BIODECHEMICAL MODELING AT MASS EXTINCTION BOUNDARIES: ATMOSPHERIC CARBON DIOXIDE AND OCEAN ALKALINITY AT THE K/T BOUNDARY

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Abstract: The causes of mass extinctions and the importance of major bio-events in the history of life are subjects of considerable scientific interest. A large amount of geological, geochemical, and paleontological information now exists for the Cretaceous/Tertiary (K/T) boundary (66 Myr BP). These data are used here to constrain a newly developed time-dependent biogeochemical cycle model that is designed to study transient behavior of the earth system. Model results suggest significant fluctuations in ocean alkalinity, atmospheric CO₂, and global temperatures at the K/T boundary, brought about by the extinction of calcareous plankton and reduction in pelagic CaCO₃ and organic carbon sedimentation rates. Oxygen-isotope analyses and other paleoclimatic data provide some evidence that such climatic fluctuations may have occurred, but stabilizing feedback processes may have acted to reduce the ocean-alkalinity and carbon dioxide fluctuations.

INTRODUCTION

Mass-extinction events have been interpreted by various workers as either: 1) geologically instantaneous catastrophes (lasting perhaps days to decades, e.g., Alvarez et al., 1980); 2) a stepwise series of short-term ecologically selective events spread out over 1 to a few million years (e.g., Hut et al., 1987), or 3) intervals of gradational extinctions at rates elevated above background extinction rates, related to increased rates of terrestrial environmental change (e.g. McKinney, 1987). A great amount of attention has been focused on the impact of an extraterrestrial body (or bodies) at the Cretaceous/Tertiary (K/T) boundary (66 Myr BP), and its possible effects on life (Alvarez et al., 1980). Discovery of anomalous iridium, and other trace metals in generally chondritic ratios, in a thin band of clay coinciding with the major mass extinction of nannoplankton and foraminifera at more than 75 sites worldwide, and subsequent discoveries of microspherules, shocked quartz and feldspar grains, and soot in the boundary clay layer have provided evidence for the impact scenario (Alvarez, 1986; 1987).

The original idea, involving a single large impactor, has been largely replaced by a model involving a 'shower' of perhaps half a dozen impactors of various sizes over a period of a few million years (Rampino & Stothers, 1984 a, b; Hut et al., 1987) which would have lead to stepped extinctions. The most complete sections at the K/T, Cenomanian/Turonian, and other boundaries commonly reveal a stepped extinction pattern (Kauffman, 1986, 1988).

During the past 250 Myr, at least eight significant mass extinction events, have occurred (Raup & Sepkoski, 1984, 1986). The most extreme event, at the Permian-Triassic boundary (about 245 Myr BP), may have wiped out an estimated 96% of the marine species then existing, and seems to have been stretched out over 5 Myr or more. A number of earlier extinction events, some also quite severe, are known from the Paleozoic record (Sepkoski, 1986). Seven extinction events during the last 600 Myr may be correlated with

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some evidence of bolide impacts, (Raup, 1988) and several seem to coincide with episodes of increased volcanism as well [e.g., the Late Cretaceous Deccan Flood Basalt eruptions at 66 Myr BP (Courtillot et al., 1986)]. A number of workers, however, maintain that strictly earthbound processes can account for some or all of the mass extinction events (see Hallam, 1987). The biogeochemical modeling described in this paper is neutral with respect to the cause of the extinction event, in the sense that it can examine the consequences of a pelagic extinction event, whatever its cause and timescale.

The mass-extinction/geologic-boundary events are also marked by significant changes in ocean/atmosphere chemistry. For example, at the K/T boundary, a strong negative shift in the carbon-isotope ratio of the surface ocean waters, and a general homogenization of deep- and surface-water chemistry, suggest a dramatic decrease in marine primary productivity — the so-called “Strangelove Ocean” effect, lasting up to 500,000 years (Zachos & Arthur, 1986). Similar carbon-isotope anomalies have been reported at other geological boundaries (Rampino & Vok, 1988). Large fluctuations in oxygen-isotope composition of carbonate derived from both planktonic and benthic organisms suggest variations in ocean temperatures, and perhaps salinity, roughly coincident with the extinction events (Hsu, 1986; Pern-Nielsen et al., 1982; Kauffman, 1986; Margolis et al., 1987; Mount et al., 1986; Hut et al., 1987). Deposition and preservation rates of CaCO₃ and organic carbon also underwent significant fluctuations at these boundaries (e.g., Zachos & Arthur, 1986). Several mass extinction events also correlate with Ocean Anoxic Events (Kauffman, 1986). These geochronological changes are indicative of severe perturbations of the global biological and ocean/atmosphere systems.

Regardless of their ultimate causes (and they may well be multi-causal), mass extinction events clearly represent major upheavals that have shaped the rate and direction of evolution of higher organisms (Raup, 1987). In each case, the extinctions were somewhat selective; certain organisms in particular environments managed to survive, and these survivors became the raw material for the reconstruction of the post-extinction biosphere (Jablonski, 1986; Raup, 1986; Valentine et al., 1986; Erwin et al., 1987). The physical, geochemical, and biological conditions before, during, and after the major faunal turnover events, therefore, represent important data that are of considerable value in determining the causes of mass extinctions and their effects on the evolution of complex life on earth, and also in judging the stability and resiliency of the biosphere to various kinds of severe environmental changes.

Raup (1987) recently identified the most critical data needed to resolve the question of the causes of mass extinction — these include detailed, high-resolution paleontological and isotopic data at mass-extinction boundaries. The establishment of such a data base has also been identified as a major goal by the International Geological Correlation Project (IGCP) 216 (Walliser, 1987). The study described here, using paleontological, isotopic, geochemical, and other types of geological data, attempts to quantify, through the use of a time-dependent biogeochemical cycle model, the changes and the processes of recovery of the physical environment and biosphere at the time of the K/T boundary.

Several major questions about the major mass extinction boundaries remain only partially answered: 1) What major changes in the physical environment take place at mass extinction boundaries, and to what extent are they unique or common to all boundaries? 2) What are the interactions between physical and biological systems (and important positive and negative feedback processes) at times of mass extinctions? 3) What are the processes and timescales of recovery of the physical environment (ocean/atmosphere) and the biosphere after individual major extinction events? Modeling studies should help answer these and other questions.
INITIAL MODEL STUDIES

Studies thus far have involved preliminary biogeochemical modeling of the possible changes in ocean/atmosphere chemistry at times of severe decreases in global biota, focusing on the K/T boundary. Of specific interest are the perturbations of the global carbon cycle caused by the mass extinction of plankton, and the extended "dead ocean" conditions of low productivity that may have prevailed for about 500,000 years after the K/T boundary event (Zachos & Arthur, 1986), and which seem to mark other mass extinctions as well (Valentine, 1986). This research involves the use of biogeochemical cycle models (Fig. 1) similar to those developed and utilized by Walker, Hays & Kasting, 1981 (WHAK); Berner, Lasaga & Garrels, 1983 (BLAG); Kump & Garrels, 1986; Kasting et al., 1986; and Volk, 1987; to study the fluxes and reservoirs of biologically and climatically important elements (C, P, N, O, S) (see Volk & Hoffert, 1985; Volk, 1987). This work differs from prior models in several important ways. For example, the model includes a reconstructed late-Cretaceous hypsometry, which is used in conjunction with computed lysocline depth and primary productivity to calculate CaCO₃ sedimentation rates. It also explicitly includes the oceanic mixed layer and deep ocean. Most importantly, detailed carbon-isotope data from planktonic and benthic foraminifera are used to estimate pelagic productivity.

PRELIMINARY MODEL EQUATIONS

The following is the preliminary set of equations for the time-dependent Biogeochemical Cycle Model used here. The model is still undergoing development. In all equations below, $k_\gamma$ represents a rate constant for a reaction involving species $\gamma$; $f_{SR}$ represents the sea-floor generation rate and is a function of time; $f_A$ represents a land-area correction factor; $f_B$ represents a weathering-rate correction factor and may be parameterized in terms of atmospheric CO$_2$, or derived from Sr weathering indicators; $V_m$ and $V_d$ represent volumes of the mixed layer and deep ocean, respectively; $f_m$ represents an oceanic mixing flux; $R_{bio}$ represents the biological fractionation of $^{13}$C; $R_{CS}$ represents the ratio of CaCO$_3$ to organic C in the oceanic detrital "rain"; and $R_{alk}$ represents the Non-Ca/Mg-alkalinity-to-carbon $^3$Redfield ratio for detrital particulate material falling from the mixed layer to the deep ocean.

1) Metamorphic and Ion-Exchange Fluxes

Metamorphism of calcite and dolomite into calcium and magnesium silicates, and the subsequent degassing of CO$_2$ to the atmosphere was parameterized in terms of the product of the sizes of the calcite and dolomite reservoirs and a measure of global tectonic activity (i.e., the sea-floor generation rate) (WHAK, 1981; BLAG, 1983). Since there is no evidence of extensive dolomite formation at the K/T boundary, there must be another sink of Mg$^{2+}$ ions in the oceans. Like the BLAG (1983) parameterization, we take that sink to be Mg$^{2+}$ for Ca$^{2+}$ exchange at the mid-ocean ridges. However, unlike the BLAG parameterization which yielded high variability in the oceanic Mg$^{2+}$/Ca$^{2+}$ ratio, we assumed that the exchange reaction proceeds at a rate proportional to the concentration of the reactant (Mg$^{2+}$) and inversely proportional to the concentration of the product (Ca$^{2+}$). In addition to being plausible, this parameterization produces Mg$^{2+}$/Ca$^{2+}$ ratios in the Cretaceous that are similar to today's value. This assumption does not directly affect ocean alkalinity or $\Sigma$ CO$_2$ content, but does affect CaCO$_3$ sedimentation rates through its impact on oceanic Ca$^{2+}$ concentration.
Calcite Metamorphism:
(M1) \[ M_C = k_{MC} \times f_{SR} \times C \]

Dolomite Metamorphism:
(M2) \[ M_D = k_{MD} \times f_{SR} \times D \]

Mg\(^{2+}\) for Ca\(^{2+}\) Exchange at Mid-Ocean Ridges:
(M3) \[ E_{CaMg} = k_{CaMg} \times f_{SR} \times \frac{[\text{Mg}\(^{2+}\)]}{[\text{Ca}\(^{2+}\)]} \]

II) Terrestrial Weathering Fluxes

Terrestrial weathering fluxes were parameterized in terms of the product of reservoir size, land area exposed to weathering, and a weathering-rate factor (WHAK, 1981; BLAG, 1983). Several methods were used to determine weathering-rate factors. In addition to the BLAG and WHAK formulations, strontium-isotope data can be used as a possible indicator of terrestrial weathering fluxes (McDougall, 1988; Palmer & Elderfield, 1985). Rates of weathering of organic carbon compounds can also be parameterized.

Calcite Weathering:
(W1) \[ W_C = k_{WC} \times f_A \times f_B \times C \]

Dolomite Weathering:
(W2) \[ W_D = k_{WD} \times f_A \times f_B \times D \]

Calcium Silicate Weathering:
(W3) \[ W_{CaSi} = k_{WCaSi} \times f_A \times f_B \times CaSi \]

Magnesium Silicate Weathering:
(W4) \[ W_{MgSi} = k_{WMgSi} \times f_A \times f_B \times MgSi \]

III) Ocean-Atmosphere Fluxes

The Time-Dependent BGCM represents the ocean with two boxes, and the atmosphere with a single box, extending two-box models developed by Broecker and Peng (1982), Keir and Berger (1983), and others. We have chosen a relatively simple two-box representation of the ocean because, in general, our information on oceanic carbon distribution is limited to benthic and planktonic \( \Sigma^{13}C \), which we take to represent deep-ocean and mixed-layer conditions, respectively.

The ocean/atmosphere portion of the model (Fig. 2) was solved somewhat differently from the rest of the model. Since our planktonic and benthic carbon isotope data appears in intervals no shorter than \(10^4\) years, we assumed that the ocean is near steady-state on these time-scales. Using an assumed ocean mixing rate, the planktonic-to-benthic \( \delta^{13}C \) gradient was used to partition ocean carbon between the mixed-layer and deep ocean. The mixed layer was allowed to exchange CO\(_2\) gas with the atmosphere. The outgassed (or ingassed) CO\(_2\) was removed from (added to) the oceanic reservoirs. A new global mean temperature was then estimated based on the newly computed atmospheric pCO\(_2\) level, and this temperature was taken to be the temperature of the mixed layer. As these changes in mixed layer temperature and total ocean carbon content will affect the partitioning of carbon in the system, the equations were iteratively solved until convergence is attained. For the steady state solution of the ocean model, sedimentation rates were assumed to balance riverine inputs, sedimentation rates were com

Mixed-Layer to Deep-Ocean:
(S1) \[ (1 + R_{CS}) f_p = \delta^{13}C \]

\( \delta^{13}C \) Mass Balance:
(S2) \[ (R_{bio} + R_{CS}) \]

The \( \delta^{13}C \) ratios comp:

\[ 13^R_R = 13^R_{PDB} (1 + \ldots) \]

Note that the value of \( ^{13}R_{PDB} \).

Ocean/Atmosphere Total Car
(S3) \[ \Sigma CO_{2 tot} = V_m \]

where \( M_{tot} \) is the moire volume layer, computed as a function presented in Peng et al. (1987)

Mixed-Layer to Deep-Ocean:
(S4) \[ R_{CS} f_p = Ca^{2+} \]

Ocean/Atmosphere Total Cal:
(S5) \[ Ca^{2+}_{tot} = V_m \]

Deep-Ocean to Mixed-Layer:
(S6) \[ R_{NaK} f_p = f_M \]

Ocean/Atmosphere Total Non:
(S7) \[ NaK_{tot} = V_m \]

IV) Carbon Deposition on the

The deep ocean carbonate using deep ocean temperature using the pressure dependenc Peng (1982). A late-Cretaceous approach presented in Scatter have changed significantly in compare additional shelf area the age-depth relationship for spreading rates of Southam at
to balance riverine inputs. For the time-rate-of-change of the total ocean/atmosphere reservoir sedimentation rates were computed using the fractional area of the ocean above the lysocline.

Mixed-Layer to Deep-Ocean Carbon Mass Balance:

\[
(1 + R_{CS}) f_P = \text{HCO}_3^{-} + f_M ([\Sigma \text{CO}_2]_d - [\Sigma \text{CO}_2]_m)
\]

& $^{13}\text{C}$ Mass Balance:

\[
(R_{\text{bio}} + R_{CS})^{13}R_m f_P = \text{HCO}_3^{-} \text{riv}^{13}R_m + f_M ([\Sigma \text{CO}_2]_d^{13}R_d - [\Sigma \text{CO}_2]_m^{13}R_m)
\]

The $^{13}\text{C}/^{12}\text{C}$ ratios computed from planktonic and benthic foraminifera data using the formula:

\[
^{13}R = R_{\text{PDB}} \left(1 + \frac{\delta^{13}C}{1000}\right)
\]

Note that the value of $^{13}R_{\text{PDB}}$ drops out of the equations (S2). We also calculate:

Ocean/Atmosphere Total Carbon Mass:

\[
\Sigma \text{CO}_2_{\text{tot}} = V_m [\Sigma \text{CO}_2]_m + V_d [\Sigma \text{CO}_2]_d + M_{\text{atm}} p\text{CO}_2_{\text{atm}}
\]

where $M_{\text{atm}}$ is the mole volume of the atmosphere and $p\text{CO}_2_{\text{atm}}$ is the partial pressure of $\text{CO}_2$ in the mixed layer, computed as a function of mixed layer temperature, alkalinity and $\Sigma \text{CO}_2$ using the algorithm presented in Peng et al. (1987)

Mixed-Layer to Deep-Ocean Calcium Mass Balance:

\[
R_{CS} f_P = \text{Ca}^{2+} + f_M ([\text{Ca}^{2+}]_d + [\text{Ca}^{2+}]_m)
\]

Ocean/Atmosphere Total Calcium Mass:

\[
\text{Ca}^{2+}_{\text{tot}} = V_m [\text{Ca}^{2+}]_m + V_d [\text{Ca}^{2+}]_d
\]

Deep-Ocean to Mixed-Layer Non-Ca/Mg-Alkalinity Charge Balance:

\[
R_{\text{NA}l} f_P = f_M ([\text{NA}l]_d + [\text{NA}l]_m)
\]

Ocean/Atmosphere Total Non-Ca/Mg-Alkalinity:

\[
\text{NA}l_{\text{tot}} = V_m [\text{NA}l]_m + V_d [\text{NA}l]_d
\]

IV) Carbon Deposition on the Ocean Floor

The deep ocean carbonate ion concentration was computed using the algorithm from Peng et al. (1987) using deep ocean temperatures estimated by Shackleton (1987). The depth of the lysocline was computed using the pressure dependence of the aragonite and calcite saturation constants outlined in Broecker and Peng (1982). A late-Cretaceous hypsometry was developed using the "mean equivalent rectangular ocean" approach presented in Sclater et al. (1979). The mean shape of the continental shelves was assumed not to have changed significantly since the Cretaceous, and we used the Haq et al. (1987) sea-level curves to compute additional shelf area due to raised sea-level. Mean ridge volume shape was computed by assuming the age-depth relationship for spreading centers developed by Parsons and Sclater (1977) and the sea-floor spreading rates of Southam and Hay (1977). Given the calculated hypsometry and the calcite and aragonite
lysocline depth, the fraction of sea floor above each of the lysoclines was calculated, and the model attributed that fraction of calcite and aragonite to calcium deposition on the ocean bottom. Shelf productivity with a detrital flux that does not reach the deep ocean is not directly reflected in surface-to-deep-ocean δ13C gradients, so a simple formulation for shelf productivity was developed that results in recovery of both today's lysocline and the inferred late-Cretaceous lysocline (Delaney & Boyle, 1988). This parameterization states that shelf productivity in the region coastward of today's 30 meter depth is 6 times higher than open-ocean productivity.

Ocean CaCO₃ Deposition:

(D1) \[ D_C = R_{CS} \times f_p \times (R_{Calcite} \times \frac{A_{Calcite}}{A_{Ocean}} + (1 - R_{Calcite}) \times \frac{A_{Aragon}}{A_{Ocean}}) \]

V) Basic Differential Equations for State Variables

All the time-derivatives of the state variables are computed in the same way: The time rate of change is the difference in the rates of the source and sink terms for a given species. (The source and sink terms have been described above.) As the model is still in development, it may grow to encompass other variables as state variables. Further modeling efforts will include the the sulfur, organic carbon and lithium cycles.

Atmospheric/Ocean Total Inorganic Carbon:

(1) \[ \frac{d CO_2}{dt} = M_C + 2M_D \cdot D_C \]

Oceamic Ca²⁺:

(2) \[ \frac{d Ca}{dt} = W_C + W_D + W_{CaSi} + E_{CaMg} \cdot D_C \]

Oceanic Mg²⁺:

(3) \[ \frac{d Mg}{dt} = W_D + W_{MgSi} \cdot E_{CaMg} \]

Calcite (CaCO₃):

(4) \[ \frac{d C}{dt} = D_C \cdot M_C \cdot W_C \]

Dolomite (CaMg(CO₃)₂):

(5) \[ \frac{d D}{dt} = M_D \cdot W_D \]

Calcium Silicate (CaSiO₃):

(6) \[ \frac{d CaSi}{dt} = M_C + M_D + E_{CaMg} \cdot W_{CaSi} \]

Magnesium Silicate (MgSiO₃):

(7) \[ \frac{d MgSi}{dt} = M_D \cdot E_C \]

VI) Numerical Methods

These equations were integrated using the 
Kasting, pers. comm., 1988).

APPLICATIONS OF THE

This model is being used to explore the effects of changes in ocean chemistry on paleo-environments through the biosphere over millions of years. We are currently using the most accurate model of the modeled include: weathering processes at mid-ocean ridges, CO₂ dissolution in the oceans, feedbacks on CO₂ solubility to variations in biological weathering, and atmospheric temperatures.

Model output includes inorganic carbon content, mean global temperatures, and a new, biogeochecmical cycle model for nanoplankton.

![Schematic Diagram](image-url)
calculated, and the model in the ocean bottom. Shelf directly reflected in surface-to-
basins developed that results in (Delaney & Boyle, 1988). This
50 meter depth is 6 times

\text{Magnesium Silicate (MgSiO}_3):\]

\[
\frac{d \text{MgSi}}{dt} = M_{12} \cdot E_{\text{CaMg}} \cdot W_{\text{MgSi}}
\]

\text{VI) Numerical Methods}

These equations were integrated using the Reverse-Euler's Method, which retains integrative stability and relative accuracy when used on sets of equations spanning a wide range of time scales (Gear, 1971; Kasting, pers. comm., 1988).

\text{APPLICATIONS OF THE MODEL}

This model is being used to study the effects of transient events on the cycling of carbon and other elements through the biosphere, oceans, atmosphere and lithosphere on time scales ranging from thousands to millions of years. We believe that it is crucial to model the transient responses since these almost certainly present the most severe conditions for life, and thus are a critical element in evolution. Processes modeled include: weathering of terrestrial carbonate and silicate rocks by \text{CO}_2, detrital flux from the mixed layer to the deep ocean, deep-ocean/mixed-layer carbon fluxes, alkalinity fluxes, \text{Mg}^{2+} for \text{Ca}^{2+} exchange at mid-ocean ridges, \text{CO}_2 gas exchange at the ocean surface, calcium carbonate precipitation and preservation in the oceans, metamorphism of carbonate rocks (calcite and dolomite), and temperature feedbacks on \text{CO}_2 solubility in the oceanic mixed layer (Fig. 1). Model runs test the sensitivity of the system to variations in biological activity, oceanic mixing rates, ocean alkalinity, and the relationships between weathering rates, atmospheric \text{pCO}_2, and global temperatures.

Model output includes temporally resolved estimates of atmospheric \text{pCO}_2, ocean alkalinity, ocean inorganic carbon content, \text{CaCO}_3 deposition rates, chemical weathering rates for terrestrial rocks, and mean global temperatures (Caldeira et al., 1988). It is important to note that unlike previous studies, the Time-Dependent BGCM is constrained with $\delta^{13}\text{C}$ data from benthic and planktonic foraminifera and nanoplankton.

\text{INVESTIGATIONS OF ATMOSPHERIC CARBON DIOXIDE FLUCTUATIONS DURING BIO-EVENTS}

On short time scales atmospheric \text{CO}_2 is greatly influenced by planktonic primary production in the world’s oceans (Broecker & Peng, 1982), whereas on longer time scales atmospheric \text{CO}_2 seems to be largely controlled by rates of tectonism and chemical weathering of silicate rocks (e.g., Lasaga et al., 1985; Berner et al., 1983 (BLAG model); Walker et al., 1981 (WHAK model). Data from the Deep Sea Drilling Project and other sources suggest changes in atmospheric carbon

\text{Figure 1: Schematic Diagram of the time-dependent biogeochemical cycle model.}
dioxide spanning a hierarchy of biological and geochemical timescales (Caldeira et al., 1988). Therefore, models of carbon dioxide changes at boundaries must be able to resolve this hierarchy of scales to investigate such questions as: What is the relative importance of biological and geochemical factors in returning the earth system to near equilibrium following a large scale perturbation? What feedback processes exist in the major biogeochemical cycles, and does life and its effects on climate have a stabilizing influence in the face of large scale disruptions of the earth system?

Most modelers of biogeochemical cycles have been parameterizing weathering rates in terms of atmospheric pCO₂ (BLAG, 1983), or atmospheric pCO₂ and surface temperature (WHAK, 1981). One important data set that could, when extended, provide excellent information on the relative fluxes of biogeochemically important chemicals to the ocean-atmosphere system is the Sr/Ca and Sr/Li ratios in pelagic calcareous fossils (Delaney & Boyle, 1986). As oceanic Sr has primarily terrestrial sources, Li has primarily mid-ocean ridge sources, and Ca, a mix of the two, dynamic models would be able to use these ratios either as constraints or for independent verification (Delaney & Boyle, 1988).

Another important data set that could provide more information on rates of chemical weathering is the strontium isotope record. Strontium in the oceans has several sources, including emissions at the mid-ocean ridges, riverine input, and diagenetic fluxes from ocean sediments (Palmer & Elderfield, 1985). If we make the assumption that the perturbation at the K/T boundary (McDougall, 1988) affected only the riverine sources of strontium, we can calculate from the ⁸⁷Sr/⁸⁶Sr isotopic excursion the rate of Strontium riverine input and therefore strontium weathering. Unfortunately, these flux estimates are very sensitive to small variation in the isotopic composition of source reservoirs. Since Sr/Ca ratios in chemical weathering are pH dependent, we can use the DSDP ⁸⁷Sr/⁸⁶Sr data, estimates of rainfall pH at the K/T boundary and the derived Strontium weathering rates to calculate a CaSO₄ weathering rate (McDougall, 1988; Stumm & Morgan, 1981; Lasaga, 1984; Prinn & Fegley, 1987). The Sr-ratio-derived weathering rates can be used to further constrain or verify the model results. Our initial Sr-isotope modeling results suggest an initial boundary period of intense weathering, followed by reduced weathering rates.

This is consistent with results of the Biogeochemical Cycle Model which suggest an initial pCO₂ at the K/T boundary, lowered by a reduction in atmospheric pCO₂. The use of the Sr-derived weathering rates should allow more accurate modeling of atmospheric pCO₂, ocean alkalinity, atmospheric O₂, planetary temperature across the K/T boundary.

RESULTS

Model results suggest an increased ocean alkalinity (balanced by deposition of terrestrial CO₃ budget) and the model calculated carbonate shell production mixing time. This yields an equilibrium CaCO₃ press

K/T Boundary Biogeochemical Cycle Model

Figure 2: steady-state ocean/atmosphere segment of the time-dependent biogeochemical cycle model.
boundary period of intense weathering, followed by reduced weathering rates. This is consistent with the results of the Biogeochemical Cycle Model which suggest an initial pCO₂ rise at the K/T boundary, followed by a reduction in atmospheric pCO₂. The use of the Sr-derived weathering rates should allow more accurate modeling of atmospheric pCO₂, ocean alkalinity, atmospheric O₂, and planetary temperature across the K/T boundary.

**RESULTS**

Model results suggest that the reduced productivity of the "Strangelove-Ocean"-period would have led to increased ocean alkalinity. The continued riverine fluxes of calcium and magnesium ions would not be balanced by deposition of pelagic carbonates. During the "Strangelove-ocean"-period (roughly 66.4 to 65.9 Myr BP) the model calculates a mean riverine alkalinity flux to the oceans of $34 \times 10^{12}$ eq/yr and a mean carbonate shell production rate of only $8.4 \times 10^{12}$ moles CaCO₃/yr using a overly rapid 1000 yr ocean mixing time. This yields a riverine alkalinity source flux that is roughly twice the alkalinity sink flux produced by biogenic CaCO₃ precipitation (Fig. 3), so ocean alkalinity should increase. Starting with inferred Late Cretaceous atmospheric pCO₂ of about 500 ppm, our model calculates that this alkalinity increase would have resulted in a reduction in atmospheric carbon dioxide to approximately 100 ppm, with a possible global cooling of about 4.5° C (Fig. 4). These low atmospheric CO₂ values might have led to further reductions in terrestrial and oceanic primary productivity. The eventual return of pelagic carbonate production should have caused a release of CO₂ from the oceans, and an increase in atmospheric CO₂ to about 1500 ppm, leading to an increase in...
global temperatures of about 2°C.

CaCO₃ shell production rate is to a first-order approximation inversely proportional to ocean mixing time, so a more realistic slower ocean would only increase the magnitude of this imbalance. The calculated increase in alkalinity would drive the calcite compensation depth (CCD) to the bottom of the ocean for an extended period of time. We see no evidence for such a sustained period of ocean calcite supersaturation, although the CCD does appear to have deepened somewhat after the boundary event. So the major question remains: What became of the excess alkalinity?

If the pelagic die-off left the oceans with phosphate rich surface waters, these waters may have fertilized the shelves and epicontinental seas. This might lead to higher shelf CaCO₃ accumulation rates during the "Strangelove-ocean" period. An indication that this may have occurred is present in the data from the Bragg's section in Alabama (Jones et al., 1987), but estimates of pre- and post-boundary global rates of CaCO₃ accumulation await further analysis. A significant drop in the organic carbon burial rate would also have the effect of supplying more carbon to the ocean, which might balance the excess alkalinity. Arthur et al. (1985) suggest that this may have occurred. Another possibility is that the eruption of the Deccan Traps in India may have provided a flux of H₂SO₄, HCl, and CO₂ that would have mitigated some of the effects of this "alkalinity crisis", but recent calculations suggest that the flux was too small to fully offset the estimated alkalinity imbalance (Caldeira & Rampino, 1989).

A number of additional effects and impacts at the K/T boundary, such as acid rain (Prinn & Fegley, 1987), rapid ocean mixing induced by tsunami (Kauffman, 1986), and possible bolide impact into carbonate rocks (O'Keefe & Ahrens, 1989) also would cause an initial atmospheric pCO₂ increase at the K/T boundary. We note, however, that rapid ocean mixing would have diluted the effects of acid rain, making it unlikely that the mixed layer would become undersaturated with respect to calcite. If the impactor struck an area of carbonate rocks, it would not only release carbonate ions, but also Ca²⁺ ions. An increased Ca²⁺ flux would increase ocean alkalinity, and cause a drawback of atmospheric CO₂ into the oceans. While there may have been a short-term atmospheric CO₂ increase due to these causes, these effects alone (i.e., without the major planktonic productivity decrease) could not have affected atmospheric pCO₂ levels for longer than several ocean mixing times (i.e., several thousand years).

The present model may overestimate the effect of the "Strangelove-ocean"-period (roughly 66.4 to 55.9 Myr BP) for several reasons. Shelf productivity is assumed to be proportional to pelagic productivity, but it is possible that this relationship does not hold. It may be that the planktonic die-off left the surface waters rich in PO₄, which may have acted to increase productivity in shelf and epicontinental sea regions. Possible changes in benthic boundary layers and in feeding habits of benthic organisms during the "Strangelove"-period have not been taken into account. Furthermore, the model calculates no oceanic productivity at 66.1 Myr BP, but, if this were the case, there would be no carbonate shells from which to get the δ¹³C data.

CONCLUSIONS

Model results suggest that the rate of pelagic production of CaCO₃ shells during the Strangelove ocean period should have fallen below the rate of riverine supply of Ca⁺²⁺ and Mg⁺²⁺ ions to the world ocean by about a factor of two (Fig. 3). These results are supported by the observed low accumulation rates of CaCO₃ at a number of DSDP and ODP drill sites. Without the flux of CaCO₃ to the sediments, ocean alkalinity should have increased, resulting in a decrease of atmospheric CO₂, lowering of the CaCO₃ lysocline, and leading to a calculated global cooling of about 4.5°C for several hundred thousand years. Eventual return of ocean productivity and increased rock weathering would have decreased ocean alkalinity, and released CO₂ to the atmosphere. Isotopic data suggest an increased excess alkalinity problem. Oxygen-isotope temperature fluctuations at the K/T boundary (Mount et al., 1987; Rampino & Cita, 1986) and other effects. It is clear that nutrient-rich waters may have flowed from the oceans, decreasing ocean alkalinity.

While the current model does not account for the processes that occur in the oceans, the model does demonstrate that the processes may have contributed to the perturbations against perturbation, and the dynamics of the system.

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proportional to ocean mixing this imbalance. The calculated the bottom of the ocean for an ocean calcite supersaturation, boundary event. So the major these waters may have fertilized accumulation rates during the present in the data from the post-boundary global rates of carbon burial rate would also be the excess alkalinity. Arthur et eruption of the Deccan Traps mitigated some of the effects of ill to fully offset the estimated as acid rain (Prinn & Fegley, bolide impact into carbonate: \( \text{pCO}_2 \) increase at the KT effects of acid rain, making it calcite. If the impactor struck \( \text{Ca}^{2+} \) ions. An increased \( \text{CO}_2 \) into the oceans. These causes, these effects alone \( \Delta \text{atmospheric } \text{pCO}_2 \) levels -period (roughly 66.4 to 55.9 to pelagic productivity, but it die-off left the surface waters continental sea regions. Possible reasons during the "Strangelove"-no oceanic productivity at 66.1 12C to get the \( \delta^{13} \text{C} \) data.

During the Strangelove ocean \( \text{Ca}^{2+} \) ions to the world ocean led low accumulation rates of \( \text{CO}_3 \) to the sediments, ocean \( \text{O}_2 \) lowering of the \( \text{CaCO}_3 \) several hundred thousand years. Would have decreased ocean alkalinity, and released \( \text{CO}_2 \) to the atmosphere causing a calculated warming of about 2°C (Fig. 4). Sr-isotope data suggest an increased weathering flux to the oceans at the KT boundary, thus exacerbating the excess alkalinity problem. Oxygen-isotope measurements and other paleoclimatic data show some evidence of temperature fluctuations at the KT boundary (possible warming and cooling, see Hsu, 1986; Margolis et al., 1987; Mouni et al., 1986; Rampino & Volk, 1988), but the interpretation of these data is complicated by diagenesis and other effects. It is also possible that some stabilizing feedbacks may have acted to reduce the variability in ocean alkalinity, and hence atmospheric \( \text{CO}_2 \) during the Strangelove period. One possibility is that nutrient-rich waters may have led to increased rates of carbonate and organic precipitation in shallow waters, decreasing ocean alkalinity.

While the current model does not yet include all of the important biogeochemical processes, it demonstrates that the processes modeled are capable of producing significant perturbations in geochemical cycles. If such large perturbations did not occur, it is because mechanisms exist that can stabilize the system against perturbation, and the dynamics of these stabilizing processes must be investigated through further modeling.

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