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## Seafloor weathering controls on atmospheric CO<sub>2</sub> and global climate

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**Abstract**—Alteration of surficial marine basalts at low temperatures (<40°C) is a potentially important sink for atmospheric CO<sub>2</sub> over geologic time. Petrologic analyses, thermodynamic calculations, and experimental weathering results point to extensive Ca leaching and consumption of marine CO<sub>2</sub> during alteration. Basalt weathering in seawater-like solutions is sensitive to temperature. The activation energy for initial basalt weathering in seawater is 41–65 kJ mol<sup>-1</sup>. If seafloor weathering temperatures are set by deep ocean fluids under high fluid to rock ratios the feedback between weathering and atmospheric CO<sub>2</sub> is indirect, but sizeable. If the bulk of seafloor weathering occurs in the presence of low-temperature hydrothermal fluids, the weathering feedback depends on the linkage between spreading rates and heat flow. In either case, the primary linkage between seafloor weathering and the global carbon cycle appears to be thermal as opposed to chemical. Copyright © 1997 Elsevier Science Ltd

### 1. LIST OF SYMBOLS

$r/r_0$	Rate of Ca,Mg-silicate weathering (mol s <sup>-1</sup> ) as a function of temperature, spreading rate, or time relative to a given base-line value $r_0$ .
$E_a$	Activation energy of Ca,Mg-silicate weathering (kJ mol <sup>-1</sup> ).
$R_{CO_2}$	The ratio of atmospheric carbon dioxide partial pressure relative to its pre-industrial value—( $P_{CO_2}/P_{CO_2,o}$ ).
$f_{sr}$	Ratio of seafloor production rate (km <sup>2</sup> y <sup>-1</sup> ) at a given time to its present value.
$f_a$	Ratio of continental surface area (km <sup>2</sup> ) to its present value.

### 2. INTRODUCTION

Interactions between submarine basalts and seawater are important controls on the long-term chemistry of the ocean and the oceanic crust (e.g., Hart, 1973; Wolery and Sleep, 1976; Holland, 1978; Edmond et al., 1979; Gregory and Taylor, 1981; Thompson, 1983). Chemical exchange between the ocean and crust probably balances the marine budgets of Mg (Holland, 1978; Edmond et al., 1979; McDuff and Morel, 1980; Edmond et al., 1981; Mottl and Wheat, 1994) and K (e.g., Thompson, 1973; Thompson and Humphris, 1977; Staudigel et al., 1981). While much attention has focused on the dramatic mineralogic changes observed at high temperature ( $T > 200^\circ\text{C}$ ) mid-ocean hydrothermal systems (e.g., Bischoff and Dickson, 1975; Hajash, 1975; Mottl and Holland, 1978), low temperature (<40°C) alteration of basalts plays a dominant role in the cycling of a number of major and minor elements, in particular Ca (e.g., Thompson, 1973; Thompson and Humphris, 1977; Seyfried and Bischoff, 1979; Thompson, 1983; Spivack and Staudigel, 1994). Isotopic evidence points to alteration of the top 600 m of crust by deep ocean water (~4°C) (e.g., Muehlenbachs, 1977; Lawrence et al., 1977; Lawrence and Drever, 1981; Böhlke et al., 1984). Low-temperature alteration of Ca-containing silicates by seawater is estimated to account for a net flux of roughly  $1\text{--}2 \times 10^{12}$  moles y<sup>-1</sup> of Ca out of abyssal basalts (McDuff and Morel, 1980; Spivack and Staudigel, 1994). Alt et al. (1986) calculated a lower value of

$0.62 \times 10^{12}$  moles y<sup>-1</sup> from DSDP hole 504B. The net flux, while imprecisely known, still appears to be somewhat similar to recent estimates of the contribution of Ca derived from the continental weathering of Ca-silicates,  $3.49 \times 10^{12}$  mol y<sup>-1</sup> (e.g., Francois and Walker, 1992). Berner and Berner (1987) calculate  $5.52 \times 10^{12}$  mol/y for Ca + Mg. Note that the dissolution of Ca-containing silicates consumes CO<sub>2</sub> and that weathering is the primary sink for atmospheric CO<sub>2</sub> over geologic time. Staudigel et al. (1989) estimate that the Ca-leaching of the seafloor at low temperatures accounts for  $2.2\text{--}2.9 \times 10^{12}$  moles of CO<sub>2</sub> drawdown per year. Relative to continental weathering, there is considerable uncertainty in the rate of Ca-leaching and CO<sub>2</sub> consumption from submarine basalts. This uncertainty is one of the more important obstacles to modeling the long-term C cycle and its role in climate evolution (see discussion of Berner, 1990). The object here is to first examine seafloor weathering using petrologic, thermodynamic, and kinetic evidence. Seafloor weathering refers to the oxidative and nonoxidative alteration which occurs when seawater comes into contact with the upper several hundred meters of the oceanic crust, as well as the alteration of exposed ocean floor by seawater. We are specifically interested in the leaching of Ca during seafloor weathering.

The balance between CO<sub>2</sub> outgassing from the mantle and CO<sub>2</sub> consumption by weathering determines atmospheric CO<sub>2</sub> levels and, through the Greenhouse Effect, global climate over geologic time. Global climate is not only the result of changes in CO<sub>2</sub>, as it also reflects the presence of other greenhouse gases, the albedo, oceanic circulation (basin configuration), the presence (or absence) of vegetation, etc. Nevertheless, for a first order model it is reasonable to treat climate in terms of atmospheric CO<sub>2</sub> levels (e.g., Berner et al., 1983). Rates of CO<sub>2</sub> production by outgassing are generally thought to be related to marine spreading rates (e.g., Berner, 1994). Continental weathering rates are complex functions of temperature (Brady, 1991; Velbel, 1993; Gwiazda and Broecker, 1994; Dorn and Brady, 1995; White

and Blum, 1995), organic activity (e.g., Volk, 1987; Schwartzman and Volk, 1989; Brady and Carroll, 1994), exposure/elevation (Stallard and Edmond, 1983; Raymo et al., 1988; Drever and Zobrist, 1992; Bluth and Kump, 1991; alternatively see White and Blum, 1995), and, in the case of basalt, age (Gíslason et al., 1995). The rate dependencies for carbon dioxide consumption by seafloor weathering are less clear.

To explain the  $^{87}\text{Sr}/^{86}\text{Sr}$  record of marine carbonates, Francois and Walker (1992) suggested that seafloor weathering rates might be proportional to  $[\text{H}^+][\Sigma\text{CO}_2]$  (bracketed terms denote aqueous concentrations in the deep ocean). Francois and Walker (1992) emphasized that a critical input in models of global C cycling may be the rate dependency of seafloor weathering. Although petrologic mass balance measurements (e.g., Thompson and Humphris, 1977; Staudigel et al., 1990; Spivack and Staudigel, 1994) give estimates of integrated weathering fluxes, they do not reveal how  $\text{CO}_2$  fluxes respond to geochemical and tectonically-induced changes elsewhere in the global C cycle. For this, the specific rate dependencies of seafloor weathering must be determined.

A feedback between weathering (continental and/or seafloor) and atmospheric  $\text{CO}_2$  (or temperature) appears to be needed if climate is to be stabilized over geologic time (Walker et al., 1981; Francois and Walker, 1992). Because of the relatively small size of the atmospheric reservoir minimal imbalances between  $\text{CO}_2$  sources and sinks would cause rapid fluctuations in atmospheric  $\text{CO}_2$  levels and global mean temperatures.  $\text{CO}_2$  consumption from continental silicate weathering is thought to be greatest when high  $\text{CO}_2$  levels cause temperatures to be high and vice versa (e.g., Walker et al., 1981; alternatively see Raymo and Ruddiman, 1992). No equivalent feedback control over  $\text{CO}_2$  consumption by seafloor weathering has been fully quantified.

Caldeira (1995) constructed a C cycle model and used laboratory dissolution rates measured in dilute solutions to estimate seafloor weathering response to changes in ocean chemistry, but not temperature. Caldeira (1995) calculated seafloor weathering to vary relatively little in response to changes in atmospheric  $\text{CO}_2$  levels, and, as a result, predicted that the continental weathering feedback has been a more important control over long-term atmospheric  $\text{CO}_2$  levels. The strength of the continental weathering feedback occurs for the most part because silicate weathering is sensitive to temperature (Brady, 1991; Gwiazda and Broecker, 1994), not because of its sensitivity to the chemistry of the weathering solutions (Brady, 1991; Gwiazda and Broecker, 1994). A true comparison of the continental and seafloor weathering feedbacks must consider the role of temperature in seafloor weathering as well. We use experimental measurements to constrain the effect of temperature on  $\text{CO}_2$  consumption by basalt weathering in seawater-like solutions. This allows some limits to be set on the linkage between seafloor weathering and climate.

### 3. LOW TEMPERATURE ALTERATION OF THE OCEAN FLOOR

#### 3.1. Thermodynamic Constraints

As seawater comes into contact with basalt at low temperature, basaltic glass, olivine, and sometimes plagioclase tend

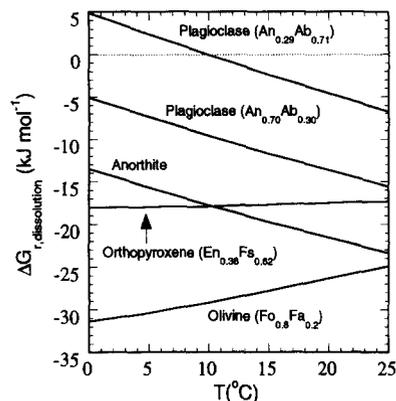


Fig. 1. Calculated Gibbs free energy ( $\text{kJ mol}^{-1}$ ) of dissolution into seawater as a function of temperature for basaltic minerals.

to dissolve. This is observed in DSDP cores (see summary of Honnorez, 1981) and predicted by solubility calculations. In Fig. 1 are shown calculated free energies of dissolution,  $\Delta G_r$  ( $\text{kJ mol}^{-1}$ ) for the various phases present in basalt in contact with seawater as a function of temperature. The WATCH program of Arnórsson et al. (1982) was used to calculate aqueous speciation for the seawater composition given in Riley and Chester (1971). The database is that given in Table 5 of Arnórsson et al. (1982) except for the addition of the aluminum hydroxy complexes (see the discussion of Gíslason and Arnórsson et al., 1993). The Gibbs free energy of formation of minerals and aqueous species involved in the dissolution reactions depicted by Fig. 1 is given in Gíslason and Arnórsson et al. (1993). Reliable thermodynamic data are not available to assess the solubility of basaltic glass in aqueous solutions. However, it is clear that such glass will have a higher solubility than any of the minerals as the glass has retained more energy (heat of crystallization) from its parent magmatic environment than the minerals. Olivines (forsterite to fayalite) are always undersaturated, increasingly so with decreasing temperature. The same trend is seen for orthopyroxene, though the undersaturation is slightly less. Plagioclase, the most abundant mineral in basalt, shows an interesting behavior. Ca-rich plagioclase ( $\text{An}_{70}$ ) is always undersaturated in seawater. Conversely to the olivines and pyroxenes, undersaturation increases with increasing temperature. Na-rich plagioclase ( $\text{An}_{29}$ ), which probably represents the composition of groundmass plagioclase in the interior of basalt pillows, is saturated below  $10^\circ\text{C}$  but undersaturated above ( $\text{An}_{29}$  stability depends also on the solution pH). Although basaltic glass, Ca-plagioclase, and possibly clinopyroxenes are probably the most important suppliers of Ca to seawater, Na-rich plagioclase may also contribute depending on the temperature.

Solubility calculations indicate that low temperature seawater ( $\sim 0^\circ\text{C}$ ) is saturated with respect to calcite and Mg-smectite, and close to saturation with zeolites and K-smectite, before reacting with ocean basalts. The most prevalent alteration minerals, as observed in DSDP cores, and summarized in Honnorez (1980) and Staudigel and Hart (1983), are palagonite, Mg- and K-smectites, K, Na, Ca-zeolites,

Ca, Mg-carbonates, and Fe-hydroxides. Dissolution of basalt results in higher levels of e.g., Ca, Mg, Si, Al, Fe, and probably an increased pH in the percolating seawater. The net result is an increase in supersaturation with respect to calcite and Mg-smectite and probably saturation with respect to zeolites and K-smectite. Accumulation of primary mineral components in solution would also decrease the thermodynamic driving force for dissolution. Nevertheless, it is fairly clear from Fig. 1 that fresh seawater has the capacity to weather primary silicates upon contact.

### 3.2. Petrologic Observations

At high seawater flushing rates (high fluid/rock ratio), Ca and Mg are lost to seawater as shown by samples dredged from the ocean floor (e.g., Thomsson, 1983). The Honnorez (1981) summary included nine studies indicating Ca loss from the basalts and eleven studies where Mg loss to seawater was documented (note that these studies represent hundreds of samples). A number of uncertainties obscure estimated fluxes though. Undoubtedly, some of the Mg goes into the formation of smectite veins. At the same time, substantial evidence points to exchange of Mg for Ca (see review of Berner and Berner, 1987), particularly at higher temperatures and in any overlying sediments (Caldeira, 1995). Calcium released by the latter process is particularly important as it doesn't affect the CO<sub>2</sub> budget. Caldeira (1995) cited evidence from hole 418A suggesting that 69% of the Ca release can be accounted for by exchange reactions. At the same time, dredged samples are always recovered from taluses associated with fault scarps, or other tectonic events, and are probably not representative of closed-off samples. These samples have been exposed to extremely large amounts of seawater from the time they were uplifted to the ocean floor by faulting to the time they were dredged (Honnorez, 1981).

A significant portion of the Ca leached from the basalt combines with bicarbonate from circulating seawater to form calcite. Although kinetic factors determine whether Ca is transported away from the weathering site, the C used to precipitate calcite must come from seawater as there is little in basalt. Inhibition of calcite precipitation by Mg may play a role (Mucci and Morse, 1983) and calcite might not precipitate until enough Mg has been consumed by smectite growth. Carbonate levels are higher in altered basalt than in pristine basalt because altered basalt values include the C addition needed to grow calcite. Net dissolution of Ca-containing silicates in the basalt is estimated by comparing the Ca content of bulk unaltered basalt with the Ca content of altered basalt and correcting for the amount of Ca associated with authigenic calcite in the latter (e.g., Thompson, 1983). Although most basalts from drill cores tend to gain Ca in the process of being altered, on a mole basis they acquire even more C. The extra Ca required to form calcite must, therefore, come from the rocks themselves (Staudigel et al., 1989). The Ca/Sr ratio of authigenic carbonates suggest that at least 50% of the Ca was derived from basalt alteration (Staudigel et al., 1981). Titanium-normalized Ca losses and CO<sub>2</sub> exchange from the basalts recovered at DSDP holes 417 and 418 (Thompson, 1983; Staudigel et al., 1990;

Spivack and Staudigel, 1994) indicate that at least 51–83% of the Ca is derived from the primary basalt. Alternatively, Caldeira (1995) has suggested that seawater Ca could also form calcite if heated sufficiently. For an extensive review of the arguments for and against Ca-leaching from basalts to form calcite see Caldeira (1995). Caldeira (1995) concluded that the actual fraction of carbonate formed by seawater Ca is not clear and used a value of  $3 \times 10^{12}$  mol/y as the rate of carbon uptake in his model. We will likewise assume that the seafloor weathering sink is substantial, though unquantified.

### 3.3. Timing of Alteration

Studied basalts from the seafloor are almost always altered (Muehlenbachs, 1980). The alteration must commence immediately after the crust is formed because the young (<3.2 m.y.) DSDP basalts are pervasively weathered (Muehlenbachs, 1977; Muehlenbachs and Hodges, 1978). The weathering proceeds for some millions of years and then appears to cease because the  $\delta^{18}\text{O}$  values of DSDP basalts do not continue to increase with age. The  $\delta^{18}\text{O}$  values of the altered basalts from both the young sites and the bottom of the deep Cretaceous holes are approximately the same as those of basalt exposed to seawater for about 10 m.y. Easy access of seawater to the crust ends by that time (Muehlenbachs, 1977). Consistent with this scenario, radiometric dating of vein smectites indicates that most of the alteration occurs within 3 m.y. (Hart and Staudigel, 1978; Richardson et al., 1980). After the open circulation of seawater ceases, some alteration continues in the top of the basalt section because  $\delta^{18}\text{O}$  gradients are observed in the basalts from the Cretaceous holes, but not in the young holes of equal depth (Muehlenbachs, 1977; Muehlenbachs and Hodges, 1978). The second stage of alteration proceeds at a much slower rate and probably with connate seawater (Muehlenbachs, 1980). Convective flow, and presumably extensive alteration, end once 100–150 m of sediment accumulates (McDuff, 1981). Sediment-seawater interaction tends to make reacting fluids more reducing (e.g., Mottl and Wheat, 1994) and possibly charged with CO<sub>2</sub>. Note that this occurs well after the peak of Ca-leaching has passed. Alteration and re-equilibration is thought to occur in the older crust at higher temperatures (20–40°C) (Muehlenbachs, 1977).

### 3.4. Temperature and Hydrologic Setting

There is a great deal of uncertainty regarding the temperature and hydrologic setting of seafloor weathering. Substantial evidence points to low temperature ( $T < 10^\circ\text{C}$ ) alteration of the top 600 m of the ocean floor by seawater at ambient temperatures (Muehlenbachs and Clayton, 1976; Muehlenbachs, 1977; Lawrence and Drever, 1981; Lawrence et al., 1977; Thompson and Humphris, 1977). Calcite veins have oxygen isotopic compositions ranging from  $\delta^{18}\text{O}$  (SMOW) 30.8–37.3‰ and carbon isotopic compositions of  $\delta^{13}\text{C}$  (PDB) of 1.6–4.6 (Lawrence et al., 1977; Muehlenbachs, 1977; it is routinely assumed that calcite formed under the same temperatures as alteration). Paleotemperatures calculated from the oxygen isotopic data point to growth at 0–

15°C in equilibrium with deep ocean water (Lawrence et al., 1977). At DSDP site 395 calculated formation temperatures are less than 6°C for all calcites sampled in the top 500 m of basalt and only exceed this value at greater depth. Nevertheless, higher temperatures have also been observed where evidence of local hydrothermal activity is present. At the same time there is evidence pointing to authigenic carbonate growth from warmer (up to 40°C) fluids (Burns et al., 1992) at up to 36 m.y. after basalt formation. This may represent the late-stage alteration cited by Muehlenbachs (1977). At the same time it may point to alteration occurring over significantly longer periods than the 0–3 m.y. time window assumed above, and at higher temperatures. Mottl and Wheat (1994) have modeled 1–4 m.y. old basement temperatures to be greater than 15°C.

The lower temperature results ( $T < 10^\circ\text{C}$ ) have been explained as being caused by high fluid/rock ratios wherein alteration of the upper 500–600 m occurred at ambient deep ocean temperatures. Lawrence and Drever (1981) estimated that volumetric fluid/rock ratios of at least 10–1000 were required to produce the observed calcite vein abundances. The high volumes of seawater required, combined with the evidence for weathering at ambient seawater temperatures, led Lawrence et al. (1977) to suggest that fluid flow was driven by convective heat loss from the crust, but that weathering of the top 400 m occurred primarily on the downgoing limb. Obviously, speculating further about the nature and extent of fluid circulation through 0–3 m.y. old ocean crust is difficult in the absence of more data. Nevertheless, the majority of data to date suggests that downwelling is vigorous enough to erase or minimize any chemical signature of large-scale hydrothermal activity. Because of the accumulated uncertainties we explicitly consider hydrothermal effects when we examine weathering-climate feedbacks below.

To summarize, a great deal of evidence points to extensive leaching of Ca from basalts on the order of  $1\text{--}2 \times 10^{12}$  moles m.y. by cold deep ocean water under fluid-dominated conditions within roughly 3 m.y. of eruption. Nevertheless, Ca carbonate formation, and presumably Ca-leaching, has been seen to occur at higher temperatures and over longer periods of time. To link the Ca (and  $\text{CO}_2$ ) flux to models of the global C cycle and long-term climate requires that the sensitivity of Ca leaching to changes in ocean chemistry and temperature be constrained. Because of the obvious difficulties involved in extracting rate dependencies from drill core data we instead draw on experimental measurements of basalt dissolution.

## 4. DISSOLUTION OF BASALT INTO SEAWATER

### 4.1. Background

Calcium leaching from basalt glass and basalt minerals is significant and measurable in the laboratory over relatively short timescales (e.g., Furnes, 1975). Seyfried and Bischoff (1979), using a seawater to crushed basalt glass mass ratio of 10:1, observed measurable increases in Ca over the high seawater background in 30 h at  $T > 70^\circ\text{C}$ . Crovisier et al. (1983) using a seawater/glass ratio of 50 (wt.) identified the primary weathering reactions at 50°C to be the release of Ca and the subsequent formation of hydroxycarbonates,

which may be precursors to phyllosilicates. Crovisier et al. (1983) specifically noted uptake of Mg by layers at the glass surface. Crovisier et al. (1987) showed that dissolution of basalt glass into seawater is stoichiometric and that palagonitic growth layers probably do not passivate the surface against further dissolution. The temperature dependence of the dissolution rate of basaltic glass in various solutions (distilled water, seawater, 0.05 M HCl-NaCl solutions, amorphous silica-saturated solutions; Berger et al., 1987, 1988, 1994; Crovisier et al., 1987; Gislason and Eugster, 1987; Guy, 1989; Guy and Schott, 1989) normalized to pH-independent rates for basaltic glass (Guy and Schott, 1989) is the same (Berger et al., 1994) and translates to 64 kJ mol<sup>-1</sup> for initial rates, and 60 kJ mol<sup>-1</sup> for long-term rates. To confirm the temperature dependence, and to constrain any effect of  $P_{\text{CO}_2}$  on rates, whole rock basalt dissolution rates were measured.

### 4.2. Experimental Methods

Unaltered pillow basalt from the Southern Rift Valley of the Eastern Galapagos Rift was provided by M. R. Perfit of the University of Florida. The sample (#50-2 in Table 1 of Embley et al., 1988) was part of a pillow basalt recovered from a depth of 2540 m. The pillow has multiple protrusions, each 8–14 cm in diameter and a well preserved, thick glassy rind. The sample is vitrophyric grading into mesocrystalline in the interior. The outer glassy rind (<1 cm) contains microlites of plagioclase and clinopyroxene that commonly exist in the cores of spherulitic intergrowths (quenched crystallites) set in fresh glass. The outer zone grades inward to a mesocrystalline region containing sub- to euhedral microphenocrysts of plagioclase and clinopyroxene (<1 mm long) set in a matrix of devitrified glass containing crystallite opaques. Some areas have a fasciculate texture with branching crystals of plag and cpx. Vesicularity is less than 1% and vesicles are generally smaller than 0.1 mm. A few zones of the sample contain fractures along which there is some palagonitization and more extensive devitrification/weathering of glass (M. R. Perfit-pers. commun., October, 1996).

The sample was ground to a sieve size fraction of 75 < diameter < 125  $\mu\text{m}$ , then ultrasonically washed in alcohol to remove any adhering fine particles produced in grinding. The BET surface area of the ground, washed basalt was measured to be 1990 cm<sup>2</sup>/gm. A chemical analysis of the basalt is given in Table 1. Dissolution rates were measured in single pass, flow-through reactors (see Knauss and Wolery, 1986) to mimic sub-seafloor circulation. Mineral dissolution rates were determined by measuring the change in dissolved silica concentration between the input ( $\text{Si} = 0$  ppm) and output solution and normalizing these to reactor flow rate and total mineral surface area. Input solutions were seawater-like solutions made to the seawater recipes of Subow (1941). Silica concentrations in the output solutions were measured by direct current plasma (DCP) atomic emission spectrometry.

Dissolution rates were measured at 25, 37, and 50°C and at  $P_{\text{CO}_2} = 10^{-3.5}$  atm. and  $10^{-2.3}$  atm. The 37 and 50°C experiments were done by thermostating the reaction chamber in a water bath.  $\text{CO}_2$  was bubbled through the input solutions for the runs at greater than atmospheric  $\text{CO}_2$  levels. The conditions for each of the experimental runs are given in Table 2. Surface area-normalized rates were calculated from Si release because of the necessary high background of Ca, Mg, Na, and K. Each element has the potential to affect dissolution rates by adsorbing to, and accelerating, or poisoning, weathering. Because the major element composition of seawater has not changed significantly over Phanerozoic time (e.g., Holland, 1984), determining general controls on  $\text{CO}_2$  by weathering does not require the unraveling of the specific effects of individual elements. Although input solutions were Si-depleted relative to seawater ( $\text{Si} \sim 4$  ppm; Riley and Chester, 1971), the steady-state outflow solutions ( $0.9 < \text{Si} < 8$  ppm) were similar in Si content. One result of the high Ca levels of seawater (and the relatively low rate of dissolu-

Table 1. Basalt composition

Oxide	%
SiO <sub>2</sub>	51.4
TiO <sub>2</sub>	1.88
Al <sub>2</sub> O <sub>3</sub>	12.5
FeO <sup>T</sup>	13.0
MnO	0.22
MgO	6.26
CaO	10.4
Na <sub>2</sub> O	2.38
K <sub>2</sub> O	0.11
P <sub>2</sub> O <sub>5</sub>	0.22
S	0.16
Total	98.5

From: Embley et al. (1988)

tion) is that in the discussion of Ca-release below, it is assumed that steady-state Ca release rates are proportional to steady-state Si release rates at each  $P_{\text{CO}_2}$  and temperature (see discussion of Crovisier et al., 1987).

As noted above, the fluid-rock ratio typical of basalt weathering is uncertain and, therefore, impossible to exactly reproduce in the laboratory (see Honnorez, 1983). The steady-state volume of fluid in the reaction cell and tubing was roughly 15 cm<sup>3</sup>, hence the mineral area to fluid mass ratio was  $1.3 \times 10^4$  cm<sup>2</sup>/L. The surface area of the dissolving basalt was found to increase slightly, to 2370 cm<sup>2</sup>/gm, in the one month duration of the experiment. The increase is probably due to: (1) calcite growth, and/or (2) dissolution-driven enhancement of surface microporosity.

#### 4.3. Results

Dissolution reactions quickly approached steady state, generally within 2–3 days. Steady state dissolution rates are shown as a function of temperature and  $P_{\text{CO}_2}$  (at 25°C) in Table 2 and Fig. 2. The 25°C  $P_{\text{CO}_2} = 10^{-3.5}$  atm basalt dissolution rate =  $10^{-14.35}$  mol/cm<sup>2</sup>s is bracketed by the olivine rate (=  $10^{-13.8}$  mol/cm<sup>2</sup>s) and enstatite rates (=  $10^{-15.1}$  mol/cm<sup>2</sup>s) measured at 25°C and  $P_{\text{CO}_2} = 10^{-3.5}$  but in more dilute solutions by, respectively, Wogelius and Walther (1991) and Brady and Walther (1989). To get an idea of the uncertainty in the rates, the error in the DCP analyses are on the order of  $\pm 5\%$ . The error in the BET analyses is on the order of  $\pm 7\%$ . Note that CO<sub>2</sub> has a minor, but measurable effect on dissolution rates. A sixteenfold increase in solution carbon dioxide content (from  $P_{\text{CO}_2} = 10^{-3.5}$  atm to  $10^{-2.3}$  atm) raised dissolution rates by roughly a factor of 2. Higher  $P_{\text{CO}_2}$ 's are associated with lower input (and output) pH's making it difficult to say whether CO<sub>2</sub> or protons accelerate dissolution. Because the latter drive dissolution of Ca and Mg silicates in dilute solutions (Brady and Carroll, 1994), we assume that basalt dissolution rates respond to changes in pH, not  $P_{\text{CO}_2}$ . This has important implications for the weathering-climate linkage as Caldeira (1995) has shown that ocean bottom pH is quite insensitive to likely changes in  $P_{\text{CO}_2}$  over geologic time. The net result is that changes in atmospheric CO<sub>2</sub> levels probably

have little direct effect on seafloor weathering rates. The activation energy for dissolution calculated from the 25, 37, and 50°C rates is 41 kJ mol<sup>-1</sup>. This value is somewhat lower than that measured for tholeiitic glass dissolution by Crovisier et al. (1987) and other workers (see above), but otherwise broadly consistent with the range of activation energies observed for Ca and Mg silicates dissolving into dilute solutions, which generally range from 41 to 82 kJ mol<sup>-1</sup> (e.g., Brady, 1991).

#### 5. SEAFLOOR WEATHERING

Our object is to use the measured dissolution rate dependencies to examine the seafloor weathering-climate feedback. This can only be done in an order of magnitude sense as it is impossible to exactly predict the temperatures or quantities of fluids that seafloor basalts interact with. In light of the Caldeira (1995) work showing minimal effects of ocean chemistry on weathering we focus on the role of temperature. We use two endmember cases to semiquantitatively assess the role of temperature in seafloor weathering. The first case builds on the work of Muehlenbachs and Clayton (1976), Muehlenbachs (1977), Lawrence and Drever (1981), Lawrence et al. (1977), and Thompson and Humphris (1977), and assumes that the temperatures of the solutions which weather the top 600 m of the oceanic crust are, in essence, those of deep ocean water. This case will be termed the cold basalt endmember. For this case it is important to note that deep ocean temperatures are particularly sensitive to atmospheric CO<sub>2</sub> levels (see below).

The second endmember we use, the hot basalt case, assumes that weathering solutions are heated by the underlying slab to temperatures above that of deep ocean water. This case envisions waters that are not really all that hot ( $10 < T < 40^\circ\text{C}$ ). The important point is that their temperature is set not by atmospheric CO<sub>2</sub> levels, directly or indirectly, but by tectonic processes which drive heat production, namely ridge spreading. Examination of the hot and cold basalt scenarios, combined with global carbon cycle models, are useful in that they point up critical data needs, and they suggest that seafloor weathering does play a role in climate control.

#### 6. WEATHERING OF COLD BASALTS

Ocean deep water is the result of thermohaline circulation originating at the poles. Deep water temperatures are largely determined by the temperatures of high latitude air masses, and with high atmospheric CO<sub>2</sub> levels these rise. Changes in global mean temperature are amplified at high latitudes. For a given  $P_{\text{CO}_2}$  polar temperatures will depend in a complex

Table 2. Experimental conditions and results

$T$ (°C)	log $P_{\text{CO}_2}$ (atm.)	log R (moles/cm <sup>2</sup> s)
25	-3.5	-14.35
37	-3.5	-14.05
50	-3.5	-13.79
25	-2.3	-14.07

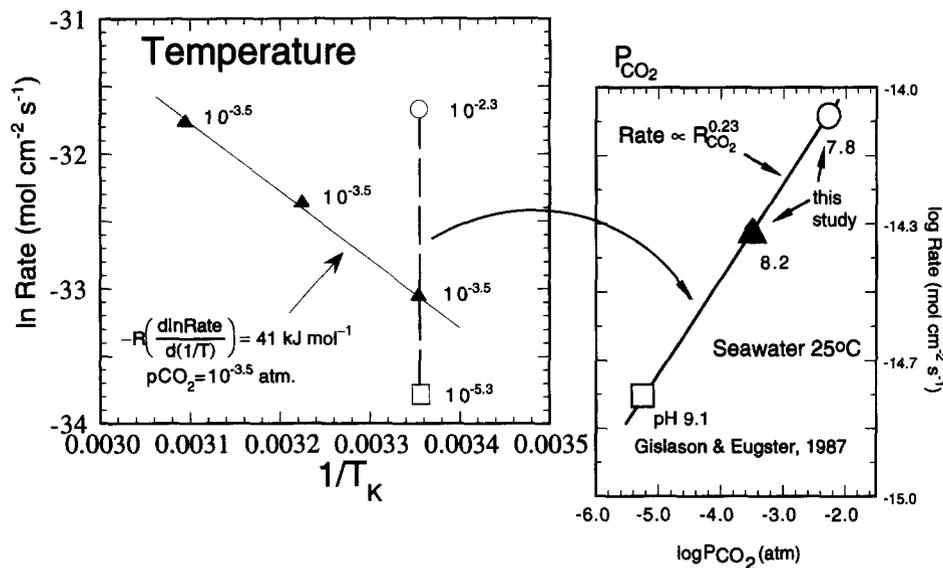


Fig. 2. Basalt dissolution rates in seawater ( $\text{mol cm}^{-2} \text{ s}^{-1}$ ) measured from Si-release as a function of temperature and  $P_{\text{CO}_2}$ .

fashion on a number of geographic factors, particularly the degree of ice coverage (e.g., Barron et al., 1980). Barron and Washington (1985) calculated that for Cretaceous geography a fourfold increase in atmospheric  $\text{CO}_2$  would give an increase in the global mean temperature of  $3.6^\circ\text{C}$ . The temperature increase was calculated to fall most heavily on the high latitudes ( $60\text{--}80^\circ$ ), though, where temperatures were calculated to increase between 5 and  $7^\circ\text{C}$ , in other words by 40–90% over the global mean. Spelman and Manabe (1984) and Manabe and Bryan (1984) also showed that  $\text{CO}_2$ -induced warming of the deep ocean is significantly larger than the area-averaged global mean and used this result to explain the divergence of  $^{18}\text{O}$  isotopic temperatures measured by benthic vs. planktonic foraminifera from the North Pacific (see Savin, 1977). The amplification of temperature changes at the poles is important because it means that over periods of time greater than the residence time of deep ocean water, small changes in global mean temperature (and atmospheric  $\text{CO}_2$ ) should result in large changes in the temperatures of deep ocean waters in contact with abyssal basalts. When atmospheric  $\text{CO}_2$  is high, high latitude temperatures would be high, as would deep ocean temperatures. In contact with such solutions seafloor weathering would be amplified, in the process causing a proportionally larger drop in  $\text{CO}_2$ . Under times of low atmospheric  $\text{CO}_2$  and cold temperatures, seafloor weathering would be low and the attendant  $\text{CO}_2$  sink minimal.

The actual strength of the feedback proposed above depends on the temperature sensitivity of each link, as well as the absolute magnitude of the seafloor weathering sink. Manabe and Bryan (1984) used a general circulation model of the ocean-atmosphere system for an idealized geography to examine the controls on deep ocean temperatures. Their calculated high and low latitude temperatures are shown in Fig. 3. Fitting their calculated near-equatorial ( $6.7^\circ$ ) surface and abyssal temperatures as logarithmic functions of atmo-

spheric  $\text{CO}_2$  pressures from  $\text{CO}_2 = 0.5\text{--}8$  times its pre-industrial value gives  $\Delta T = (T - T_0) = 4.85 \ln R_{\text{CO}_2}$ .  $\Delta T$  is the change in temperature from its pre-industrial value ( $16^\circ\text{C}$ ). Note the much greater sensitivity of this function compared to that between  $\text{CO}_2$  and ocean surface temperatures,  $\Delta T = 2.58 \ln R_{\text{CO}_2}$ . Because the results of Manabe and Bryan (1984) are quantitatively consistent with the independently calculated values of Barron and Washington (1985), it is reasonable to apply the results of their work as a first approximation to model weathering-climate response.

To determine the strength of the cold seafloor weathering- $\text{CO}_2$  feedback the relation between atmospheric  $\text{CO}_2$  and abyssal ocean temperatures is substituted into the Arrhenius

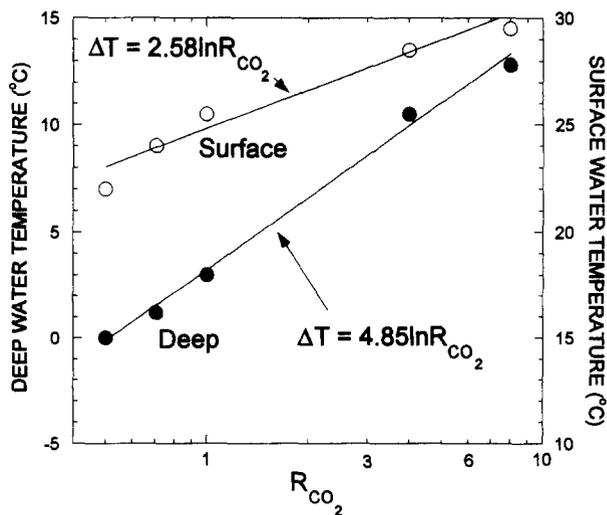


Fig. 3. Deep ocean and surface water temperatures calculated from the global climate energy balance model of Manabe and Bryan (1984).

relation describing rates as a function of temperature,  $f_{sr}$ , the ratio of seafloor spreading rate in the past to its present value, and  $R_{CO_2}$ :

$$\begin{aligned} r/r_0 &= f_{sr} \exp[(E_a/R)(T_0^{-1} - T^{-1})] \\ &= f_{sr} \exp[(41000/R)(T - T_0/TT_0)] \\ &= f_{sr} \exp[T - T_0/15.12] \\ &= f_{sr} \exp[4.85 \ln R_{CO_2}/15.12] \\ &= f_{sr} R_{CO_2}^{0.32} \end{aligned} \quad (1)$$

The weathering response is calculated for the activation energy measured here (41 kJ mol<sup>-1</sup>). Seafloor weathering is set proportional to spreading rate on the assumption that the total amount of basalt 0–3 m.y. in age available for weathering scales linearly with the rate at which it is produced.

### 7. SEAFLOOR VS. CONTINENTAL WEATHERING

For comparison, the continental weathering feedback is calculated using an activation energy of 63 kJ mol<sup>-1</sup> (see Brady, 1991 and Berner, 1994). Attendant increases in runoff are accounted for with the expression of Berner et al. (1983) where runoff increases proportionally to  $\exp(\Delta T/17.85)$ . Changes in continental surface area over time are accounted for in  $f_a$ , the ratio of exposed continental area to its present value. The amplification by organic activity (higher plants, microbes etc.) is tracked using a Michaelis-Menton function and weathering is set proportional to  $[2R_{CO_2}/(1 + R_{CO_2})]^{0.4}$  (Berner, 1991). The Greenhouse relation,  $\Delta T = 2.7 \ln R_{CO_2}$ , is substituted to express weathering response as a function of  $P_{CO_2}$ .

$$\begin{aligned} r/r_0 &= f_a \exp[(63000/R)(T - T_0/TT_0)] \\ &\quad \exp[T - T_0/17.85] [2R_{CO_2}/(1 + R_{CO_2})]^{0.4} \\ &= f_a \exp[T - T_0/10.95] \exp[T - T_0/17.85] \\ &\quad [2R_{CO_2}/(1 + R_{CO_2})]^{0.4} = f_a \exp[2.7 \ln R_{CO_2}/10.95] \\ &\quad \exp[2.7 \ln R_{CO_2}/17.85] [2R_{CO_2}/(1 + R_{CO_2})]^{0.4} \\ &= f_a R_{CO_2}^{0.40} [2R_{CO_2}/(1 + R_{CO_2})]^{0.4} \end{aligned} \quad (2)$$

For comparison the weathering response functions (Eqns. 1 and 2) are plotted as a function of  $R_{CO_2}$  in Fig. 4.  $f_a$  and  $f_{sr}$  were set equal to one to point out the relative strengths of the CO<sub>2</sub>-temperature-weathering feedbacks. One of the primary conclusions to be drawn from Fig. 4 is that seafloor weathering is probably less sensitive to changes in atmospheric CO<sub>2</sub> relative to continental weathering. A fourfold increase in atmospheric CO<sub>2</sub> levels, in the absence of changes in continental surface area and spreading rate, would cause a near doubling of continental weathering, but only a 50% increase in seafloor weathering.

Although the response of seafloor weathering to changes in atmospheric CO<sub>2</sub> is less than that of continental weathering, it is not orders of magnitude (Caldeira, 1995) smaller. This is probably true, even if hot basalt weathering occurs at temperatures greater than that of the deep ocean. High spreading rates are generally associated with times of ele-

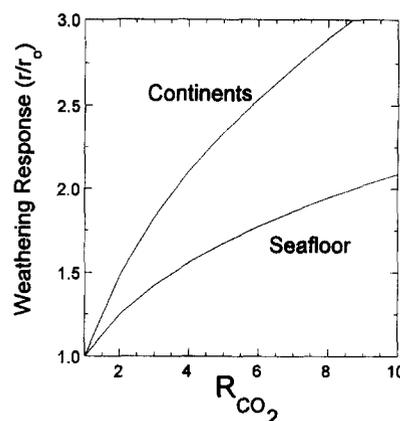


Fig. 4. Sensitivity of continental and seafloor weathering to changes in atmospheric CO<sub>2</sub>. Lines were calculated from Eqns. 1 and 2.

vated atmospheric CO<sub>2</sub> (Berner et al., 1983) and lead to increased heat fluxes. The added heat flux can be taken up by increased fluxes of fluid through the basalts and/or by higher temperatures in the weathering solutions. Both would lead to increased weathering. As a result high spreading rates, high atmospheric CO<sub>2</sub> levels and elevated seafloor weathering should occur at the same time. This might constitute a feedback wherein the increase in CO<sub>2</sub> production by ridge spreading would be compensated by seafloor weathering accelerated by the added heat flow. The actual strength of such an apparent feedback can only be quantified if the linkage between weathering fluid fluxes, temperatures, and spreading rates is better understood. The absolute size of any seafloor weathering sink for CO<sub>2</sub> also remains unclear (see review of Caldeira, 1995). Recent work by Snow and Dick (1995) points to a possible  $2 \times 10^{12}$  eq/y of CO<sub>2</sub> consumption by weathering of abyssal peridotites, which might amplify the total. The absolute size of the sink and the thermal regime which drives it, therefore, remain critical questions. Nevertheless, our results demonstrate a significant feedback between seafloor weathering and climate. Our results also support the notion that seafloor weathering might have moderated climate in the continent-free world of the Archean (Walker, 1990).

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