Influence of late Cenozoic mountain building on ocean geochemical cycles

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ABSTRACT

In a steady-state ocean, input fluxes of dissolved salts to the sea must be balanced in mass and isotopic value by output fluxes. For the elements strontium, calcium, and carbon, rivers provide the primary input, whereas marine biogenic sedimentation dominates removal. Dissolved fluxes in rivers are related to rates of continental weathering, which in turn are strongly dependent on rates of uplift. The largest dissolved fluxes today arise in the Himalayan and Andean mountain ranges and the Tibetan Plateau. During the past 5 m.y., uplift rates in these areas have increased significantly; this suggests that weathering rates and river fluxes may have increased also. The oceanic records of carbonate sedimentation, level of the calcite compensation depth, and $\delta^{13}\mathrm{C}$ and $\delta^{87}\mathrm{Sr}$ in biogenic sediments are consistent with a global increase in river fluxes since the late Miocene. The cooling of global climate over the past few million years may be linked to a decrease in atmospheric CO₂ driven by enhanced continental weathering in these tectonically active regions.

INTRODUCTION

Changes in sea-floor-spreading rates, land-sea distribution, and rates of outgassing have been proposed as primary causes of the decline in global temperatures over the past 100 m.y. (e.g., Hays and Pitman, 1973; Berner et al., 1983). On shorter time scales, tectonic changes in oceanic sill depths (Keigwin, 1982), increased volcanism (Kennett and Thunell, 1975), and epeirogenic uplift in highland regions of northern Canada (Birchfiel et al., 1982) have been invoked as possible causes of the late Pliocene appearance of continental ice sheets in the Northern Hemisphere. It has been proposed that rapid uplift of the Himalayan-Tibetan Plateau region and the plateau and mountain regions of the southwest United States could also have caused climates to cool duirng the past 3 m.y. (Ruddiman and Raymo, 1988). Increased elevation in these areas may have enhanced the meridionality of Northern Hemisphere atmospheric waves and allowed greater southward penetration of polar air masses over east-central North America and Europe.

Here, we propose that increasing rates of uplift and erosion in the Himalayas, Andes, and Tibetan Plateau have contributed to a significant increase in the global rate of chemical weathering since the late Miocene. We focus on the Himalayan-Tibetan region and the Andes because their associated rivers carry the greatest dissolved and particulate loads to the sea, and thus large changes in the amount of erosion in these areas would have the greatest global effect. However, we note that rates of uplift have increased during the late Neogene for many other areas, including the southwest United States, the Swiss Alps, and the Southern Alps of New Zealand.

Using simple one-box ocean models of the geochemical cycles of strontium (Sr), calcium (Ca), and carbon (C), we show that the marine records of carbonate sedimentation, calcite compensation depth (CCD), δ^{87} Sr, and δ^{13} C are consistent with increased fluxes of weathering products to the sea over the past 5 m.y. We propose that this increase in the rate of global chemical weathering could have lowered atmospheric CO₂ concentrations. This view differs from recent geochemical models that ignore relief as a factor controlling global weathering rates and atmospheric CO₂ (e.g., Berner et al., 1983; Volk, 1987).

EVIDENCE FOR PLIOCENEPLEISTOCENE MOUNTAIN UPLIFT

Mineralogic and biologic evidence suggests that rates of uplift and erosion have increased substantially in the Himalayas since the early Pliocene. Rb/Sr, K/Ar, and fission-track ages of minerals in the Siwalik formation and other molasse deposits along the southern margin of the Himalayan range indicate that progressively faster rates of uplift, erosion, and sedimentation have occurred during this interval (e.g., Saini et al., 1979; Burbank and Johnson, 1983). These formations coarsen progressively upward from early Pliocene silts to middle and late Pleistocene conglomerates, consistent with increasing uplift through the past 5 m.y. Mammalian distributions (the Hipparion fauna) also suggest that the Himalayas were not an effective barrier to north-south migration until the late Pliocene (West, 1984).

On the Tibetan Plateau, late Miocene and early Pliocene subtropical pollen assemblages, indicative of elevations below 1.5 km, are found today at elevations higher than 4 km (Hsu,

1978). Results from 12 additional pollen and vegetation studies spanning the Cenozoic are summarized in Figure 1a. Over the past 5 m.y., uplift rates have been at least twice as great (curves 2N and 2S) as those of the previous 5 m.y., and may have increased more than fivefold (curve 1).

In the eastern Cordillera and Altiplano of the Bolivian Andes, Benjamin et al. (1987) used dated pairs of apatite and zircon to estimate Neogene uplift rates. Their results (Fig. 1b) showed that uplift rates have approximately doubled over the past 5 m.y. To the south, the Puna Plateau of Argentina also underwent a major phase of uplift, beginning between 10 and 5 Ma, which culminated at approximately 2 Ma (Allmendinger, 1986). To the north, in western Colombia, the timing of major uplift centered on 3 to 4 Ma (McCourt et al., 1984). As in the Tibetan-Himalayan region, uplift rates appear to have increased significantly since the late Miocene, even though the exact timing and magnitude of these changes are still poorly constrained.

UPLIFT AND CHEMICAL WEATHERING RATES

Increased rates of vertical movement in the Himalayas, Tibet, and the Andes could have a significant effect on chemical weathering rates and the global flux of dissolved material to the sea. Today, the three largest sources of dissolved materials are the Yangtze, Amazon, and Ganges-Brahmaputra rivers (Berner and Berner, 1987). These three rivers, which drain the Tibetan Plateau, Andes, and Himalayas, respectively. account for about 20% of the total dissolved plus suspended solids and water discharges to the ocean. Including all the other rivers draining these three areas, chemical erosion in the Himalayas, Andes, and Tibet makes a substantial contribution to the flux of dissolved material reaching the sea.

Relief influences rates of chemical weathering and dissolved fluxes to the sea for three reasons:

(1) Rapid mechanical breakdown of rocks in areas of rapid uplift enhances exposure of primary minerals to chemical weathering (Stallard and Edmond, 1983). Abrasion in mountain streams also removes iron-oxide coatings that inhibit chemical attack and retard weathering.

(2) Dissolved loads are highest in areas dominated by easily eroded sedimentary rocks. In general, areas of active tectonism are character-

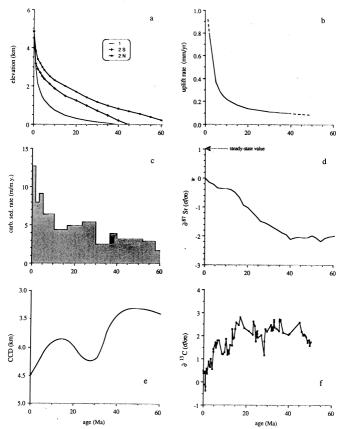


Figure 1. a: Estimated elevation of Tibet over past 60 m.y. based on 12 vegetation studies (after Mercier et al., 1987). Curve 1 shows maximum rates of upilit since Miocene; curves 25 and 2N show minimum upilit rates for southern and northern Tibetan Plateau, respectively. b: Mineralogic estimates of upilit in Peruvina Alliplano (after Berjamin et al., 1987) show that upilit rates have more than doubled in these over past 5 m.y. c: Global CaCO₃ sedimentation rates (after Delaney and Boyle, 1988). d: Average marine δ⁸ 'S values plotted at 2 m.y. increments over past 50 m.y.; arrow shows taddy-attel value for current measured S' inputs (data from Elderfield, 1988). e: Average jobal calcit. Increments over past 50 m.y.; arrow shows taddy-attel value for current measured S' inputs (data from Elderfield, 1988). e: Average jobal calcit seprensation depth (Cover Conzolo (fafter Delaney and Boyle, 1988). e: Δ³C of bulk carbonate recovered from Deep Sea Drilling Project Sites 525 and 528, South Allantic (Shackleton, 1957).

ized by uplifted sedimentary formations typical of continental margins, whereas thick, well-weathered soils and more resistant crystalline rocks characterize peneplained, continental low-lands (Stallard and Edmond, 1983). (3) Chemical and physical weathering rates increase with runoff, which tends to be greatest in mountainous areas because of the orographic influence of mountain ranges on precipitation patterns. Schmitz (1987) estimated that the annual rainfall associated with the Asian monsoon may have increased as much as tenfold in conjunction with Himalayan uplift.

The above effects have been well documented in the Amazon River system, where over 75% of the discharged dissolved solids are eroded from the Andean highlands (Gibbs, 1967; Stallard and Edmond, 1983). Thus, increasing rates of uplift in the Himalayan-Tibetan and Andean regions could have significantly enhanced dissolved fluxes in rivers to the ocean since the late Miocene and early Pliocene. Are sea-floor records of δ^{87} Sr, carbonate sedimentation, CCD, and δ^{13} C consistent with such an increase?

RIVER FLUXES AND OCEAN GEOCHEMICAL CYCLES

We use steady-state, one-box models of the ocean to estimate the direction and approximate magnitude of changes in river fluxes needed to explain the evolution of the δ^{87} Sr and carbonate accumulation output records over the past 5 m.y. The record of δ^{13} C cannot be used to constrain estimates of past river fluxes for reasons discussed below. Mass-balance equations for the oceanic constituents Sr, Ca, and C are given in Appendix 1. Over thousands of years, the ocean achieves a steady-state mass balance by adjusting outputs so that they equal inputs. Potential oceanic feedback mechanisms that govern changes in output rates have been discussed by Broecker and Peng (1982).

The modern input and output fluxes, as well as isotopic values of the Sr and C fluxes, are given in Table 1. The flux and isotopic values of river Sr are based on recent measurements of rivers draining the Himalayan and Andean regions (Edmond, 1987, and unpub. data). These values are higher than those measured in previous studies of limited areal extent (e.g., Martin and Meybeck, 1979; Wadleigh et al., 1985) and are consistent with the hydrothermal fluxes based on ³He loss from the ocean crust (Edmond, 1987). The Sr and Ca output fluxes are calculated from measured input fluxes, and C fluxes are based on a 4:1 burial ratio of C in carbonate and organic matter (Broecker and Peng, 1982), with the additional constraint that the output fluxes of C and Ca in carbonate sediments must be equal.

In Table 1, our isotopic value of Sr in modern carbonate (and hence seawater) is not the current measured seawater value (δ^{87} Sr = $0.0^{\circ}/_{00}$; Palmer and Elderfield, 1985). The oceanic isotopic value for Sr cannot be at steady state because the residence time of Sr in the ocean is ~5 m.y. (Broecker and Peng, 1982) and the oceanic record of Sr isotopes (Fig. 1d) shows a continual increase over the past 5 m.y. (indicating that inputs and/or outputs are changing). If the ocean were allowed to reach steady state with the measured river, redissolution, and hydrothermal inputs (Table 1), we calculate that the seawater-carbonate δ^{87} Sr value would be about 1.01 $^{\circ}$ /₀₀. We adopt this value to represent the modern ocean. The isotopic value for river carbon (δ^{13} C = -3.9 0 /₀₀) was determined from the isotopic value of bulk marine carbonate $(\delta^{13}C = +0.38^{\circ})/_{00}$; Shackleton, 1987) and deepsea sediment organic carbon ($\delta^{13}C = -21^{-0}/_{00}$; Degens, 1969) and from the fractions of each being deposited in the modern ocean (Broecker and Peng, 1982).

For each element in Table 1, rivers dominate

TABLE 1. MASS BALANCE FLUX ESTIMATES

TABLE I. MASS BALANCE FLOX ESTIMATES					
auto and student relations and the set of Land. It is	Sr (10 ¹⁰ mol/yr)	δ ⁸⁷ Sr (0/00)	Ca (10 ¹² mol/yr)	C (10 ¹² mol/yr)	δ13 _C (o/oo)
Modern Oceans	manufacture and the second	A Control of the Cont	annan magis - milligrad (5 - 1915) — milligh - 1945, 1975, milligh distribution millight	and a second sec	A CONTRACTOR OF THE PROPERTY O
River input	2.9(a)	+5.36(a)	13(e)	20	-3.9
Hydrothermal input	1.2(b)	-8.74(d)	3(f)	- "	-
Redissolution input	0.5(c)	-0.85(c)	-	-	-
Hydrothermal output	1.2(b)	+1.01	-		-
Organic output	- ` ′	-	-	4(g)	-21(h)
Carbonate output	3.4	+1.01	16	16	+0.38(i)
5 Ma Oceans					
River input	1.85	5.36*	9	16.2	-3.9*
Hydrothermal input	1.2*	-8.74*	3*	-	-
Redissolution input	0.5*	-0.85*	-	•	-
Hydrothermal output	1.2*	-0.28	•	<u>-</u>	-
Organic output	•	-	-	4.2	-19.8
Carbonate output	2.35	-0.28(j)	12(k)	12	+1.6(i)

Note: Letters with values indicate references: a--Edmond (unpub. data and 1987); b--Palmer and Elderfield (1985), Edmond (1987); c--Elderfield and Gieskes (1982); d--Albarede et al. (1981); e--Martin and Meybeck (1979); f--Von Damm et al. (1985); g--Broecker and Peng (1982); h--Degens (1969); i--Shackleton (1987); j--Elderfield (1986); k--Davies et al. (1977), with timescale corrections of Delaney and Boyle (1988) assuming 50% preservation effects and 50% true changes in sedimentation rates. Values with no reference were determined by mass-balance difference.

* Values assumed to be equal to modern.

the inputs to the oceanic reservoir. Hydrothermal and redissolution inputs are less significant. Output fluxes occur primarily by biogenic sedimentation of carbonates. To avoid the possibility of large variations in spreading rates and hydrothermal fluxes (which we assume remain constant), we restrict this study to the past 5 m.y., and we specifically address the influence of rapid vertical tectonics on erosional fluxes. Output fluxes for the 5 Ma ocean (Table 1) are estimated below.

Strontium

The δ^{87} Sr record of oceanic carbonate is shown in Figure 1d. Unlike the present-day value, the 5 Ma Sr isotopic value (δ^{87} Sr = -0.28 ⁰/₀₀) is assumed to be near steady state because of the relative constancy of $\delta^{87} Sr$ values over the previous 10 m.y. (15-5 Ma). This implies an early Pliocene river Sr flux of 1.85×10^{10} mol/yr. We assume no change with time in the isotopic value of the river input and, thus, in the proportion of silicates to carbonates being weathered on the continents. If the fraction of carbonates being weathered has increased since the early Pliocene (as might be expected from the geology of Tibet, the Andes, and the Himalayas), then our 5 Ma river Sr flux would be slightly overestimated. Holding all else constant, the Sr isotopic values indicate that the river flux of Sr has increased by about 55% since the early Pliocene.

Calcium

Because we do not know the fraction of biogenic aragonite deposited in the past or even its bulk average Sr/Ca ratio, we cannot use the Sr/Ca ratio in foraminifera to estimate past river fluxes of Ca. The global record of carbonate accumulation, however, provides some constraints on estimates of dissolved river inputs.

Davies et al. (1977) estimated average CaCO₃ sedimentation rates in the world's oceans over the Cenozoic by using core data recovered by Legs 1-34 of the Deep Sea Drilling Project (DSDP). Their compilation, with the revised time scale used by Delaney and Boyle (1988), is plotted in Figure 1c. Davies et al. (1977) suggested that increases in CaCO3 sedimentation rates were caused by greater river delivery of Ca. Taken at face value, the trends in Figure 1c would indicate that global CaCO₃ sedimentation rates have approximately doubled since the early Pliocene, and therefore, the output flux of Ca in CaCO3 sediments has also doubled. This would imply that river erosional fluxes of Ca have increased by as much as 160% (using mass-balance equations in App. 1).

The true increase, however, is probably smaller than is suggested by Figure 1c. Moore and Heath (1977) argued that the late Cenozoic increase in CaCO₃ sedimentation was an artifact of enhanced preservation of younger sediments and not due to increased river fluxes. Accept-

ing this model of age-dependent preservation, Davies and Worsley (1981) recompiled the carbonate data and found that the increase in sedimentation rates since the Miocene was greatly reduced.

Despite the preservation effect, several arguments suggest that a late Concorci increase in carbonate deposition is plausible. First, dissolution of CaCO₃, and hence destruction of sediment, can occur either shortly after deposition (below the CCD) or much later, long after burial (by a shoaling of the CCD). The fact that the CCD has deepened by ~350 m since the early Pliocene (Fig. 1e) suggests that dissolution may have been more widespread at 5 Ma than today. Increased preservation of CaCO₃ over this interval would then be not solely a function of age but a consequence of the CCD deepening, possibly in response to increased river fluxes of Ca.

Second, in their evaluation of preservation effects, Moore and Heath (1977) defined a hiatus as any DSDP section that accumulated at rates less than 1 m/m.y. If, on average, sedimentation rates were much lower in the past, as suggested by Figure 1c, then sediments accumulating at less than 1 m/m.y. would greatly expand in areal coverage. This would increase the frequency of sediments assigned as hiatuses in the Moore and Heath analysis and create an artificial preservation effect.

Thus, it is unclear what fraction of the increase in carbonate sedimentation is due to increased river inputs and what fraction is an artifact of age and preservation. We suggest that Figure 1c represents the maximum possible increase in global carbonate sedimentation over that past 5 m.v.; the true increase is probably lower because of the preservation effect discussed by Moore and Heath (1977). In Table 1. we ascribe 50% of the apparent increase in Figure 1c to preservation and 50% to a true increase in carbonate sedimentation rates. This model implies that river Ca fluxes have increased by ~45% since the early Pliocene. This estimate is more in keening with the increase in river fluxes suggested by the Sr data, but larger (or smaller) increases cannot be ruled out. If, indeed, carbonate burial rates have increased since the early Pliocene and the level of the CCD has dropped from 4150 to 4500 m (Fig. 1e), then the CaCO3 production rate would have increased from 25×10^{12} mol/yr to 28×10^{12} mol/yr (calculation in App. 2). Thus, enhanced oceanic carbonate productivity would also have accompanied an increase in dissolved fluxes in rivers.

Carbo

Because equal amounts of Ca and C are buried with CaCO₃, the output flux of C in carbonates will equal the output flux of Ca in carbonate sediments at 5 Ma. But to independently constrain the river flux of C at this time also requires calculation of the burial of organic matter from two of the following three parameters: (1) the burial ratio of carbonate to organic matter in the ocean; (2) the δ^{13} C of the buried bulk-marine organic matter, (3) the δ^{13} C of the buried bulkmarine carbonate. Unfortunately, only the bulk carbonate δ^{13} C record is known in sufficient detail

The δ^{12} C of bulk carbonate from DSDP Sites 525 and 528 is shown in Figure 1f. Parts of this record have been reproduced in several areas (Shackleton, 1987), suggesting that it is a representative global signal. Likewise, the present-day value (δ^{12} C = 40.38 40.28 $^{\prime}$ Ms. Shackleton, 1987) is found over a wide range of latitudes in three oceans, suggesting that the decline in bulk carbonate δ^{12} C from the Miocene to the present is also global.

Shackleton (1987) estimated burial rates of marine organic matter through the Cencozoic from his bulk carbonate δ¹²C record alone (Fig. 1) by assuming that (1) the earbon isotope fractionation δ¹³Cog. σ¹³Cog. his remained constant, (2) the burial flux of CaCO₃ was constant, and (3) the δ¹³Cof the river input was constant. His assumptions led directly to his conclusion that Cog. burial, organic carbon/carbonate burial ratios, and river-C inputs decreased toward the present.

Here, we recalculate Corg burial at 5 Ma, also using Shackleton's bulk carbonate δ13C record (Fig. 1f). Instead of assuming a constant burial flux of CaCO3, however, we use the lower carbonate output flux at 5 Ma (12 × 1012 mol/yr; Table 1) derived in the previous section. By using $\delta^{13}C_{carb} = +1.6^{\circ}/_{00}$ at 5 Ma (from Fig. 1f), we estimate the Core sedimentation flux in the early Pliocene to be 4.2 × 1012 mol/yr (vs. 4 × 1012 mol/vr today), and the river-C flux to be 16.2×10^{12} mol/yr (vs. 20×10^{12} mol/yr today). Both Shackleton's and our estimates imply that a greater fraction of C was deposited in organic matter at 5 Ma and that total organic carbon deposition was also greater (although our estimate of the latter difference is much less than Shackleton's). However, the calculated river fluxes differ significantly. When we allow carbonate sedimentation rates to increase toward the present, river-C fluxes also increase (in the model presented here, by about 25%), whereas in Shackleton's model, which assumes constant carbonate sedimentation rates, river-C fluxes decrease toward the present.

One potential problem with both treatments of the C cycle is the assumption that ¹³C fractionation factors remain constant. Measurements of δ^{13} C within single species of planktonic foraminfers suggest that surface-water δ^{13} C has not changed significantly since the late Miocene (Sanged significantly since the late Miocene δ^{13} C implies that biological fractionation effects must have changed. If so, then it is no longer must have changed. If so, then it is no longer

possible to estimate the relative proportions of carbonate and organic sedimentation and hence past river fluxes of C, without data for 61³² C of bulk organic matter. If, rather than assuming constant fractionation factors, one assumes a constant organic carbon Carbonate output ratio, then the organic matter and river-C fluxes both must increase by 33% toward the present, as prescribed by the change in the carbonate flux. This would imply that fractionation factors were larger in the early Pliocene cocan, possibly because of elevated CO₂ concentrations in the ocean (Arthur et al., 1985).

DISCUSSION

The Sr isotope record and carbonate sedimentation curve are both consistent with an increase in dissolved fluxes in rivers over the past 5 m.v. The bulk carbonate δ13C record is also consistent with increased river fluxes, provided the model invoked to explain this record does not assume constant burial fluxes a priori. Such an increase in the rate of global chemical erosion could have been caused by increased rates of tectonic uplift in the Himalayas and Andes and on the Tibetan Plateau, as well as in other active tectonic regions such as the western United States and the Alps. However, alternative mechanisms could have produced the observed δ87Sr and carbonate records. The increase in the 87Sr/86Sr ratio could have been caused by a 40% decrease in hydrothermal fluxes over this interval, or by a 95% decrease in the redissolution flux. Increasing the proportion of silicates weathered on land by ~16% could also explain the evolution of Sr isotopes since the late Miocene (Palmer and Elderfield, 1985). Yet all these explanations would require constant or decreasing Ca-input fluxes, opposite to the trend suggested by both the CaCO3 sedimentation and CCD records.

The apparent increase in global erosional fluxes has also been attributed to the growth of continental ice sheets and their effect or erosion, both directly through the exposure and grinding of rock (Amstrong, 1971) and indirectly through lowering sea level and increasing land area subject to erosion (DePaolo, 1986). Both mechanisms have probably influenced fluxes to the sea, although the relative importance of these sources compared to low-latitude rivers (that dominate the dissolved chemical influx today) remains uncertain.

The increase in chemical weathering that we ascribe to uplift may have influenced atmospheric CO₂ either by consumption of CO₂ during weathering reactions or by influencing the oceanic carbon cycle. The increased supply of cations associated with enhanced continental erosion would tend to drive ocean alkalinity up and CO₂ down (Broccker and Peng, 1982). In-deed, if relief is an important factor in continental weathering, as we argue here, then CO₂

levels may be controlled not only by the balance between sea-floor spreading rates, land-sea distributions, and atmospheric CO2 feedbacks on weathering rates (e.g., Berner et al., 1983; Volk, 1987) but also by relative rates of sea-floor spreading (CO₂ production) and continental orogeny (CO2 consumption)

Ultimately, the onset of Northern Hemisphere glaciation may have been related to mountain uplift through the impact of high plateaus and mountain ranges on atmospheric circulation patterns (Ruddiman and Raymo, 1988) and the impact of enhanced rates of chemical erosion on the oceanic C cycle and atmospheric CO2. At present, we cannot adequately quantify how changes in weathering rates, silicate/carbonate weathering ratios, carbonate/organic carbon burial ratios, and ocean ventilation rates might alter Earth's CO2 budget. Nevertheless, uplift and erosion of mountain ranges can clearly influence chemical fluxes through the oceans and atmosphere, and thus climate, on scales of 106-107 yr.

APPENDIX 1. STEADY-STATE MASS-BALANCE EQUATIONS

Ca
$$F_{riv} + F_{hyd} = F_{carbi}$$

C $F_{riv} \delta_{riv} = F_{org} \delta_{org} + F_{carb} \delta_{carbi}$
Sr $F_{riv} \delta_{riv} + F_{hyd} \delta_{hyd} + F_{rediss} \delta_{rediss} = (F_{hyd} + F_{carb}) \delta_{oo}$

where δ = isotopic enrichment/depletion compared to modern seawater (per mille), F = fluxes to/from ocean, riv = river, hyd = hydrothermal, org = organic matter, carb = calcium carbonate, rediss = redissolution of carbonates, and oc = ocean reservoir.

APPENDIX 2. CALCULATION OF SHELL PRODUCTION RATES

Shell production rate = Fcarb + fractional area above calcite compensation depth (CCD), where $F_{carb} = 16 \times 10^{12} \text{ mol/yr (present)}$ and $= 12 \times 10^{12} \text{ mol/yr (5 Ma)}$: CCD = 4.50 km (present) and = 4.15 km (5 Ma); fractional area above CCD (fractional area above a given depth, $A[z] = [4.8z^2 - 13.9z + 23.2] \div 100$ when $z \ge 2 \text{ km}$ = 0.58 (present) and 0.48 (5 Ma); and shell production rate = $28 \times 10^{12} \text{ mol/yr (present)}$ and = 25 × 1012 mol/yr (5 Ma) (after Delaney and Boyle, 1988).

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