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LONG-TERM CONTROL OF ATMOSPHERIC CARBON DIOXIDE: LOW-TEMPERATURE SEAFLOOR ALTERATION OR TERRESTRIAL SILICATE-ROCK WEATHERING?

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ABSTRACT. Accumulation of authigenic carbonate in the basaltic ocean basement during low-temperature alteration has been proposed as a major sink for carbon in the oceans and atmosphere. François and Walker (1992) suggested that seafloor alteration, and not the terrestrial silicate-rock weathering feedback, is the most important factor determining long-term steady-state atmospheric CO_2 concentrations. They suggested that basalt dissolution and carbonate accumulation in the ocean basement is proportional to the deep-ocean hydrogen-ion and total carbon concentrations; however, they recognized that their parameterization was a first estimate that should be improved. In this work, I develop an improved parameterization and incorporate it in a global carbon-cycle model. Silicate-mineral dissolution rates have been found to be nearly independent of *p*H in the *p*H range 5 to 8 in a wide variety of experiments. Because deep-ocean *p*H is >7.5, low-temperature seafloor basalt alteration is not likely to be an effective feedback on atmospheric CO_2. If proposed terrestrial silicate-rock weathering formulations are at least approximately correct, then CO_2 consumption by terrestrial weathering is several orders of magnitude more sensitive to changes in atmosphere and ocean CO_2 concentration than is CO_2 consumption by low-temperature seafloor alteration. This suggests that silicate-rock weathering on land, and not low-temperature seafloor basalt alteration, has been the primary control on long-term atmospheric CO_2 content. Nevertheless, ocean basement carbonate accumulation should be included in global carbon budgets and may impact atmospheric CO_2 content by affecting the degassing of CO_2 during subduction zone metamorphism.

INTRODUCTION

In 1981, Walker, Hays, and Kasting published an influential paper suggesting that silicate-weathering feedbacks stabilized planetary temperature over Earth history. Atmospheric CO_2 is consumed in silicate-rock weathering on land and subsequent sedimentary carbonate accumulation. They suggested that the global rate of silicate weathering is positively correlated with global mean temperature and atmospheric CO_2 concentration, resulting in a negative feedback that modulates Earth's climate. In 1983, Berner, Lasaga, and Garrels extended this approach, taking factors such as changing seafloor generation rates, land area, and rock reservoir sizes into consideration to estimate the atmospheric CO_2 concentration over the past 100 my. Other works that extend or apply the basic principles introduced by Walker, Hays, and Kasting (1981) and

Berner, Lasaga, and Garrels (1983) include: Lasaga, Berner, and Garrels (1985); Kasting and Richardson (1985); Kasting and others (1985); Volk (1987, 1989); Schwartzman and Volk (1989); Marshall, Walker, and Kuhn (1988); Berner (1991, 1994); Caldeira and Rampino (1990, 1991, 1993); and Brady (1991). In these models, atmospheric CO_2 tends toward the concentration needed to balance atmospheric CO_2 sources and sinks, where the primary CO_2 sources are metamorphic and magmatic, and the primary CO_2 sink is terrestrial silicate-weathering and subsequent carbonate accumulation.

Staudigel and others (1989) suggested that these carbonate-silicate cycle models ignore a flux of $\sim 3 \times 10^{12}$ mol C yr^{-1} from seawater associated with the formation of authigenic carbonate in the upper layers of the ocean crust during low-temperature alteration. Authigenic carbonate cements are a widespread feature of basalt recovered from the upper layers of the basaltic ocean basement (Honnorez, 1981) and from ophiolites (Gillis and Robinson, 1990). However, the accuracy of the global flux estimate is limited primarily by the paucity of high recovery holes drilled deep into old ocean basement.

François and Walker (1992) suggested that low-temperature seafloor-basalt alteration, and not terrestrial silicate weathering, exerts the dominant long-term control on atmospheric carbon dioxide concentration. They developed a mathematical parameterization of low-temperature seafloor alteration in which the seawater-to-ocean-basement carbon flux was modeled as being proportional to the product of the deep-ocean hydrogen-ion and total dissolved inorganic carbon concentrations. François and Walker (1992) implicitly assumed that the net flux of alkalinity into the interstitial waters from basalt dissolution was equal to the flux of alkalinity to authigenic carbonate in the ocean crust.

In this work, after reviewing low-temperature seafloor alteration and silicate mineral dissolution studies, I develop a parameterization for seafloor basalt dissolution rates as a function of *p*H. Using this parameterization, I examine the likelihood that this kind of relation could be an effective feedback on long-term atmospheric CO_2 content. Then, I use this parameterization in a series of calculations, designed to compare the relative importance of seafloor basalt dissolution and silicate-rock weathering on land in modulating long-term climate. These calculations are relatively simple and schematic but qualitatively indicate that low-temperature alteration of the seafloor is unlikely to be an effective control on long-term atmospheric CO_2 content.

LOW-TEMPERATURE SEAFLOOR ALTERATION

Staudigel, Hart, and Richardson (1981) proposed a four stage model of low-temperature seafloor alteration:

Stage 1: Formation of palagonites
Stage 2: Formation of smectites
Stage 3: Formation of carbonates
Stage 4: Compaction and dehydration of the crust.

Seafloor basalt alteration commences immediately after the crust is formed as shown by the pervasive alteration of young (< 3.2 my) basalts (Muehlenbachs, 1977). During stage 1, basaltic glass is altered to palagonite, involving the formation and growth of smectite/proto-celadonite nuclei (Staudigel, Hart, and Richardson, 1981). In stage 2, more crystalline smectites, zeolites (for examples, analcite) and micas (celadonite) are formed (Burns, Swart, and Baker, 1990). Stages 1 and 2 may be complete within 3 my (Staudigel and others, 1981) but may last as long as 10 to 20 my, overlapping the stage 3 formation of carbonate minerals (Staudigel and Hart, 1985; Staudigel, Gillis, and Duncan, 1986; Staudigel, Kastner, and Sturze, 1986). Stage 3 alteration generally follows the first stages 1 and 2, as indicated by the crosscutting of vein minerals and Rb/Sr and $^{87}Sr/^{86}Sr$ dating (Burns and others, 1990). Stage 3 carbonate forms to depths of at least 550 m into the ocean basement (Staudigel, Hart, and Richardson, 1981), over a period generally lasting 10 to 15 my (Staudigel, Gillis, and Duncan, 1986; Staudigel, Kastner, and Sturze, 1986), although lasting up to 40 my in some cases (Burns, Baker, and Elderfield, 1992). Ocean basement carbonate precipitates from seawater-derived solutions involving a major contribution of basalt Ca, as indicated by elevated Ca concentrations in the interstitial waters and lower Ca content of alteration products such as smectite, palagonite, and chlorite (Staudigel, Hart, and Richardson, 1981). Stage 4 alteration, involving dehydration and settling of the ocean crust, does not cause significant changes in crustal bulk composition (Staudigel and others, 1981). For reviews of low-temperature alteration of the seafloor see Thompson (1991), Wolery and Sleep (1988), and Honnorez (1981).

Based on oxygen isotope analyses, Muehlenbachs (1980) concludes that ~ 10 percent of the seafloor is weathered to a depth of 600 m by cold seawater within about the first 10 my. After that massive circulation ceases, but some alteration of the upper parts of the crust may continue, perhaps to 20 percent, at a much slower rate, perhaps for another 25 to 50 my (Muehlenbachs, 1980).

Several studies have concluded that Ca is released to seawater during low-temperature basalt alteration (Honnorez, 1978; Lawrence, Gieskes, and Broecker, 1975). The concentration of Ca in the pore water is higher than the concentration in seawater; hence, exchanges of pore water for seawater create a net transport of Ca to the seawater. (The increases in bulk Ca content reported by Staudigel and others (1989) could be explained by lateral transport of Ca in the ocean crust, as the seafloor near hole 417A may have been a conduit for pore fluids derived from rocks whose bulk composition show Ca depletion.)

A significant, and unresolved, question is: How much of the Ca depletion in altered basalt is the result of cation exchange and how much is the result of proton adsorption? A single borehole water sample, 329 m into layer 2, was obtained from hole 418A eight yrs after it was first drilled into ~ 120 Ma seafloor (Gieskes, Hart, and Peretsman, 1988; Mottl and Gieskes, 1990). This single measurement suggests that about two thirds (69 percent) of the charge represented by the release of Ca^{2+} to the bore

hole fluids may be balanced by the uptake of Mg^{2+}, K^+, Na^+, and SO_4^{2-} by the basalts and/or clays. At Site 395A, in 10 my old seafloor, far more Mg^{2+} is removed from the bore hole fluids than Ca^{2+} is added. This may be explained by Mg^{2+}-for Ca^{2+} exchange, followed by Ca^{2+} uptake by precipitating carbonate (McDuff, 1984).

Ocean basement carbonate precipitation generally seems to occur in relatively open systems, with seawater circulating rapidly enough to maintain pore-fluid chemistry, $\partial^{18}O$, and $^{87}Sr/^{86}Sr$ ratios similar to that of contemporaneous seawater (Anderson and Lawrence, 1976; Anderson, 1980; McKenzie, 1980; Staudigel, Hart, and Richardson, 1981; Staudigel and others, 1981). Hence, the timing and duration of carbonate precipitation can be estimated by comparing the $^{87}Sr/^{86}Sr$ ratios in the precipitated carbonate with Cenozoic/Mesozoic Sr-isotope curves (Hart and Staudigel, 1978, 1979, 1983; Staudigel, Kastner, and Sturze, 1986). The circulation of seawater through the seafloor would permit the transport of seawater Ca to the interstitial waters.

The deepest ocean waters typically have carbonate-ion concentrations within 10 to 20 μmol $[CO_3^{2-}]$ kg^{-1} of calcite saturation, with a typical $[CO_3^{2-}]$ in the range of 80 to 100 μmol kg^{-1} (Broecker and Peng, 1983). During stage 3 alteration, carbonate minerals accumulate in the upper layers of the ocean crust at temperatures up to 40°C. As seawater is heated from 2° to 40°C, the carbonate-ion concentration increases by over 20 percent (calculated from Stumm and Morgan (1981) and references therein), and the apparent solubility product of calcite decreases by over 5 percent (Mucci, 1983). Hence, temperature effects alone could saturate seawater flowing through cracks in the ocean crust and cause the calcium and carbonate-ion in the seawater to precipitate. This would require rapid exchange of seawater for interstitial water (that is, an interstitial water residence time, τ, of less than 100 yr); otherwise, the removal of 3×10^{12} mol yr^{-1} of calcium carbonate from the interstitial water would quickly undersaturate the interstitial water with respect to calcite. However, the alkalinity and Ca concentrations in the interstitial waters are generally higher than in seawater (Sayles and Manheim, 1975; Garrison, 1981; Gieskes, Hart, and Peretsman, 1988; Mottl and Gieskes, 1990); hence, the net alkalinity and Ca transport is probably from seafloor basalt to ocean basement carbonate. Nevertheless, it is not clear what fraction of the alkalinity flux to ocean basement carbonate is derived from the basement and what fraction is from seawater.

One approach to the problem of assessing the net flux of materials into or out of basalts at low-temperature has been to examine pore water profiles in the overlying sediments. In sediment-covered ocean basement, submarine weathering of basalt to authigenic clays or zeolites increases calcium and alkalinity in the interstitial waters (Sayles and Manheim, 1975; Garrison, 1981). Lawrence, Gieskes, and Broecker (1975) estimated chemical and isotopic gradients in sediment pore waters, which they interpreted as the result of fluxes from low-temperature alteration of the underlying seafloor, near the Equatorial Pacific Clipper-

ton Fracture Zone. These sites show pore water concentrations indicating that the charge flux from the ocean basement associated with Ca^{2+} diffusion is balanced by a comparable charge flux from Mg^{2+} and K^{+} to the basement. This suggests that cation exchange and not hydrogen-ion adsorption is the primary mode of ocean crust alteration at this site. The Ca^{2+} gradients may be explained by exchange of Mg, K, or Na for Ca during low-temperature basalt alteration. At nearby DSDP Sites 42, 69, 72, 73, and 74, Ca^{2+} and Mg^{2+} concentration gradients are much less than that observed at sites nearer the fracture zone (sites 70 and 71) indicating that the permeability of the basement is a dominant factor in determining the extent of low-temperature basalt alteration. Other sediment porewater studies have also concluded that cation exchange can best explain the inferred major ion fluxes into and out of the underlying basalts (Thompson, 1973; Robinson and others, 1977; Kastner and Gieskes, 1976; Sayles and Manheim, 1975). Hence, much of the alkalinity flux to ocean basement carbonate may ultimately derive from the ocean and not seafloor basalt.

ESTIMATING ELEMENTAL MASSES AND FLUXES

While carbonate veins, vesicles, amygdules, and cements in and among seafloor basalts are relatively common, there are remarkably few data to constrain the net fluxes of materials into or out of the seafloor during low-temperature alteration (see Wolery and Sleep, 1988, for review). Many studies of low-temperature seafloor alteration have been made (Hart, 1970, 1973; Staudigel, Hart, and Richardson, 1981; Staudigel and others, 1989; Burns, Swart, and Baker, 1990; Gillis and Robinson, 1990). Nevertheless, elemental fluxes into and out of the seafloor basement during low-temperature seafloor alteration are poorly constrained because: (1) many studies of seafloor basalt have proceeded with the intent of gaining an understanding of mantle and/or mid-ocean-ridge processes, therefore the least altered samples were selected for study; (2) many studies have chosen to focus on a particular seafloor component (for example, basalts, clays, zeolite, or carbonate) and have not attempted to develop an estimate of the bulk composition of the upper layers of the basaltic seafloor basement; (3) most drill holes have had poor recovery in basalts, introducing possible sampling biases; (4) most drill holes have not penetrated very deep into old seafloor basalts, hence measurements of the upper layers of the ocean crust must be extrapolated to depth; (5) in sediment pore-water studies, it is often difficult to segregate fluxes into and out of the seafloor from the diagenetic fluxes in the sediments; (6) borehole fluid studies have been hampered by vertical mixing and the difficulties of segregating alteration signals from the effects of drilling. Furthermore, studies applying these varying techniques often lead to contradictory conclusions regarding fluxes into or out of the seafloor. Some of these apparent contradictions may point to an inherent heterogeneity in low-temperature alteration of the seafloor.

Staudigel and others (1989) is the only study at the time of this writing that has attempted to quantify the global rate of formation of carbonate in the veins, vesicles, amygdules and cements in and among seafloor basalts. For that study, a "Super Composite" bulk rock was developed using representative samples from the upper 200 m of Deep Sea Drilling Project hole 417A, the upper 295 m of hole 417D, and the 536 m of hole 418A. Hole 417A penetrated 206 m into the oceanic basement, recovering among the most altered basaltic lava ever drilled by DSDP. Basalt recovered from this hole exhibited the most extensive alteration of any DSDP site studied by Muehlenbachs (1986) with a basaltic $\partial^{18}O$ of 13.9 permil, indicating that ~40 percent of the original rock mass recovered at this site has been weathered. Analyses of the top one-third of site 417A indicate that this interval is nearly totally weathered. The least altered sample is a massive flow near the bottom of the hole indicating 5 to 10 percent weathering (Muehlenbachs, 1980). The material that was recovered from hole 417D, only 450 m away from hole 417A, was generally much less altered, and very fresh samples of ocean basalt were recovered from hole 418A, only 7.5 km away (Honnorez, 1981). Hole 417A was drilled into a topographic high that may have functioned for ~20 my as a conduit for thermally driven circulation of warm (30°C) seawater (Donnelly, Thompson, and Richardson, 1979).

I developed an exponential least squares curve fit to the "depth composite" data of Staudigel and others (1989), yielding the following equation for bulk CO_2 wt percent as a function of depth, z, below the ocean basement/sediment interface:

$$CO_2 \text{ wt } \% = 5.27\% \text{ Exp}\left(\frac{-z}{280 \text{ m}}\right). \quad (1)$$

According to this expression, the value of degassed mid-ocean-ridge basalt (=0.045 wt percent CO_2; Gerlach, 1989) is reached at a depth of 1334 m. Using this regression equation, a basalt density of 2.6 g cc^{-1} and a seafloor production rate of 3.45 $km^2\ yr^{-1}$, I calculate that carbon uptake by degassed seafloor basalts may be $\sim 2.9 \times 10^{12}$ mol yr^{-1}. Based on $\partial^{18}O$ analyses, hole 417A is the most heavily altered seafloor drilled by the DSDP, whereas holes 417D and 418A appear typical of old seafloor (Muehlenbachs, 1986). However, eliminating the highly altered hole 417A from the analysis reduces the estimated seafloor carbon uptake by less than 5 percent.

The method of Staudigel and others (1989) produces an estimated degassed seafloor carbon uptake of 3.2×10^{12} mol yr^{-1}. The similarity of these two estimates (no surprise, since they were computed from the same data by a different method) suggests that the rate of carbon uptake by degassed basalts may be $\sim 3 \times 10^{12}$ mol yr^{-1}. Whereas there may be questions about sampling biases (Staudigel and others, 1989) and the appropriateness of extrapolating to the entire planet based on three closely spaced holes, nevertheless, an estimate of 3×10^{12} mol yr^{-1} will be

adopted for this study as today's accumulation rate of carbonate carbon in the ocean basement ($F^{C}_{ic,0}$).

Most of this carbon flux to the seafloor is probably the result of advected, not diffusive, transport of seawater into the seafloor. Lawrence and Gieskes (1981) found that the average Ca^{2+} gradient in sediments overlying the basaltic basement were ~ 8 mol m^{-3} per 100 m sediment. The Ca^{2+} gradients were accompanied by oxygen-isotope gradients indicating that both gradients were produced by the alteration of volcanic ash or seafloor basalts. The Ca^{2+} concentrations measured nearest the ocean basement ranged from 10.2 to 145 mol m^{-3} and averaged 35.4 mol m^{-3}, similar to the basalt pore water value measured in hole 418A. These porewater gradients are present in the sediments because the primary mode of transport in sediment porewater is diffusion and not advection. Using a diffusion coefficient of 5×10^{-6} cm^2 s^{-1} (Lawrence, Gieskes, and Broecker, 1975), we can calculate a diffusive Ca flux of $\sim 1.3 \times 10^{-3}$ mol m^{-2} yr^{-1} or less than 0.5×10^{12} mol yr^{-1} if this flux were maintained over the entire ocean. The diffusion coefficient for HCO_3^- is ~ 1.5 times that for Ca^{2+} (Li and Gregory, 1974), but the concentration gradient is at least an order of magnitude less—a difference of ~ 25 mol m^{-3} for Ca, compared to < 2.5 mol m^{-3} for HCO_3^-. Hence, the diffusive flux of CO_2 into the ocean basement is less than 0.1×10^{12} mol yr^{-1}. If the diffusive flux of carbon through seafloor sediments is $< 0.1 \times 10^{12}$ mol yr^{-1} and we accept a value of $\sim 3 \times 10^{12}$ mol yr^{-1} for the carbon flux from seawater to ocean basement cements, then advective transport must be the primary mode of transferring ocean carbon to basement interstitial waters. If the stage 3 carbonate flux is $\sim 3 \times 10^{12}$ mol yr^{-1} and if this carbon comes from seawater with a total dissolved carbon values of ~ 2.3 mol m^{-3}, then the flux of seawater into the basaltic basement during low-temperature alteration must be at least 1.3×10^{12} m^3 yr^{-1}. This estimate would be twice as high if only half the seawater ΣCO_2 is precipitated as carbonate.

ESTIMATING GLOBAL LAYER 2A PORE SPACE

In order to model ocean basement pore waters, it is important to quantify the size of this reservoir. Only one hole has penetrated to a depth of more than 700 m in the ocean crust (DSDP hole 504B), and the density of only one hole in basement older than 10 my has been thoroughly investigated (DSDP hole 418A; Salisbury and others, 1986). Because of the lack of *in situ* data, porosity of ocean basement must be largely inferred from seismic velocity data (Carlson and Herrick, 1990). Seismic studies indicate that the ocean basement may be divided into two layers: layer 3 corresponds to gabbro complex constituting the bulk of the ocean crust, and layer 2 corresponds to the extrusive pile overlying the gabbro complex. Layer 2 shows some stratification into three layers: layer 2a, 2b and 2c, corresponding to seismic velocities of about 3.6, 5.2, and 6.1 km s^{-1}, respectively (Houtz and Ewing, 1976). In hole 504B, layer 2a represents the interval of high permeability and porosity and low-temperature alteration (Carlson and Herrick, 1990). As the ocean

crust ages, velocities in layer 2a increase and the layer gradually disappears (Purdy and Ewing, 1986), owing to the infilling and sealing of cracks and voids by alteration products (Carlson and Herrick, 1990). Layer 2b is an interval of lower porosity, markedly reduced permeability, and higher temperature alteration. The top of layer 2c corresponds to the top of the sheeted dike complex, the first appearance of greenschist facies, and markedly reduced porosity (Anderson and others, 1982; Alt, Laverne, and Muehlenbachs, 1985).

The trend in oxygen isotopes as a function of age observed in seafloor basalts is similar to the age trend in seismic velocity measured in the acoustic basement. This indicates that both trends may be explained by low-temperature alteration or weathering of the ocean basement (Muehlenbachs, 1980). As layer 2a becomes progressively altered, it thins and becomes less porous. Carlson and Herrick (1990) re-analyzed the data of Houtz and Ewing (1976) and concluded that the fractional porosity (f_p) of layer 2a may be represented:

$$f_p = (0.35 \pm 0.02) - (0.005 \pm 0.001 \text{ my}^{-1})t, \quad (2)$$

where t is the age of seafloor in my, and 0 my $< t <$ 30 my. Carbonate sediments may fill in some small fraction of the pore space in the uppermost part of the ocean basement. For example, DSDP hole 373A penetrated 187 m of basaltic breccias and flow rock in the central Tyrrhenian basin. Bernoulli, Garrison, and McKenzie (1978) found pelagic sediment in quantity in voids in the ocean basement to depths of ~40 m and in small amounts to at least 70 m. If this effect is important generally, its importance is probably limited to the uppermost part of the ocean basement and, hence, will not be considered here.

Carlson and Herrick (1990) concluded that layer 2a thickness (z) for Atlantic ridges may be represented:

$$z_{Atl} = (1.66 \pm 0.18 \text{ km}) - (0.034 \pm 0.012 \text{ km my}^{-1})t, \quad (3)$$

and, for Pacific ridges,

$$z_{Pac} = (0.77 \pm 0.04 \text{ km}) - (0.020 \pm 0.003 \text{ km my}^{-1})t. \quad (4)$$

If the carbonate percentages measured in the drilled portion of the seafloor continued to the original depth of layer 2a, then the 3×10^{12} mol carbonate yr^{-1} estimate could be low by nearly a factor of 2. Layer 2a in young Atlantic ocean floor is generally twice as thick as it is in young Pacific ocean floor, but Atlantic seafloor produces approximately half as fast as Pacific seafloor. Hence, layer 2a may be produced at approximately the same rate at both Atlantic and Pacific ridges (Houtz and Ewing, 1976). This suggests that the production rate of pore space in layer 2a may be independent of seafloor generation rate.

Atlantic ridges spread at an average rate of 1.7 cm yr^{-1}, whereas Pacific ridges spread at an average rate of 4.8 cm yr^{-1} (calculated from data in Kominz, 1984). From these data and the above formulations we

can calculate that Atlantic ridges produce ~ 9.9 km^3 my^{-1} of pore space per km of ridge length and Pacific ridges ~ 12.9 km^3 my^{-1} of pore space per km of ridge length. Whereas the above regressions are based on data from seafloor younger than 30 my old, they may be integrated to the zero porosity intercepts (Atlantic = 48.8 my, Pacific = 38.5 my) to get a rough idea at the total unfilled layer 2a pore space. This integration yields 217 km^3 of unfilled layer 2a pore space per km Atlantic ridge and 229 km^3 of unfilled pore space per km Pacific ridge—virtually identical given the magnitude of possible errors introduced in such a calculation. Total ridge length is $\sim 4.9 \times 10^5$ km (Kominz, 1984), which suggests that there is on the order of 10^7 km^3 of pore space in layer 2a—roughly equivalent in volume to a layer under the entire ocean of ~ 35 m depth. Dividing the pore space by the pore production rate yields time constants of 21.9 my (Atlantic) and 17.8 my (Pacific) for the reduction in porosity with age. Given the possible errors involved, the difference in these time constants is probably not significant. On a basis of these calculations, we can estimate that globally ~ 0.5 km^3 of layer 2a pore space is created and filled by authigenic materials each year.

ESTIMATING DISSOLUTION RATES AS A FUNCTION OF *PH* AND $[\Sigma CO_2]$

Several factors have been suggested as being important in determining the rate and extent of alteration of ocean crust at low temperature. Honnorez (1981) proposed that, for a given temperature and pressure, the rate and intensity of seafloor weathering is essentially controlled by the rate at which unaltered seawater flows through the upper layers of the ocean basement. The flow of seawater increases with the effective porosity and permeability of the rock. Muehlenbachs (1980) concluded that the rate and timing of low-temperature seafloor alteration are governed by changes in the permeability of layer 2 of the ocean crust and the rate of reaction of seawater with basalt. The process of low-temperature seafloor basalt alteration can proceed as long as the seafloor basalts remains open to the circulation of seawater, allowing the removal of altered solutions from the sites of alteration. The burial of the seafloor basalts by pelagic sediments and younger lavas and the sealing off of cracks and intergranular spaces by authigenic materials will tend to reduce seawater circulation and reduce the rate and intensity of seafloor alteration (Honnorez, 1981).

François and Walker (1992) suggested that the seafloor "weathering" rate of basalt is proportional to the product of the hydrogen ion (H^+) and total dissolved inorganic carbon (ΣCO_2) concentrations:

$$F = 3 \times 10^{12} \text{ mol yr}^{-1} \left(\frac{[H^+]}{[H^+]_0}\right)\left(\frac{[\Sigma CO_2]}{[\Sigma CO_2]_0}\right) \quad (5)$$

The rationale behind this parameterization was that two hydrogen ions may replace a divalent cation (principally Ca^{++} or Mg^{++}), and then carbonate may precipitate in fractures or within the matrix of the seafloor

basalt. The proportionality with $[H^+]$ may have been intended to capture the seafloor weathering step, and the proportionality with $[\Sigma CO_2]$ may have been intended to capture the carbonate precipitation step. This formulation was an attempt to capture controls on large-scale seafloor alteration processes.

By assuming that the rate scales directly with the hydrogen-ion concentration, François and Walker (1992) suggested that the dissolution rates of plagioclase, pyroxene, and olivine are directly dependent on hydrogen-ion concentration. Direct comparison to laboratory experiments may not be justified; yet, given the paucity of evidence directly from the natural system, laboratory experiments constitute the primary body of available information. Such laboratory experiments have been shown to yield insight into the dynamics of silicate weathering on land (Velbel, 1993a) and may yield similar insight into the dynamics of low-temperature seafloor alteration.

Ample evidence in the literature suggests that the rate dependence for silicate dissolution can be modeled by the following equation:

$$\text{Rate} = k_H[H^+]^{n_H} + R_T + k_{OH}[OH^-]^{n_{OH}}, \quad (6)$$

(Helgeson, Murphy, and Aagaard, 1984; Wollast and Chou, 1984; Wogelius and Walther, 1991), where each term represents a different independent mechanism of dissolution: k_H is the hydrogen-ion dependent rate constant (usually the dominant term in the acid *p*H-dependent region), R_T is the dominant term in the dissolution rate in the *p*H-independent region, and k_{OH} is the hydroxyl-ion dependent rate constant (usually the dominant term in the basic *p*H-dependent region). The general shape of many silicate mineral dissolution curves is roughly U-shaped when plotted in log dissolution rate-*p*H space (Lasaga, 1984). Typically, dissolution rates in dilute solutions increase as *p*H increases above about 8 and increase as *p*H decreases below about 3 to 6, depending on the mineral under consideration.

Silicate dissolution rates generally show no strong dependence on *p*H in waters of near neutral *p*H, and, in cases where silicate dissolution rates do show a *p*H dependence in the seawater *p*H range ($7.5 < p\text{H} < 8.4$;Sverdrup, Johnson, and Fleming, 1942), dissolution rates generally decrease with increasing hydrogen-ion concentration. For example, Helgeson, Murphy, and Aagaard (1984) concluded that feldspar dissolution rates at 25°C are not sensitive to *p*H variation in the range from *p*H 3 and 8. Knauss and Wolery observed that the rate of albite dissolution at 70°C showed no dependence on *p*H when $5 < p\text{H} < 8$. Chou and Wollast (1985) also showed no *p*H dependence for albite dissolution between a *p*H of 5 and 8. However, Blum and Lasaga (1991) suggest that albite dissolution rates, in the presence of dissolved atmospheric pCO_2, are inversely correlated with hydrogen-ion concentration when *p*H is greater than ~7 but are correlated with hydrogen-ion concentration when *p*H is less than ~7. Within the limits of the data,

nepheline exhibits dissolution behavior similar to that observed in albite (Tole and others, 1986). Blum and Lasaga (1988) did not do experiments in the *p*H range between about 5 and 9; however, they found that olivine dissolution rates were negatively correlated with *p*H for *p*H < 5 and positively correlated with *p*H for *p*H > 9. Wogelius and Walther (1991) found very little *p*H dependence for olivine dissolution between *p*H 6 and 8 for olivine at 25°C. Quartz dissolution rates show no *p*H dependence in the acid *p*H range and are positively correlated with *p*H in the basic range (Brady and Walther, 1989).

Rimstidt and Dove (1986) did find a very slow wollastonite dissolution rate for which they could find no obvious explanation in an experiment at *p*H = 7.93. This led them to suggest that wollastonite dissolution rates may be proportional to hydrogen-ion concentration in the *p*H range of about 6 to 8. However, this suggestion was largely based on a single data point, this dissolution behavior has not been observed in other experiments or in other minerals, and seafloor basalts are not composed of wollastonite. For these reasons, it is unlikely that seafloor basalt dissolution would follow such a rate law.

By assuming that the rate scales directly with the total dissolved carbon concentration, François and Walker (1992) suggested that the dissolution rates of plagioclase, pyroxene, and olivine are correlated with total dissolved carbon concentration. However, from a study of olivine dissolution at 25°C in water in equilibrium with the atmosphere, it appears that in basic solutions with dissolved CO_2, carbonate-ions are adsorbed from the fluid forming a complex on the mineral surface that protects the rate-limiting Si–O bond from solvent attack (Wogelius and Walther, 1991). In waters that are virtually free of dissolved CO_2 ($pCO_2 < 10^{-4.5}$) with *p*H > 8, the $[OH^-]$ term in eq (4) usually dominates the dissolution rate, but with CO_2, the $[OH^-]$ term becomes negligible. Dissolved CO_2 appears to have no effect on olivine dissolution rates in the neutral or acid *p*H range. Hence, in interstitial waters in the ocean basement, the $[OH^-]$ dependent term in eq (6) is probably not a significant factor, and, following Wogelius and Walther (1991), the dissolution rate may be described by an equation of the form:

$$\text{Rate} = k_H[H^+]^{n_H} + R_T. \tag{7}$$

In addition, if we were to allow the $[OH^-]$ dependent-term as in eq (6), increasing the oceanic hydrogen-ion concentration from present values would tend to decrease seafloor basalt dissolution rates, which is opposite to the direction suggested by François and Walker (1992). Hence, the assumption that the [OH] dependent term is not important in low-temperature seafloor alteration is conservative, because a negative correlation between *p*H and dissolution rates in the *p*H range of interstitial waters in the ocean crust would work against the hypothesis of François and Walker (1992).

The value of n_H is typically less than unity. Schweda (1990) studied the dissolution rate of sanidine at *p*H 5.7, 4, and 3, both in pure HCl and 10^{-2} M NaCl. He found that increasing the ionic strength of the solution did not affect dissolution rate at *p*H 5.7. However, at *p*H 4 and 3, the dissolution rates in the NaCl solution was 68 and 45 percent, respectively, that of the pure HCl solution. This indicates that the value of n_H may be lower in high ionic strength solutons such as seawater. However, Brady and Walther (1992) suggest that n_H may increase with ionic strength. Despite this uncertainty, the value of n_H will be 0.5 in this model. The qualitative results of this model are insensitive to the value of n_H; they depend only on the dissolution rate of seafloor basalts being relatively insensitive to *p*H changes near deep-ocean seawater *p*H values (*p*H > 7.5; for example, Sverdrup, Johnson and Fleming, 1942).

For the purpose of this model, we will assume (1) that at *p*H = 6, the rate contribution to basalt dissolution from the R_T term in eq (7) is equal to the hydrogen-ion concentration term, and (2) that at low *p*H, seafloor basalt weathering rates scale with the square-root of hydrogen-ion concentration. These considerations yield the following parameterization for relative basalt dissolution rate per unit mineral surface area:

$$f_{bi} = k_{bi}([H^+]_i^{0.5} + 10^{-3}), \tag{8}$$

where k_{bi} is a normalization constant such that $f_{bi} = 1$ at the present (that is, $k_{bi} = ([H^+]_{i,0}^{0.5} + 10^{-3})^{-1}$), and $[H^+]_i$ is the hydrogen-ion concentration in the ocean-crust interstitial water. This formulation produces an increase in dissolution rate of ~80 percent as *p*H in solution drops from 8 to 6. This is approximately the increase in dissolution rate in the curve fit of Wogelius and Walther (1991) to olivine dissolution data at 25°C in solutions at equilibrium with atmospheric CO_2.

ESTIMATING SENSITIVITIES TO CHANGES IN ATMOSPHERIC CO_2 CONTENT

To estimate the relative sensitivity of low-temperature seafloor alteration versus silicate-rock weathering on land to changes in atmospheric CO_2 content, I employ a hierarchy of models (fig. 1). The first and simplest calculation (using ocean pH model) makes the approximation that seafloor-basalt interstitial water chemistry is the same as that of deep-ocean water. Given a change in oceanic dissolved inorganic carbon concentrations, using Berner's (1991) silicate-rock weathering formulation, I estimate the relative change in the alkalinity flux from both terrestrial silicate weathering and seafloor basalt dissolution. The second calculation (using a simple porewater model) is like the first, except that ocean-basement interstitial water is represented by a single box whose chemistry is determined by seawater composition and the rates of basalt dissolution and carbonate precipitation in the ocean basement. Both these calculations hold ocean alkalinity constant. The third calculation (the carbonate-silicate with porewater reservoir model) is like the first two, except that it utilizes parameterizations of riverine fluxes and shallow- and deep-water carbonate accumulation to estimate changes in

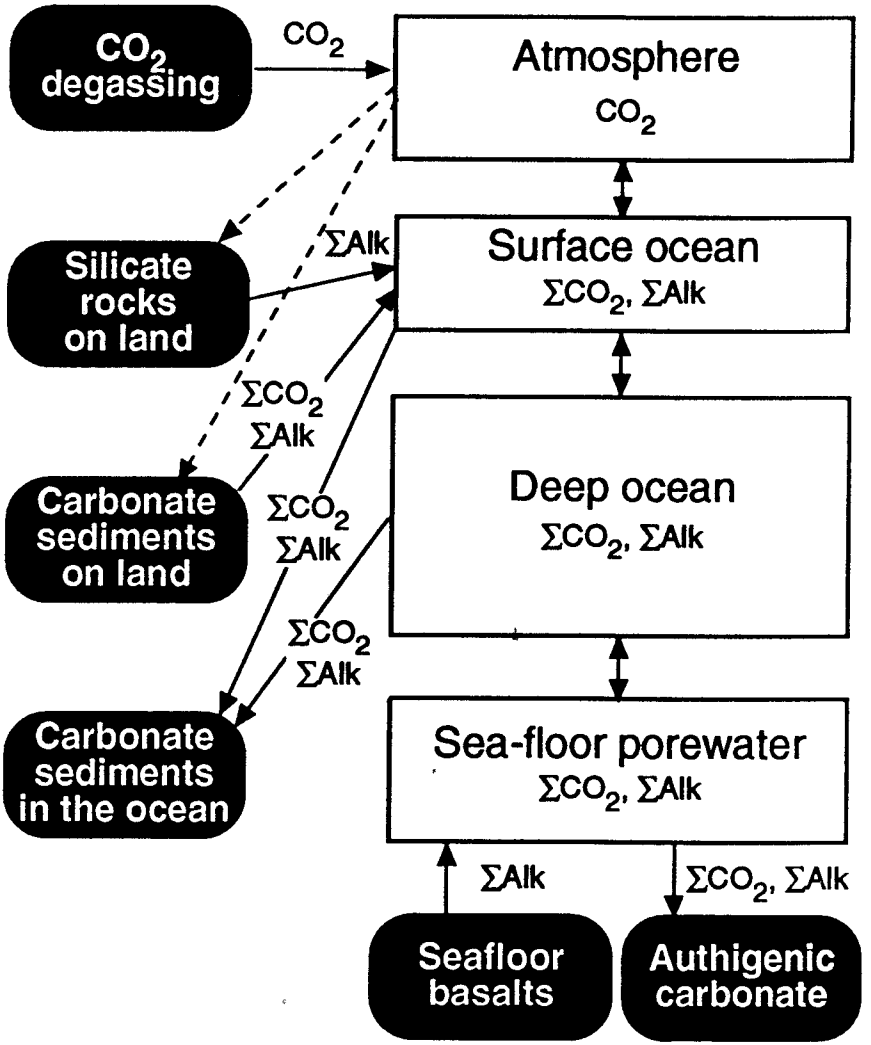

Fig. 1. Conceptual framework for the three calculations performed here. Solid lines represent fluxes of carbon and/or alkalinity. Dashed lines indicate rate controlling influences. (1) In the first calculation ("Approximating seafloor-basalt interstitial water with deep-ocean water"), the chemistry of seafloor basalt interstitial water is approximated as being the same as that of the deep-ocean. The concentration of total dissolved CO_2 (ΣCO_2) is varied by the same amount in the surface and deep ocean, at constant alkalinity. The atmospheric partial pressure of CO_2 is taken to be the same as that in the surface ocean. This partial pressure of atmospheric CO_2 is used to estimate the alkalinity flux from the weathering of silicate rocks on land using the formulation of Berner (1991). The change in deep-ocean $[\Sigma CO_2]$ is used to calculate a change in deep-ocean pH, which is then used to estimate the alkalinity flux from the basalt weathering in the seafloor using a formulation developed here. (2) In the second calculation ("A simple seafloor-basalt interstitial water model"), the interstitial water total alkalinity and $[\Sigma CO_2]$ vary due to basalt dissolution, authigenic carbonate formation; and exchange between seawater and the interstitial pore water. (3) In the third calculation ("A carbonate-silicate model with seafloor-basalt interstitial water"), ocean alkalinity is permitted to change due to silicate rock weathering on land, and interactions involving the sedimentary carbonate system.

ocean alkalinity. That all these calculations give the same qualitative result indicates that the basic conclusions are robust and do not rely on any single model parameter.

Approximating Seafloor-basalt Interstitial Water with Deep-ocean Water

A simple calculation can answer the question of how much deep ocean pH would have to change to compensate for a 50 percent increase in the total CO_2 degassing rate, if the terrestrial silicate-rock weathering feedback did not function. (Cretaceous CO_2 degassing rates may have been greater than this, Berner, 1991.) If today's degassing rate balances the present day riverine silicate-weathering fluxes ($\sim 6 \times 10^{12}$ mol CO_2 yr^{-1}) and seafloor basalt dissolution ($\sim 3 \times 10^{12}$ mol CO_2 yr^{-1}), then today's degassing flux (without that fraction associated with the organic carbon cycle) may be $\sim 9 \times 10^{12}$ mol CO_2 yr^{-1}. Hence, to balance a 50 percent increase in degassing rates ($\sim 4.5 \times 10^{12}$ mol CO_2 yr^{-1}), seafloor basalt dissolution would have to increase by ~ 150 percent. Using the conservatively constructed eq (8) and a deep-ocean pH of 8, we can calculate that this 150 percent increase would require a pH shift of ~ 2.5 pH units. If the carbonate-ion concentration is fixed by the sedimentary carbonate system, then calcite saturated ocean with a pH of 5.5 would have a dissolved aqueous CO_2 concentration and pCO_2 that is $\sim 10^5$ times today's concentration. Such a CO_2 partial pressure for the Cretaceous would be unreasonably high.

The question may be posed: in a situation where oceanic alkalinity and surface-to-deep carbon concentration gradients are constant, which would be more sensitive to changes in CO_2 concentrations: proposed terrestrial silicate rock weathering rate formulations or the seafloor basalt dissolution rate formulation proposed here? A more detailed analysis is to follow, but a simplified approach can yield an answer to this question.

The sensitivity of this seafloor basalt alkalinity flux to changing ocean total carbon concentration can be roughly estimated using (1) the estimate of $\sim 3 \times 10^{12}$ mol yr^{-1} for the ocean basement carbonate accumulation rate, (2) the implicit assumption of François and Walker (1992) that the net alkalinity flux to this authigenic carbonate is equal to the net alkalinity flux to the interstitial waters from basalt dissolution, (3) the parameterization of this flux as proportional to the seafloor basalt dissolution rate as represented by eq (8), and (4) deep water pH as a proxy for interstitial water pH. This last simplification is conservative, because interstitial pore waters generally have a higher pH and alkalinity than seawater (Sayles and Manheim, 1975; Garrison, 1981), putting the interstitial waters into a pH region in which basalt dissolution is less sensitive to pH variation.

Using the equations in app. 1, the change in both terrestrial silicate-rock weathering rate and seafloor basalt dissolution rate can be calculated for any specified change in surface and deep ocean ΣCO_2 concentration. Changing oceanic ΣCO_2 concentrations changes deep-ocean pH

and mixed-layer pCO_2. The results are plotted against both these variables in figure 2.

These results indicate that, in response to a change in ocean carbon content, the alkalinity flux from terrestrial weathering will change over an order of magnitude more than the alkalinity flux from seafloor alteration. Because the uncertainty in the response of silicate-rock weathering to changing atmospheric pCO_2 is greater than 10 percent, a first order approximation of the functional relation between CO_2 consumption and ocean-atmosphere CO_2 concentrations, for ocean pH > 7, may ignore variations in low-temperature seafloor alteration rates.

A Simple Seafloor-basalt Interstitial Water Model

Motivation and description.—The chemical composition of the interstitial waters are influenced by the composition of the incoming seawater, the weathering of seafloor basalts, and the accumulation of authigenic carbonate. It is important to distinguish ocean basement carbonate accumulation from ocean basement basalt dissolution. Authigenic ocean basement carbonate formation would be promoted by high carbonate-ion concentrations, typical of seawater with low ΣCO_2 concentrations or high alkalinity. Seafloor basalt dissolution would be promoted by low pH (<5), which would be characteristic of altered seawater with very high ΣCO_2 concentrations, or very low alkalinity. Hence, factors that promote greater authigenic carbonate formation may impede seafloor basalt dissolution.

Convection of fluids in layer 2a is the primary mode of water transport (Lawrence and Gieskes, 1981). Unfortunately, it is difficult to make quantitative bulk estimates of this fluid flow in old crust (Staudigel and Hart, 1985), and the residence time of interstitial water in the ocean basement is not well constrained. Authigenic carbonate is thought to precipitate from relatively unaltered seawater, as indicated by fluid chemistry, $\partial^{18}O$, and $^{87}Sr/^{86}Sr$ ratios (Anderson and Lawrence, 1976; Anderson, 1980; McKenzie, 1980; Staudigel, Hart, and Richardson, 1981; Staudigel and others, 1981). Two constraints on the interstitial water residence time (τ) are that τ be short enough, so that the chemistry and isotopic composition of the interstitial waters are not markedly different from contemporaneous seawater values, and τ be long enough so that weathering of seafloor basalts can alter the chemistry of the interstitial waters sufficiently to promote the observed calcite precipitation. If τ were greater than 10^4 yr, then a carbonate precipitation rate of 3×10^{12} mol C yr^{-1} would more than exhaust the available flux of seawater carbon to the seafloor. If τ were less than 10^2 yr and basalt dissolution produced an alkalinity flux of $\sim 6 \times 10^{12}$ eq yr^{-1}, then basalt dissolution would not alter pore water chemistry sufficiently to saturate the interstitial waters with respect to calcite at 25°C. In this study, we use a value for τ of 10^3 yr.

To prevent a major imbalance in the Ca cycle, the return flow of altered seawater to the ocean must have Ca concentrations within a few

mol m^{-3} of the seawater value. Interstitial fluids from holes 418A and 395A had Ca^{2+} concentrations 37.3 and 1.8 mol m^{-3}, respectively, greater than the seawater value of ~10.6 mol m^{-3} (Mottl and Gieskes, 1990; Gieskes and Peretsman, 1988; McDuff, 1984). If we take this lower value as representative of layer 2a pore fluids during low-temperature alteration and the interstitial water flux out of the ocean basement is at least 1.3×10^{12} m^3 yr^{-1}, then the net Ca flux to the ocean would be 2.3×10^{12} mol yr^{-1}. If the mean Ca^{2+} concentration in the layer 2a pore fluids were on average very much higher than seawater values such as at hole 418A, then the calculated flux of Ca^{2+} to the oceans would greatly exceed all other known Ca sources—an unreasonable situation. This indicates that, as seawater is advected into the ocean basement, CO_3^{2-} concentration increases are likely to be much more important than Ca concentration increases in promoting authigenic carbonate precipitation.

In this model, layer 2a interstitial waters are represented by a single reservoir (fig. 1). This is no doubt a gross simplification as there are likely micro-environments in layer 2a with fluid chemistry differing markedly from the bulk interstitial water chemistry. The heterogeneity of $^{87}Sr/^{86}Sr$ ratios measured in some DSDP cores (hole 504B; Staudigel and Hart, 1985) indicates that some of the interstitial waters in layer 2a are relatively isolated from exchange with ocean waters. Nevertheless, a simple, single pore-water reservoir model should be able to capture some of the basic dynamics of chemical exchanges associated with low-temperature seafloor alteration and carbonate precipitation.

The net flux of alkalinity from seawater to the basement interstitial waters (F_{di}^{A}) is poorly constrained. The net negative charge flux of carbonate and bicarbonate-ions transported to the basement porewaters may be largely balanced by a corresponding flux of cations, such as Mg^{2+}, K^+, and Ca^{2+}, or by a corresponding flux of protons. Because pore water alkalinities are often greater than seawater values, there may be a net flux of alkalinity from the ocean basement to seawater, which would require the net proton flux from the ocean to layer 2a to exceed the charge flux carried by carbonate and bicarbonate ions. For the purpose of this study we will adopt the implicit assumption of François and Walker (1992) that the negative charge flux of carbonate and bicarbonate ions transported to ocean crust is balanced by a corresponding proton flux; hence, in the present-day steady state, there is assumed to be no net transfer of alkalinity between the ocean and the ocean crust at low-temperature. Because some of the alkalinity flux to ocean basement carbonate probably comes from seawater and not from seafloor basalts, this assumption probably overestimates the importance of seafloor alteration in the global alkalinity cycle. This assumption makes low-temperature alteration of the seafloor roughly equivalent to terrestrial weathering followed by sedimentary carbonate accumulation, in the sense that it provides a sink for ocean-atmosphere carbon without extracting alkalinity from the ocean reservoir.

The equations describing this model may be found in app. 2.

Results and discussion.—The steady-state response of this model to varying deep-ocean total dissolved carbon concentration at constant alkalinity are presented graphically in figures 2 and 3. Model results for the dimensionless rates of authigenic seafloor carbonate precipitation (f_{ic}) and basalt dissolution (f_{bi}) rates are plotted against deep ocean *p*H in figure 3A. The model results are unlikely to be numerically accurate, nevertheless, the qualitative results may represent how the upper layers of the seafloor would respond to a change in ocean carbon concentration and *p*H. Low *p*H and high total dissolved carbon could be expected if the CO_2 supply to the ocean-atmosphere system were enhanced and terrestrial weathering did not supply an additional flux of alkalinity from silicate weathering. In this case, the deep-ocean and interstial water carbonate-ion concentrations are greatly reduced; hence, the interstitial waters become undersaturated with respect to calcite, and authigenic carbonate precipitation stops. The lower *p*H causes only a modest increase in seafloor basalt dissolution rates.

There are two primary reasons the basalt dissolution rate responds so little to changes in deep-ocean *p*H. The first is that silicate-rock weathering is generally insensitive to *p*H changes in the range of 5 to 8. The second is that basalt dissolution and carbonate precipitation tend to buffer the *p*H of the interstitial waters (fig. 3B). As the deep-ocean *p*H is reduced below present-day seawater values, carbonate precipitation diminishes, reducing the flux of alkalinity from the interstitial fluids to authigenic cements, and basalt dissolution increases slightly, increasing the flux of alkalinity to the interstitial fluids. Both these processes buffer the *p*H of the interstitial fluids, tending to keep interstitial waters in the *p*H range in which basalt dissolution would be relatively insensitive to *p*H change.

A rough estimate of the relative contributions of the alkalinity flux to the ocean/interstitial waters due to terrestrial weathering and seafloor weathering can be made in the following manner: by assuming that surface- to deep-ocean alkalinity and dissolved carbon differences remain the same as today, and equilibrium atmospheric pCO_2 can be computed for surface-ocean conditions corresponding to the deep-ocean condition plotted in figure 2A. For these calculations, I used a surface temperature of 18°C, surface and deep alkalinities, and the surface-to-deep total dissolved carbon difference as calculated from GEOSECS data by Volk and Hoffert (1985). To estimate terrestrial weathering fluxes as a function of atmospheric pCO_2, I used Berner's (1991) silicate-weathering formulation (eq A.1.2). The use of other formulations from the literature would not alter the basic conclusions of this study.

The computed alkalinity flux from silicate-rock weathering on land and seafloor basalt dissolution versus atmospheric pCO_2 are plotted in figure 2B. In the present-day steady state, the alkalinity flux from silicate weathering is taken to be 12×10^2 eq yr^{-1} (compare Berner and others, 1983) and, from basalt dissolution in seawater, 6×10^{12} eq yr^{-1}. At an

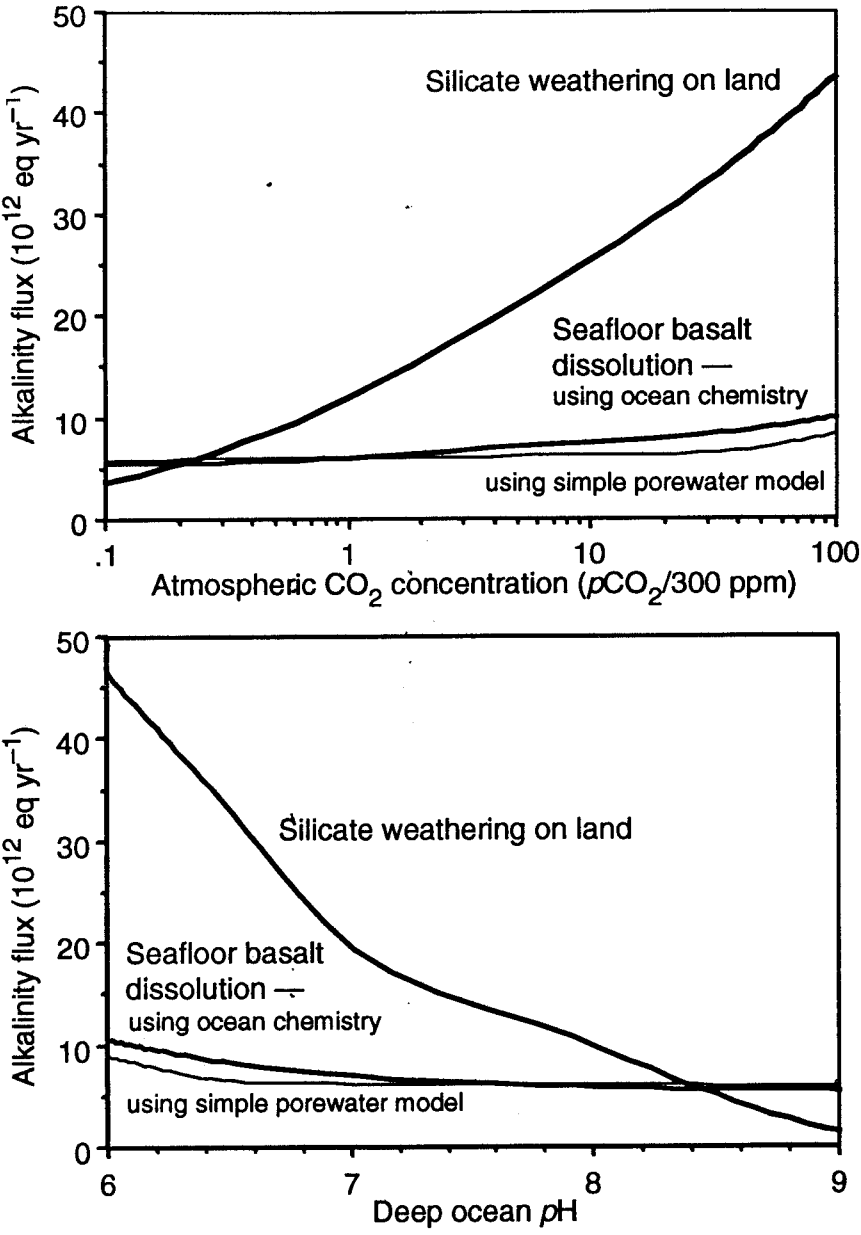

Fig. 2. Alkalinity fluxes from silicate-rock weathering on land and seafloor basalt dissolution, as a function of (A) atmospheric pCO_2 and (B) deep-ocean pH. Calculated as described in the text using modern ocean alkalinity and changing ocean pH and atmospheric pCO_2 by adding or removing CO_2 from the ocean and atmosphere. For the thin seafloor basalt dissolution line (labeled "using ocean pH"), seafloor basalt interstitial water pH is approximated as equal to deep-ocean pH. For the thick seafloor basalt dissolution line (labeled "using simple porewater model"), seafloor basalt interstitial water pH is calculated using the simple porewater model described in the text. In this model, carbonate precipitation, and to a lesser extent basalt dissolution, buffer interstitial water pH, making the basalt dissolution rates less sensitive to variation in deep ocean pH.

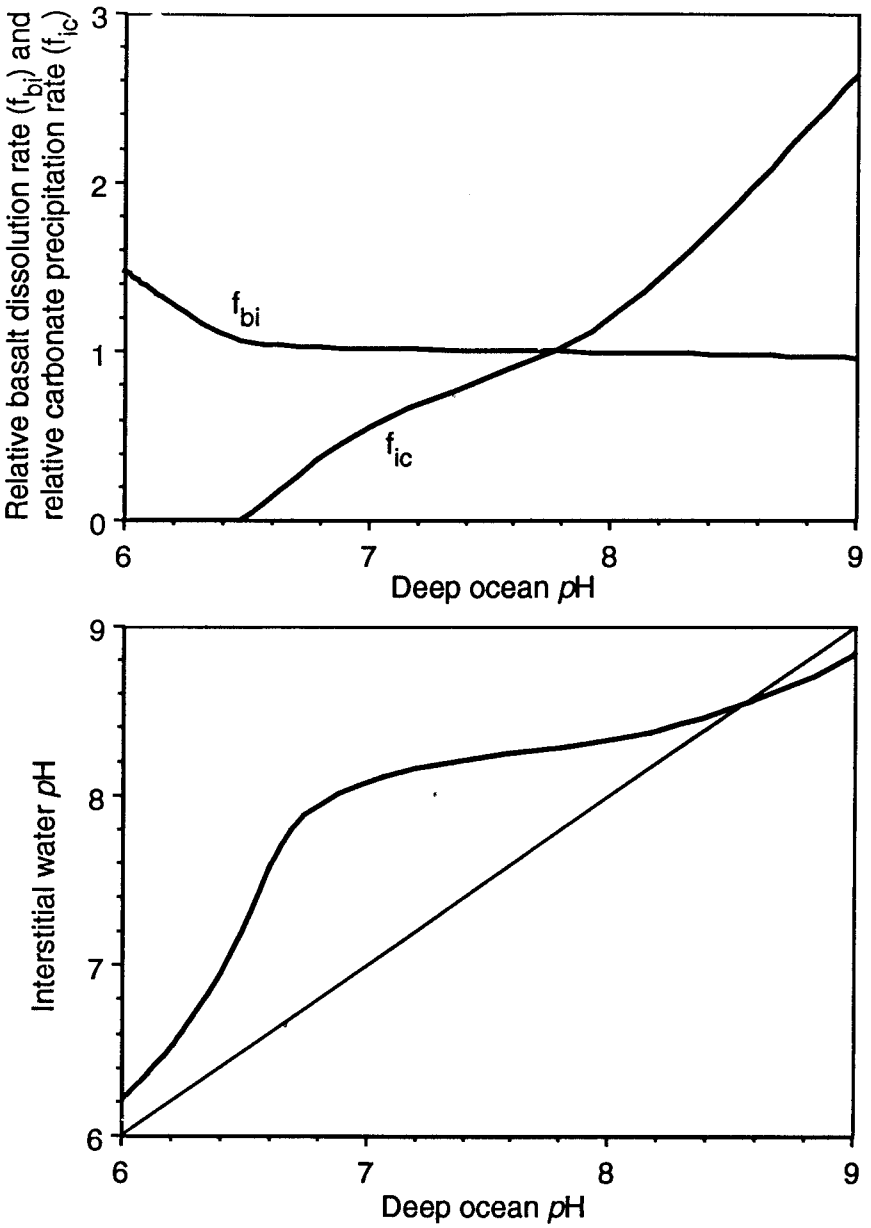

Fig. 3. Results of the one-box interstitial water model. (A) Relative rates of ocean basement basalt dissolution and carbonate precipitation as a function of deep ocean *p*H. (B) Interstitial water *p*H as a function of deep ocean *p*H. In the model, carbonate precipitation, and to a lesser extent basalt dissolution, buffer interstitial water *p*H, making the basalt dissolution rates less sensitive to variation in deep ocean *p*H.

atmospheric pCO_2 of 300 ppm (= 1 PAL), the analytically computed sensitivity of the silicate weathering alkalinity fluxes to pCO_2 changes is 1.7×10^{10} eq ppm^{-1}. At this pCO_2, the numerically computed sensitivity of the seafloor basalt dissolution alkalinity flux is 1.5×10^{8} eq ppm^{-1}. Hence, in response to ocean/atmosphere CO_2 changes, the alkalinity flux from terrestrial siliate weathering may be two orders of magnitude more sensitive than the flux from seafloor basalt dissolution. This again indicates the seafloor weathering may not be an important feedback in modulating atmospheric pCO_2 variation. The primary reason the results of the simple porewater model differ from the calculation using ocean pH is that in this model carbonate precipitation buffers pore water pH (fig. 3B), and, therefore, seafloor basalt dissolution rates are less sensitive to variations in deep-ocean pH.

A Carbonate-silicate Model with Seafloor-basalt Interstitial Water

Motivation and description.—In the above analysis, ocean alkalinity remains constant. Under high atmospheric pCO_2 and high dissolved CO_2 conditions, enhanced alkalinity fluxes to the oceans from terrestrial weathering and/or basalt dissolution may change ocean alkalinity. Could this enhance low-temperature seafloor alteration relative to terrestrial weathering and thus provide cause to believe that low-temperature alteration of the seafloor has been the primary control on ocean-atmosphere carbon concentrations?

To investigate this question, I developed a model (fig. 1) consisting of a two-box ocean model with a one-box atmosphere and a seafloor-basalt interstitial water box. Description of all model parameters and variables may be found in table 1, and the equations are in app. 3. In this model, for simplicity, the sedimentary organic carbon cycle is not considered. The ocean and interstitial water boxes are described by two state variables each, total dissolved inorganic carbon and alkalinity. The atmosphere is described by a single state variable indicating the atmospheric CO_2 concentration. One ocean box refers to the surface ocean, including shallow-shelf areas, and the other ocean box refers to the deep ocean. This highly simplified scheme is not intended to be numerically accurate but is intended to provide an indication of the relative importance of terrestrial weathering versus low-temperature seafloor alteration as a control on atmospheric CO_2 concentration.

There is a net flux of CO_2 from the surface ocean to the atmosphere via gas exchange processes at the ocean surface, and another net flux of CO_2 to the atmosphere from metamorphism and magmatism. Much of this CO_2 flux is undoubtedly subaqueous—at mid-ocean-ridges, from submarine volcanoes, in fluids expelled in subduction zones, and the like. However, the residence time of CO_2 in the oceans and atmosphere is long relative to the mixing time of the ocean; hence, model results are highly insensitive with regard to which box this metamorphic and magmatic CO_2 flux is injected.

There is a flux of CO_2 to the surface ocean associated with the weathering of carbonate and silicate rocks (Berner, Lasaga, and Garrels, 1983). When a mole of carbonate or silicate rocks are weathered, one or two moles, respectively, of atmospheric CO_2 are transported to the surface ocean as dissolved riverine bicarbonate. In steady-state, for each mole of carbonate or silicate rock weathered, one mole of CO_2 is degassed from the surface ocean to the atmosphere.

The riverine flux to the surface ocean carries bicarbonate carbon from the dissolution of terrestrial carbonate. Carbon leaves the surface ocean either as: (1) shallow-water sedimentary carbonate accumulation; (2) biogenic detritus transported to the deep-ocean; or (3) dissolved inorganic carbon transported to the deep-ocean with advective or diffusive water fluxes. Some of the biogenic carbonate transported from the surface-ocean to the deep-ocean settles on seafloor that lies in calcite saturated waters. This fraction of the biogenic detrital carbonate flux is considered to be accumulating on the seafloor. In this model, there is net transport of carbon to the interstitial waters in the seafloor basalts (Staudigel and others, 1989). This net flux is a result of higher total dissolved carbon concentrations in waters entering the basalt interstices than in waters leaving these interstices. In steady-state, this net flux is equal to the rate of carbonate precipitation in the seafloor. The rate of carbonate precipitation in the ocean basement is computed as a function of the carbonate-ion concentration in the interstitial waters.

With the exception of exchanges with the atmosphere, alkalinity fluxes largely parallel the carbon fluxes described above. The riverine alkalinity flux in equivalents is considered to be numerically equal to the riverine bicarbonate flux in moles (Berner, Lasaga, and Garrels, 1983). Sedimentary carbonate fluxes carry two equivalents of alkalinity for each mole of carbon. Detrital alkalinity fluxes from the mixed-layer to the deep ocean are calculated to reproduce the observed oceanic alkalinity distribution (Volk and Hoffert, 1985).

Results and discussion.—The principal results of this global carbon-cycle model are represented in figures 4 and 5. These model results indicate that silicate-rock weathering on land is more sensitive than seafloor basalt dissolution to changes in ocean-atmosphere CO_2 content, by several orders of magnitude. Hence, seafloor basalt dissolution is unlikely to be a major factor controlling atmospheric CO_2. The dynamics of silicate-weathering and carbonate accumulation in the ocean acts to buffer ocean chemistry in the neutral to basic *p*H range for the range of CO_2 degassing rates investigated here ($0.5\ FCO_{2,0} < FCO_2 < 2\ FCO_{2,0}$). Because silicate dissolution rates have been found to be largely independent of *p*H in the neutral to basic *p*H range, and the chemistry of the interstitial waters is similar to that of contemporaneous seawater, seafloor basalt dissolution rates may be largely independent of ocean *p*H.

The basic conclusions that can be drawn from this exercise are as follows: (1) Seafloor-basalt dissolution rates are insensitive to *p*H variation in the pH range of $6 < pH < 8$. (2) Seawater that enters the cracks

TABLE 1

Parameter definitions

(A) Dimensionless parameter definitions

f_{bi}	seafloor basalt dissolution rate ($=F^A_{bi}/F^A_{bi,0}$).
f_{CCD}	fraction of seafloor above the calcite compensation depth.
f_{ic}	seafloor basalt interstitial carbonate accumulation rate ($=F^C_{ic}/F^C_{ic,0}$).
f_{sc}	shallow-water carbonate accumulation rate ($=F^C_{sc}/F^C_{sc,0}$).
f_{sw}	silicate-rock weathering rate ($=F^C_{sw}/F^C_{sw,0}$).
k_{ic}	seafloor basalt interstitial carbonate effective rate constant ($=([CO^{2-}_3]_{i,0}/(90 \times 10^{-6}\ \text{mol}\ l^{-1})) - 1)^{-1.7}$).
k_{sc}	shallow-water carbonate effective rate constant ($=([CO^{2-}_3]_{m,0}/(66 \times 10^{-6}\ \text{mol}\ kg^{-1})) - 1)^{-1.7}$).
p	atmospheric carbon dioxide concentration ($=P/P_0$).
Ω^{arag}_m	mixed-layer aragonite saturation state.
Ω^{calc}_i	ocean basement interstitial water calcite saturation state.

(B) Dimensional parameter definitions (unreferenced values are either discussed in the text or determined from other parameters and the set of equations in the text)

A_{ocean}	m^2	ocean surface area ($=3.49 \times 10^{14}\ m^2$; Levitus, 1982).
$[CO^{2-}_3]_d$	mol m^{-3}	deep-ocean carbonate-ion concentration.
$[CO^{2-}_3]_i$	mol m^{-3}	seafloor-basalt interstitial water carbonate-ion concentration ($[CO^{2-}_3]_{i,0} = 0.238$ mol m^{-3}; determined from steady state).
$[CO^{2-}_3]_m$	mol m^{-3}	ocean mixed-layer carbonate-ion concentration ($[CO^{2-}_3]_{m,0} = 0.221$ mol m^{-3}; determined from steady state).
A_d	eq m^{-3}	concentration of total alkalinity in the deep ocean.
A_i	eq m^{-3}	concentration of total alkalinity in the seafloor-basalt interstitial waters.
A_m	eq m^{-3}	concentration of total alkalinity in the ocean mixed-layer.
C_d	mol m^{-3}	concentration of total dissolved inorganic carbon in the deep ocean.
C_i	mol m^{-3}	concentration of total dissolved inorganic carbon in the seafloor-basalt interstitial waters.
C_m	mol m^{-3}	concentration of total dissolved inorganic carbon in the ocean mixed-layer.
F_{CO_2}	mol yr^{-1}	metamorphic plus magmatic CO_2 release rate $\left(F_{CO_2,0} = F^C_{sw,0} + \frac{0.5\ \text{mol}}{\text{eq}} F^A_{bi,0}\right)$.
F^A_{bi}	eq yr^{-1}	alkalinity flux from seafloor basalts to the ocean-basement interstitial waters ($F^A_{bi,0} = 6 \times 10^{12}$ eq yr^{-1}).
F^A_{carb}	mol yr^{-1}	flux of alkalinity in the biogenic carbonate flux from the mixed-layer to the deep ocean ($=62.8 \times 10^{12}$ eq yr^{-1}).
F^A_{di}	eq yr^{-1}	total alkalinity flux to the seafloor basalt interstitial waters.
F^A_{ic}	eq yr^{-1}	alkalinity flux from the ocean-basement interstitial waters to ocean basement authigenic carbonate ($F^A_{ic,0} = 6 \times 10^{12}$ eq yr^{-1}).
F^A_{md}	mol yr^{-1}	alkalinity flux from the ocean mixed-layer to the deep-ocean transported by biogenic organic carbon fluxes ($=81.5 \times 10^{12}$ eq yr^{-1}).
F^A_{sw}	eq yr^{-1}	alkalinity flux from silicate-rock weathering on land to the ocean-mixed layer ($F^A_{sw,0} = 12 \times 10^{12}$ eq yr^{-1}).

TABLE 1

(continued)

F^C_{carb}	mol yr^{-1}	biogenic carbonate flux from the mixed-layer to the deep ocean ($=31.4 \times 10^{12}$ mol yr^{-1}).
F^C_{ma}	mol yr^{-1}	net CO_2 flux from exchange from the ocean-mixed layer to the atmosphere.
F^C_{md}	mol yr^{-1}	carbon flux from the ocean mixed-layer to the deep-ocean transported by biogenic organic carbon fluxes and by the "solubility pump" ($=368.9 \times 10^{12}$ mol yr^{-1}).
F^C_{cw}	mol yr^{-1}	carbonate-rock weathering rate ($F^C_{cw,0} = 12 \times 10^{12}$ mol C yr^{-1}).
F^C_{dc}	mol yr^{-1}	deep-water sedimentary carbonate accumulation rate ($F^C_{dc,0} = 0.6\,(F_{CO_2,0} + F^C_{cw,0} - F^C_{bi,0})$).
F^C_{di}	mol yr^{-1}	ΣCO_2 flux to the seafloor basalt interstitial waters.
F^C_{sc}	mol yr^{-1}	shallow-water sedimentary carbonate accumulation rate ($F^C_{sc,0} = 0.4\,(F_{CO_2,0} + F^C_{cw,0} - F^C_{bi,0})$).
F^C_{sw}	mol yr^{-1}	silicate-rock weathering rate ($F^C_{sw,0} = 6 \times 10^{12}$ mol C yr^{-1}).
F^C_{ic}	mol yr^{-1}	seafloor basalt authigenic carbonate accumulation rate ($F^C_{ic,0} = 3 \times 10^{12}$ mol C yr^{-1}).
$[H^+]_d$	mol l^{-1}	deep-ocean hydrogen-ion concentration.
$[H^+]_i$	mol l^{-1}	ocean-crust interstitial water hydrogen-ion concentration.
k_{gas}	mol C m^{-2} yr^{-1} ppm^{-1}	ocean gas exchange constant ($=0.07$ mol C m^{-2} yr^{-1} ppm^{-1}; area weighted average of gas exchange rates from Wenk and Siegenthaler [1985]).
M_{atm}	mol	Molar mass of the atmosphere ($=1.773 \times 10^{20}$ mol).
P	ppm	atmospheric carbon dioxide concentration ($P_0 = 300$ ppm).
P_m	ppm	ocean mixed-layer partial pressure of carbon dioxide.
W	m^3 yr^{-1}	Volumetric ocean mixing flux ($=1.3 = 10^{15}$ m^3 yr^{-1}).
V_d	m^3	deep-ocean volume ($=(3500\text{ m})A_{ocean}$).
V_m	m^3	Ocean mixed-layer volume ($=(200\text{ m})A_{ocean}$).
ΔC^T_m	mol m^{-3}	difference in carbon concentration between mean dissolved inorganic carbon concentration in ocean mixed-layer water transported to the deep-ocean and mean mixed-layer dissolved inorganic carbon concentration.
τ	yr	residence time of altered seawater in the ocean basement.

and fractures in seafloor basalts is buffered in this *p*H range by the sedimentary carbonate system. (3) Seafloor-basalt interstitial waters are further buffered in this range by authigenic carbonate in the seafloor and, to a lesser extent, by basalt dissolution. These factors suggest that *p*H dependence of seafloor-basalt dissolution rates is unlikely to be an important factor regulating the global carbon cycle.

SUMMARY AND DISCUSSION

The primary conclusion of this study is that the *p*H dependency of seafloor weathering is not a dominant mechanism regulating atmo-

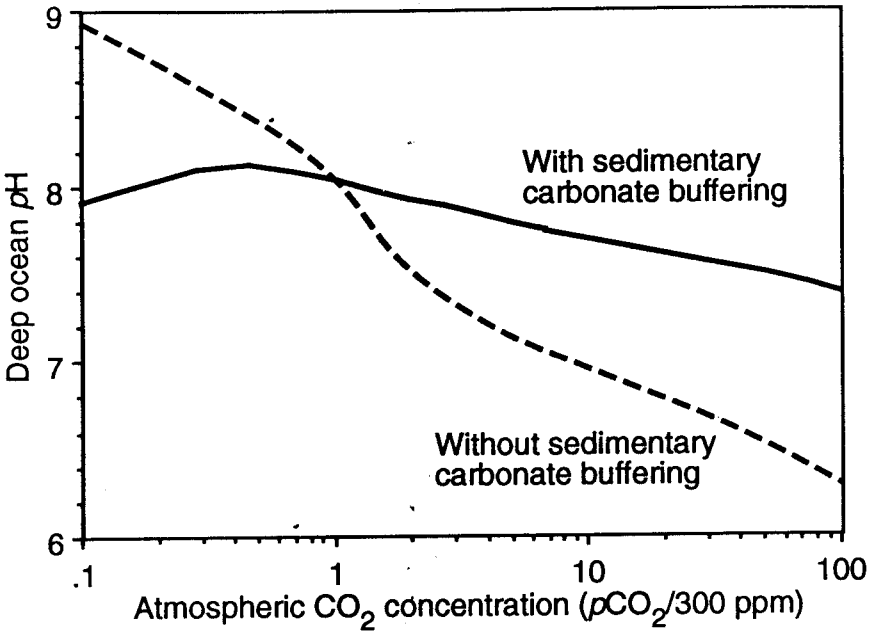

Fig. 4. Results of the four-box ocean-atmosphere-porewater carbonate-silicate model described in the text and pictured in figure 1, showing deep-ocean pH as a function of atmospheric pCO_2. The dashed curve marked "Without sedimentary carbonate buffering" represents ocean pH and atmospheric pCO_2 calculated by adding or removing CO_2 from the ocean at constant alkalinity. The solid curve marked "With sedimentary carbonate buffering" represents model results when ocean alkalinity changes as calculated by the model. In this case, the sedimentary carbonate system buffers ocean pH in the range at which silicate mineral dissolution rates are not sensitive to pH variation.

spheric carbon content. This suggests that silicate-weathering on land is the dominant control on long-term atmospheric CO_2 content.

Ocean chemistry (and atmospheric CO_2 content) would have had to vary widely in order for seafloor weathering to compensate for even minor variation in the global CO_2 degassing rate, because silicate-mineral dissolution rates tend to be insensitive to ocean pH and total carbon concentrations near present-day ocean values. If published terrestrial silicate-rock weathering rate formulations (Walker, Hays, and Kasting, 1981; Berner, 1991) are at least approximately correct, then changes in ocean-atmosphere carbon content that would affect silicate-rock weathering on land would be several orders of magnitude more sensitive to seafloor weathering. The primary assumption critical to the conclusions reached here is that the pH sensitivity exhibited in silicate mineral dissolution experiments, at least in an order of magnitude sense, may be applied to silicate minerals in the upper layers of the ocean basement exposed to relatively unaltered seawater.

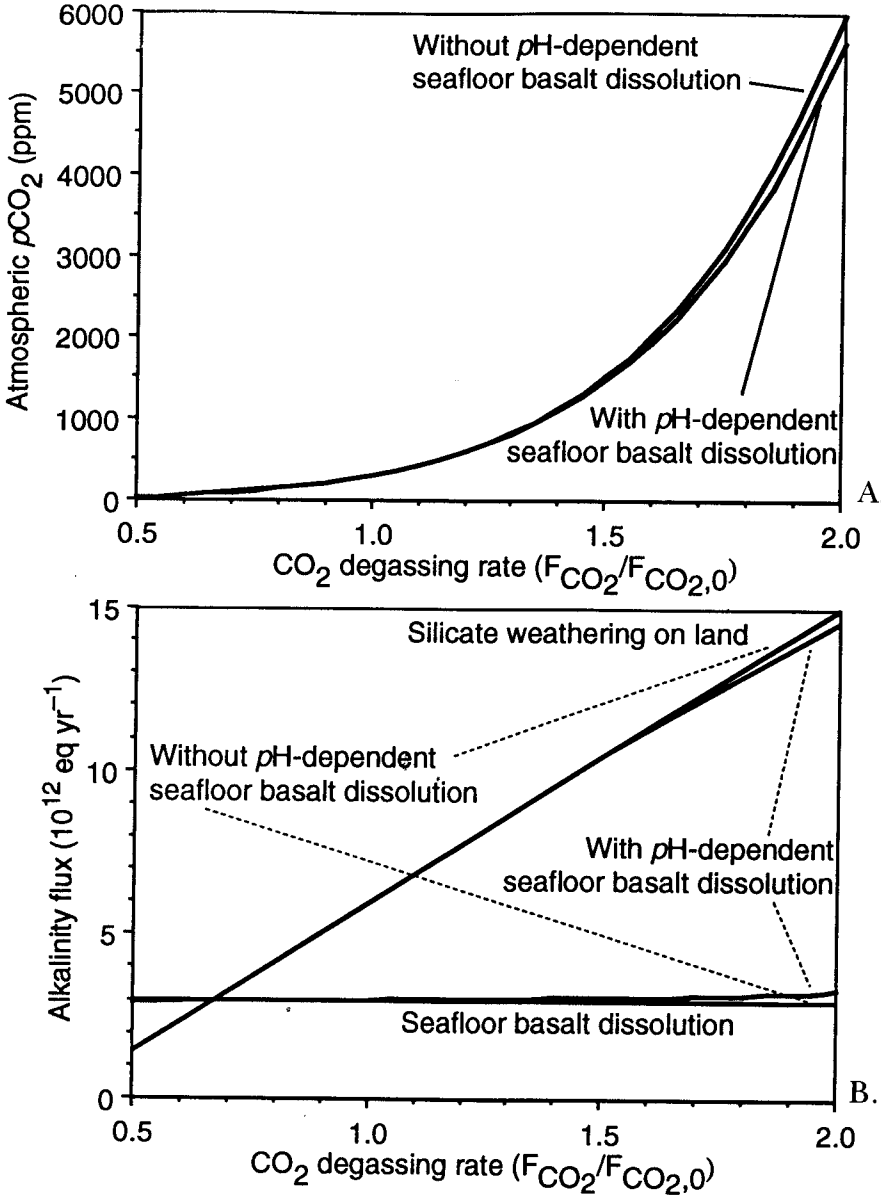

Fig. 5. Results of the four-box ocean-atmosphere-porewater model described in the text. (A) Atmospheric pCO_2 as a function of metamorphic plus mantle CO_2 degassing rate with and without *p*H dependent seafloor basalt dissolution. (B) Calculated alkalinity fluxes from silicate weathering on land and basalt dissolution in the seafloor, both with and without *p*H dependent seafloor basalt dissolution. Consideration of the *p*H dependency of seafloor basalt dissolution has little effect on estimated atmospheric CO_2 content.

The "approximating seafloor-basalt interstitial water with deep-ocean water" calculation indicates that the alkalinity flux from seafloor basalt dissolution is relatively insensitive to changes in deep-ocean pH. In the "simple seafloor-basalt interstitial water model," carbonate precipitation in the ocean basement buffers interstitial water pH, further reducing the sensitivity of seafloor basalt dissolution to changes in ocean pH. In the "carbonate-silicate model with porewater reservoir," marine sedimentary carbonate accumulation buffers ocean pH and indirectly buffers interstitial water pH even further, indicating that the pH shifts that would be needed to markedly change seafloor basalt dissolution rates probably have not occurred, at least since the Archean.

Nevertheless, seafloor basalt dissolution may be a significant, but highly uncertain, flux in the oceanic alkalinity budget (perhaps, some fraction of 6×10^{12} eq yr^{-1})—but this flux is probably not sensitively dependent on ocean pH or carbon content.

Processes not modeled here may affect chemical fluxes from seafloor basalt dissolution. The formation of a sedimentary layer on the seafloor greatly limits the advection of water into the ocean basement, and without advection the flux of carbon to the ocean basement is limited to $< 0.1 \times 10^{12}$ mol yr^{-1} by diffusion. The development of a sedimentary carbonate layer over the ocean basement limits the rate at which unaltered seawater is supplied to the ocean-basement porewaters, which limits the rate of seafloor basalt dissolution. In an ocean with a low carbonate-ion concentration (that is, low pH or low total dissolved inorganic carbon), the development of a sedimentary carbonate layer would be inhibited. Hence, prior to the onset of widespread pelagic carbonate accumulation late in the Jurassic (Boss and Wilkinson, 1991; Wilkinson and Walker, 1988), ocean basement basalts may have seen more seawater before being sealed off by carbonate sedimentation.

The schematic model developed here is intended to illustrate only the most basic chemical dynamics. Many other factors deserve consideration, including: (1) Slowly spreading ridges may create more pore space than rapidly spreading ridges per–unit–area of seafloor. Hence, there may be more seafloor basalt dissolution per–unit–area, when seafloor generation rates are low. This would leave less of an alkalinity deficit to be balanced by terrestrial silicate weathering, tending to make atmospheric pCO_2 somewhat more sensitive to changes in seafloor generation rates. (2) Pore space is created with basalt dissolution and is lost when it is infilled with various authigenic cements. The permeability of layer 2a is reduced by an order of magnitude by the formation of authigenic cements (Johnson, 1979). This will increase the residence time of the interstitial water in the seafloor. Carbonate cements will tend to form more slowly if ocean carbonate-ion concentrations are low, which may tend to increase the extent of basalt dissolution. (3) The role of authigenic clays in filling veins and competitive vein filling between clays and carbonate deserves further inquiry. (4) As seafloor ages the heat flux

driving convection is reduced. A more complete treatment would investigate all of these factors.

Ocean basement carbonate precipitation may be a significant flux in the oceanic alkalinity and carbon budgets, and this flux may depend on the ocean carbonate-ion concentration. However, pelagic sedimentary carbonate accumulation also depends sensitively on the deep-ocean carbonate-ion concentration. Both carbonate accumulation fluxes correlate with the ocean carbonate-ion concentrations; hence, possibly important subduction zone processes aside, seafloor basalt carbonate accumulation probably does not have a major impact on the carbon cycle. If the carbonate did not precipitate in the ocean basement, the oceanic carbonate-ion concentration would probably be a little higher, allowing biogenic calcite to accumulate on a broader expanse of seafloor.

Perhaps the greatest importance of ocean basement carbonate lies in its fate at subduction zones, an area that deserves further study. As this carbonate is transported through metamorphic environments in subduction zones, the subduction rate may influence the partitioning of the devolatilized carbon among the mantle, atmosphere, and other carbon reservoirs (for example, accretionary wedges). These factors may produce variations in the fluxes of CO_2 into and out of the oceans and atmosphere and may influence atmospheric pCO_2, without regulating it.

François and Walker (1992) made the assumption that all the carbonate in the ocean basement is returned to the mantle at subduction zones. While this is still an open question, there is some reason to believe that the carbon in ocean basement carbonate may not be returned to the oceans. First, this carbonate is in close proximity to silicate rocks and clays, so the carbonate may react with silicate materials in subduction zone environments, permitting metamorphic CO_2 degassing. Second, the carbonate in layer 2a may abut or be close to the decollemont zone between the accretionary wedge and the subducting slab. The decollemont zone may act as a conduit through which fluids can be transported to the ocean (Le Pichon, Kobayashi, and Kaiko-Nankai Scientific Crew, 1992). The highly fractured nature of the upper layers of the ocean basement may promote the formation of conduits to the decollemont zone for metamorphically derived fluids. As Berner (1991) has pointed out, if all the ocean basement carbonate is degassed to the ocean or atmosphere in subduction zone environments, then on very long timescales ($> 10^8$ yr) the "new" carbon sink is balanced by a "new" carbon source, and there is little net effect on the dynamics of the long term carbon cycle.

Further study is needed to determine what fraction of subducting ocean basement carbonate is returned to the mantle, and whether the fate of authigenic ocean basement carbonate in subduction zone environments differs from that of sedimentary carbonate. Some of the consequences of the recycling of carbonate to the atmosphere/oceans and/or mantle have been discussed by Volk (1989) and Caldeira (1991, 1992).

There may be some interesting dynamics relating to the subduction rate. In rapidly subducting slabs, the slab may penetrate deep into the

mantle prior to reaching isotherms at which the carbonate could be expected to degas CO_2 (Staudigel and King, 1992). Hence, the fraction of seafloor carbonate returned to the mantle may be a function of subduction rate. Furthermore, because the rate of layer 2a pore space production may be largely independent of the seafloor spreading rate (Houtz and Ewing, 1976) and the extent of layer 2a carbonate accumulation is related to initial layer 2a porosity, the amount of carbon stored in the seafloor may be a function of the seafloor generation rate.

CONCLUSIONS

1. There is no evidence indicating that pH dependence of low-temperature seafloor alteration is an important regulator of atmospheric pCO_2.

2. The pH of the deep ocean is between 7.5 and 8, and silicate mineral dissolution rates are generally insensitive to pH variation in the pH range of about 5 to 8; hence the pH of the deep ocean would have to shift by over two pH units to increase dramatically the rate of seafloor basalt dissolution. However, ocean pH is buffered by the sedimentary carbonate system, indicating that ocean basement basalt dissolution rates have not been sensitively dependent on variations in deep-ocean pH or total dissolved inorganic carbon concentration, at least, since the Archean.

3. Carbonate precipitation and basalt dissolution may buffer the pH of the ocean basement interstitial fluids, tending to keep interstitial waters in the pH range in which basalt dissolution would be relatively insensitive to pH change.

4. Much of the alkalinity flux to ocean basement carbonate may derive from the ocean and not seafloor basalt.

5. More drill holes with high recovery into old seafloor are needed to constrain elemental fluxes into and out of the ocean basement at low-temperature, and more data are needed to constrain the fate of carbonate transported to subduction zones.

ACKNOWLEDGMENTS

I thank Lee Kump and Robert Berner for their helpful reviews and Sue Brantley for instructive conversation. This work was supported by an NSF grant from the Geologic Record of Global Change program. This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

APPENDIX 1

Calculations approximating seafloor-basalt interstitial water with deep-ocean water

The following set of calculations are designed to estimate the relative sensitivity of silicate-weathering on land versus basalt weathering in the seafloor to changes in ocean total dissolved carbon content and atmospheric CO_2 content. In this initial calculation, the

chemistry of seafloor basalt interstitial water is approximated as being identical to deep-ocean water.

The change in the alkalinity flux from the seafloor basalt to the interstitial waters (F^A_{bi}), given a change in deep-ocean ΣCO_2 concentration (C_d), is approximately the product of today's alkalinity flux from seafloor basalt dissolution ($F^A_{bi,0}$), the change in the basalt dissolution rate brought on by a change in hydrogen-ion concentration, and the change in hydrogen-ion concentration brought on by a change in C_d:

$$\frac{\partial F^A_{bi}}{\partial C_d} = F^A_{bi,0} \frac{\partial f_{bi}}{\partial [H^+]_d} \frac{\partial [H^+]_d}{\partial C_d}. \tag{A.1.1}$$

Based on the estimate of 3×10^{12} mol yr^{-1} for the ocean basement carbonate accumulation rate and the implicit assumption of François and Walker (1992) that the net alkalinity flux to this authigenic carbonate is equal to the net alkalinity flux to the interstitial waters from basalt dissolution, we use a value for $F^A_{bi,0}$ of 6×10^{12} eq yr^{-1}. Using the boron concentration, carbonate and borate chemistry, and dissociation constants from Stumm and Morgan (1981) and references therein, the average deep-ocean alkalinity and carbon concentrations from GEOSECS as computed by Volk and Hoffert (1985), $\partial F^A_{bi}/\partial C_d$ may be calculated to less than 2×10^{12} eq yr^{-1} (mol C m^{-3})$^{-1}$. This number is probably high by at least a factor of two, as will be discussed later.

The alkalinity flux from silicate-rock weathering on land (F^A_{sw}) can be parameterized as being proportional to

$$f_{sw} = \left(\frac{2p}{1+p}\right)^{0.4} p^{0.22} \tag{A.1.2}$$

(Berner, 1991), where p is the partial pressure of atmospheric CO_2 (P) divided by a reference pre-industrial value (P_0), here taken to be ~300 ppm, and $f_{sw} = F^A_{sw}/F^A_{sw,0}$, where $F^A_{sw,0} = \sim 12 \times 10^{12}$ eq yr^{-1} (Berner, Lasaga, and Garrels, 1983). The rationale for this formulation can be found in Berner (1991) and references therein. This equation differs in detail, but functions in a way that is qualitatively similar to more recent chemical weathering formulations (Berner, 1994; Brady and Carroll, 1994; Velbel, 1993b). The partial derivative of the alkalinity flux from silicate-rock weathering with respect to ocean mixed-layer carbon concentration (C_m) is

$$\frac{\partial F^A_{sw}}{\partial C_m} = F^A_{sw,0} \frac{\partial f_{sw}}{\partial p} \frac{\partial p}{\partial C_m}. \tag{A.1.3}$$

Using the average surface-ocean alkalinity from GEOSECS as computed by Volk and Hoffert (1985), at 18°C, with an atmospheric pCO_2 of 300 ppm, $\partial F^C_{sw}/\partial C_m$ may be computed to be over 2×10^{13} (eq yr^{-1})/(mol C m^{-3})$^{-1}$.

Appendix 2

Simple seafloor-basalt interstitial water model equations

The following set of calculations is designed to estimate the relative sensitivity of silicate-weathering on land versus basalt weathering in the seafloor to changes in ocean total dissolved carbon content and atmospheric CO_2 content. In this calculation, the chemistry of seafloor basalt interstitial water is computed as a function of seafloor basalt dissolution rates, authigenic carbonate precipitation rates, and exchange with the overlying deep-ocean water. Rates of seafloor basalt dissolution and authigenic carbonate precipitation are themselves modeled as a function of interstitial water chemistry.

For a given volume (V_i) of ocean-basement interstitial water exchanging fluids with the overlying seawater, a differential equation for the alkalinity (A_i) in the interstitial waters may be written:

$$\frac{d\,A_i}{d\,t} = \frac{F^A_{bi} + F^A_{di} - F^A_{ic}}{V_i}, \tag{A.2.1}$$

where F^A_{bi} is the alkalinity flux from seafloor basalt dissolution to the interstitial waters, F^A_{di} is the alkalinity flux from the deep ocean to the interstitial waters, and F^C_{ic} is the alkalinity flux from the interstitial waters to the authigenic carbonate. A corresponding equation for ΣCO_2 concentration in the interstitial waters (C_i) may be written:

$$\frac{d\,C_i}{d\,t} = \frac{F^C_{di} - F^C_{ic}}{V_i}, \tag{A.2.2}$$

where F^C_{di} is the flux of carbon from the ocean to the interstitial waters, and F^C_{ic} is the flux of carbon from the interstitial waters to the authigenic carbonate. F^A_{di} and F^C_{di} may be parameterized in terms of the concentration differences between the deep-ocean and the interstitial waters times the exchange flux between the interstitial waters and the deep ocean (W_{id}):

$$F^A_{di} = W_{id}(A_d - A_i), \tag{A.2.3}$$

and

$$F^C_{di} = W_{id}\,(C_d - C_i). \tag{A.2.4}$$

Using $V_i = 10^7$ km^3, with $\tau = 10^3$ yr, W_{id} is set to V_i/τ.

The alkalinity flux from the alteration (weathering) of seafloor basalt is parameterized by f_{bi} (see eq 8) times the present-day net flux of alkalinity from the seafloor basalts to the interstitial waters ($F^A_{bi,0}$):

$$F^A_{bi} = f_{bi}\,F^A_{bi,0}. \tag{A.2.5}$$

The accumulation rate of carbonate carbon in the upper layers of the ocean crust is related to the calcite saturation state of the interstitial fluids. This saturation state is increased by the adsorption of protons by the seafloor basalts and release of other cations and is affected by the initial carbonate-ion concentration of the seawater flowing through the ocean basement. The above discussion indicates that carbonate-ion concentration changes in the ocean-basement interstitial waters are more important that Ca concentration in changes in affecting the calcite saturation state of the interstitial waters. Using the type of precipitation rate formulation used to represent experimental results (Burton and Walter, 1987), in this model, the seafloor carbonate accumulation rate (non-dimensionalized as $f_{ic} = F^C_{ic}/F^C_{ic,0}$) is parameterized as:

$$f_{ic} = k_{ic}(1 - \Omega_i^{calc})^{1.7}, \tag{A.2.6}$$

where Ω_i^{calc} is the calcite saturation state of the layer 2a interstitial waters, and k_{ic} is a normalizing constant such that $f_{ic} = 1$ (that is, $k_{ic} = (1 - \Omega^{calc}_{i,0})^{-1.7}$). In this model, Ω_i^{calc} is a function of the interstitial-water carbonate-ion concentration only. The carbonate-ion concentration is calculated using the carbonate and borate chemistry and dissociation and Henry's law constants from Stumm and Morgan (1981) and references therein. The

alkalinity flux to authigenic seafloor carbonate is two equivalents for each mole of carbon, that is,

$$F^{A}_{ic} = \frac{2\ eq}{mol} F^{C}_{ic}. \tag{A.2.7}$$

This seafloor alteration model is highly simplified and intended only to demonstrate the most fundamental dynamic aspects of basalt dissolution (weathering) and authigenic carbonate precipitation at low-temperature. Numerous other possible feedbacks exist, but an attempt to model all these feedbacks without sufficient data would result in a complicated model with an excess of unconstrained parameters. In such a model, robust fundamental results might get lost in a sea of complexity.

For the present-day steady state, the flux of alkalinity from the basalts to the interstitial waters ($F^{A}_{bi,0}$) equal to the flux of alkalinity from the interstitial waters to the authigenic carbonate ($F^{A}_{ic,0}$), that is, $F^{A}_{bi,0} = F^{A}_{ic,0}$. For this set of model runs, deep-ocean alkalinity (A_d) will be held constant at 2.474 mol m^{-3} (Volk and Hoffert, 1985; at 35 permil salinity, using 1025 kg m^{-3} as the density of seawater), and C_d will be varied. Based on carbon mass balance considerations, as estimated in the text, a minimum volumetric flow rate of seawater into the ocean basement interstices is $\sim 1.3 \times 10^{12}$ m^3 yr^{-1}. Pore-water temperature is fixed at 25°C.

Appendix 3

Carbonate-silicate model with seafloor-basalt interstitial water equations

The following calculations are designed to estimate the relative sensitivity of silicate-weathering on land versus basalt weathering in the seafloor to changes in ocean total dissolved carbon content and atmospheric CO_2 content. In this calculation, ocean alkalinity varies such that fluxes from alkalinity fluxes from carbonate and silicate weathering are balanced by alkalinity fluxes to sedimentary and authigenic carbonate reservoirs. This four box model (fig. 1) incorporates eqs 7, A.1.2, and A.2.1 through A.2.7, in conjunction with the following expressions:

The calcite compensation depth (CCD) depth (z_{CCD}) may be represented (Broecker and Peng, 1982):

$$z_{CCD} = 4\ km + 6.25\ km \ln\left(\frac{[CO_3^{2-}]_d}{0.9 \times 90\ umol\ kg^{-1}}\right), \tag{A.3.1}$$

where the calcite compensation depth (CCD) is considered to be the point of 90 percent calcile saturation (Berger and Spitzy, 1988), and $[CO_3^{-2}]_d$ is the deep-ocean carbonate-ion concentration. A least-square exponential curve-fit, with a mean-square error less than 2 percent, to hypsometric data in Sclater, Boyle, and Edmond (1979) produces the equation:

$$f_{CCD} = 0.07\ Exp\ (z_{CCD}/2.2\ km), \tag{A.3.2}$$

for the fractional of sea-floor above the CCD, for 0.2 km $> z_{CCD} >$ 5.85 km. Deep-ocean carbonate accumulation rate (F^{C}_{dc}) may then be represented:

$$F^{C}_{dc} = f_{CCD}\ F^{C}_{carb}, \tag{A.3.3}$$

where F^{C}_{carb} is the rate of pelagic carbonate productivity. A more detailed treatment would consider calcite and aragonite separately, but this would not change the qualitative results of this model.

The time rate of change of the partial pressure of CO_2 in the atmosphere in ppm yr^{-1} may be represented:

$$\frac{d\,P}{d\,t} = \left(\frac{1}{M_{atm}}\right)(F_{CO_2} + F^C_{ma} - 2\,F^C_{sw} - F^C_{cw}), \tag{A.3.4}$$

where the variables are represent metamorphic and mantle CO_2 releases (F_{CO_2}), net gas exchange from the ocean-mixed layer to the atmosphere (F^C_{ma}), and silicate (F^C_{sw}) and carbonate (F^C_{cw}) weathering. The rationale for this formulation can be found in Berner, Lasaga, and Garrels (1983) and Kasting and others (1985).

The time rate of change of ocean mixed-layer ΣCO_2 concentration in mol C m^{-3} yr^{-1} can be represented:

$$\frac{d\,C_m}{d\,t} = \left(\frac{1}{V_m}\right)(2(F^C_{sw} + F^C_{cw}) + W_{md}(C_d - C_m) - F^C_{ma} - F^C_{md} - F^C_{sc} - F^C_{carb}). \tag{A.3.5}$$

The sources of ΣCO_2 to the ocean mixed-layer are the flux of riverine carbon from carbonate and silicate weathering here represented by 2 (F^C_{sw} + F^C_{cw}) and the flux of carbon mixed up from the deep ocean ($W_{md}C_d$). The sinks of mixed-layer total dissolved carbon are: the flux of mixed-layer carbon mixed down to the deep ocean ($W_{md}C_m$); the net flux of CO_2 degassed to the atmosphere (F^C_{ma}); the flux of carbon transported to the deep ocean (F^C_{md}) as sinking particles, as dissolved organic matter, or as a result of the enhanced CO_2 solubility in cold deep-water forming regions; and the flux of mixed-layer carbon accumulating as shallow-water carbonate sediments (F^C_{sc}) or deep-water carbonate sediments (F^C_{dc}). The analogous expression for the time rate of change in ocean mixed-layer alkalinity in units of eq m^{-3} yr^{-1} is:

$$\frac{d\,A_m}{d\,t} = \left(\frac{1}{V_m}\right)(F^A_{sw} + F^A_{cw} + W_{md}(A_d - A_m) - F^A_{md} - F^A_{sc} - F^A_{carb}), \tag{A.3.6}$$

where, except for F^A_{md}, the alkalinity flux terms are equal to (2 eq mol^{-1}) times the corresponding carbon flux term.

The time rate of change in deep-ocean ΣCO_2 concentration is:

$$\frac{d\,C_d}{d\,t} = \left(\frac{1}{V_d}\right)(W_{md}(C_m - C_d) + W_{id}(C_i - C_d) + F^C_{md} + (1 - f_{CCD})F^C_{carb}), \tag{A.3.7}$$

where exchange with the mixed-layer and basalt interstitial waters and biogenic reduced C and carbonate dissolution fluxes are represented. The corresponding expression for the time rate of change in deep-ocean alkalinity is:

$$\frac{d\,A_d}{d\,t} = \left(\frac{1}{V_d}\right)(W_{md}(A_m - A_d) + W_{id}(A_i - A_d) + F^A_{md} + (1 - f_{CCD}). \tag{A.3.8}$$

The ocean mixed-layer partial pressure of CO_2 (P_m) and carbonate-ion concentration and the deep-ocean hydrogen-ion and carbonate-ion concentrations are calculated from mixed-layer or deep-ocean carbon and alkalinities using the dissociation constants for the carbonate and borate systems and the Henry's law constant for CO_2 as described by Stumm and Morgan (181), Gieskes (1974), and Edmond and Gieskes (1970). Ocean borate

concentrations were taken from Stumm and Morgan (1981). The constants used are for a mixed-layer at 1 bar pressure at 18°C and for a deep-ocean at 400 bar at 2°C. These constants are held constant for all runs. The net flux of CO_2 from the mixed-layer to the atmosphere (F^C_{ma}) is calculated to be:

$$F^C_{ma} = k_{gas} A_{ocean} (P_m - P), \tag{A.3.9}$$

where k_{gas} is a globally averaged gas exchange constant, and A_{ocean} is the area of the ocean.

In a study comparing shallow-water carbonate-accumulation rates with ocean mixed-layer carbonate-ion concentration, Opdyke and Wilkinson (1993) concluded that sea-surface carbonate-ion concentration is a major control on shallow-water carbonate accumulation. This conclusion is somewhat suspect because the strong correlation between sea-surface temperature and carbonate-ion concentration makes it difficult to separate the two signals. The picture is further complicated because long-term carbonate accumulation rates are limited by subsidence rates (Opdyke and Wilkinson, 1988), however, it is possible that the area of carbonate accumulation would increase at higher carbonate-ion concentrations. At higher surface-water carbonate-ion concentrations, globally averaged shallow-water carbonate accumulation rates may be higher; hence, we adopt a functional form for the dimensionless shallow-water carbonate accumulation rate (f_{sc}) suggested by the study of Opdyke and Wilkinson (1993):

$$f_{sc} = k_{sc} (\Omega^{arag}_m - 1)^{1.7}. \tag{A.3.10}$$

The saturation state of the mixed-layer with respect to aragonite, Ω^{arag}_m, is defined as $[CO_3^{2-}]_m$ divided by 66×10^{-6} mol kg^{-1} (Broecker and Peng, 1982). The parameter, k_{sc}, is specified such that $f_{sc} = 1$ when $[CO_3^{2-}]_m = [CO_3^{2-}]_{m,0}$. The present-day shallow-water carbonate flux ($F^C_{sc,0} = \sim 7.4 \times 10^{12}$ mol C yr^{-1}) is specified as being 40 percent (Wilkinson and Walker, 1988) of the total sedimentary carbonate flux ($=18 \times 10^{12}$ mol C yr^{-1}; compare Berner, Lasaga, and Garrels, 1983). The elimination of eq (A.3.10) from the model, substituting $f_{sc} = 1$, does not change the basic dynamics of the model for minor variations in the CO_2-degassing rate. However, if at high CO_2-degassing rates the riverine sources of alkalinity exceed shallow-water carbonate accumulation plus pelagic carbonate productivity, then, without eq (A.3.10), the additional carbonate is forced to accumulate in the seafloor; with eq (A.3.10), it accumulates both in shallow-water environments and in the seafloor. Without eq (A.3.10), at low CO_2-degassing rates, the riverine plus seafloor basalt alkalinity fluxes are less than the shallow-water carbonate accumulation flux, and the model "blows up" because the alkalinity fluxes out of the ocean exceed alkalinity fluxes to the ocean.

For ocean alkalinity and dissolved inorganic carbon concentrations, we use values from the GEOSECS data set for the surface and deep ocean normalized to 35 permil salinity as summarized by Volk and Hoffert (1985), converting to volumetric units using a seawater density of 1025 kg m^{-3}. Deep-ocean carbonate-ion concentrations are calculated using a temperature of 2°C, a pressure of 400 bars, and the carbonate and borate chemistry as described above. The present-day riverine alkalinity flux ($F^A_{sw} + F^A_{cw}$) is taken to be 36×10^{12} eq yr^{-1} (Berner, Lasaga, and Garrels, 1983), and 60 percent of this flux is taken to accumulate as sedimentary carbonate in pelagic environments (Wilkinson and Walker, 1988). The ocean mixing time scale is ~1000 yr (Broecker and Peng, 1982). The ocean volume is $\sim 1.3 \times 10^{18}$ m^3 (Levitus, 1982), suggesting an ocean mixing flux (W_{md}) of $\sim 1.3 \times 10^{15}$ m^3 yr^{-1}. With these values specified, the model is completely constrained.

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