

SEDIMENTARY CARBONATE RECORD OF CALCIUM—MAGNESIUM CYCLING

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ABSTRACT. Mass-age data on sedimentary carbonate sequences define decay parameters for principal reservoirs which, in conjunction with tabulated dolomite abundances, allow for the determination of Ca and Mg sediment fluxes over the past 560 my. Cation transfer through oceans is approximated by balances: (1) between Mg supplied by rivers and removed at ridges and during carbonate accumulation, (2) between Ca delivered by rivers and ridges and removed by carbonate deposition, and (3) between ridge Ca for Mg exchange during hydrothermal alteration. Moreover, possible excursions of river Mg/Ca are constrained by bulk compositions of surficial rocks. Employing these relations, calculated fluxes for rivers, ridges, and carbonate reservoirs indicate rates of seawater Ca-Mg transfer have varied by no more than a factor of ± 120 percent over Phanerozoic time. Actual values are dependent on estimates of dolomite volume, carbonate accumulation rate, marine versus burial dolomitization, riverine Mg/Ca ratio, and the stoichiometry of Ca-Mg exchange during hydrothermal alteration.

Mass-age and composition data require an average Mg flux of 1.8×10^{18} m/my to dolostone reservoirs. The magnitude of this rate and estimates of Ca-Mg contribution by different rock types of global rivers indicate that most sedimentary dolomite is a syndepositional marine precipitate, as significant burial dolomitization would require provenance Mg/Ca values far in excess of ratios typical of dominant crustal lithologies.

Although hydrothermal alteration at ocean ridges is presently the dominant sink for seawater Mg, dolomite precipitation accounted for nearly the entire inventory of riverine Mg over much of Phanerozoic time. Rate of marine dolomite formation has been the most important Earth-surface process in controlling marine Mg concentration and seawater Mg/Ca ratio, far outweighing any influence of Mg removal by hydrothermal alteration.

INTRODUCTION

The sedimentary record of carbonate deposition is but part of a larger system that collectively includes transfer of calcium and magnesium between various hydrospheric and lithospheric reservoirs (fig. 1). Although principal sources, sinks, and transfer rates of Ca and Mg are well constrained for modern oceans (Holland, 1984), knowledge of past fluxes is more limited because the importance of hydrothermal basalt and deep-sea sediment alteration has only recently been appreciated (Drever, 1974; Lister, 1972). In addition, the extant record of cation removal during carbonate deposition is now only a fraction of original mass (Veizer and Jansen, 1985), and the importance of synsedimentary

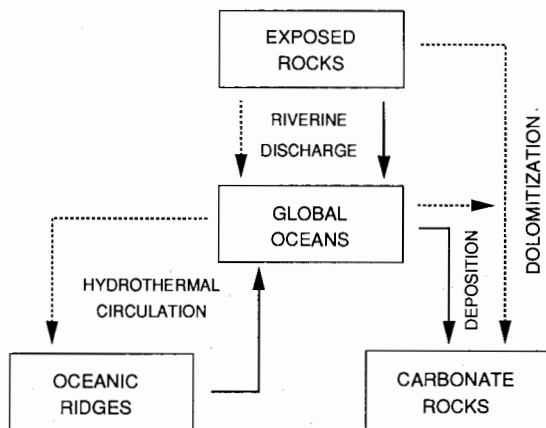


Fig. 1. Principal reservoirs and mechanisms of Ca and Mg transfer at the Earth's surface. Ca pathways shown as solid arrows, Mg fluxes as dotted arrows. Note that Ca is delivered to oceans from rivers and ridges but is only removed during limestone accumulation, while Mg is only supplied by rivers but is removed both at ridges and during dolomite formation. In theory, dolomite precipitation may occur in either marine or burial settings; both transfer paths are shown here.

versus burial diagenetic processes in dolomite formation is still poorly understood (Land, 1985).

In spite of these limitations, major reservoirs and mechanisms of transfer comprise few principal rock types and flux pathways. Perhaps most importantly, estimates of the age, volume, and composition of carbonate rock that serves as the principal sink for divalent cations have now been tabulated (Davies and Worsley, 1981; Hay, 1985; Ronov, 1980). Moreover, study of present transfer among carbonate and silicate reservoirs has been the focus of intense investigation for over a decade, and this information serves as an important temporal reference point for evaluating the history of Ca-Mg fluxes through global oceans.

Herein, the history of cation cycling at the Earth's surface is delimited from constraints imposed by mass-balances among the principal sources and sinks for Ca and Mg ions. Past rates of seawater cation removal during limestone/dolostone accumulation serve to limit significantly variation in cation cycling rate via river discharge and hydrothermal alteration.

MODERN FLUXES

In general, weathering of crustal rocks yields Ca and Mg ions that are transferred to oceans via river and groundwater discharge. Marine Mg is either incorporated into magnesian carbonate or is removed during submarine hydrothermal alteration as seawater comes into contact with hot basalt and overlying sediment at oceanic ridges. In the latter case, Mg exchanges for Ca which, in addition to Ca delivered by

ivers, is removed during carbonate deposition. Virtually all Ca is delivered to oceans from rivers and oceanic ridges but is only removed during limestone accumulation, while virtually all Mg is supplied by rivers but is removed both at ridges and during dolomitization (fig. 1).

Present fluvial fluxes, as well as the importance of different rock types in determining river water composition, have been discussed by many (fig. 2A); the present river Ca flux is about 13.2×10^{18} m/my (moles per million years) derived from the weathering of carbonate (67 percent), silicate (26 percent), and evaporite (7 percent) minerals (Meybeck, 1987). Riverine Mg delivery is about 5.2×10^{18} m/my, derived in roughly equal proportions from the weathering of carbonates (42 percent) and silicates (48 percent), with the balance from evaporite sequences (Meybeck, 1979). Collectively, rivers now supply about 18.4×10^{18} m/my of divalent cations to global oceans.

Field measurement of hydrothermal fluids (Edmond and others, 1979), laboratory experiments (Bischoff and Dickson, 1975; Mottl and Holland, 1978), and interstitial water studies (Gieskes and Lawrence, 1981; Perry, Gieskes, and Lawrence, 1976) demonstrate that basalt alteration is presently the primary sink for marine Mg ions (fig. 2B); the stoichiometry of hydrothermal reactions is such that each mole of Mg removed from seawater is accompanied by the release of between 0.7

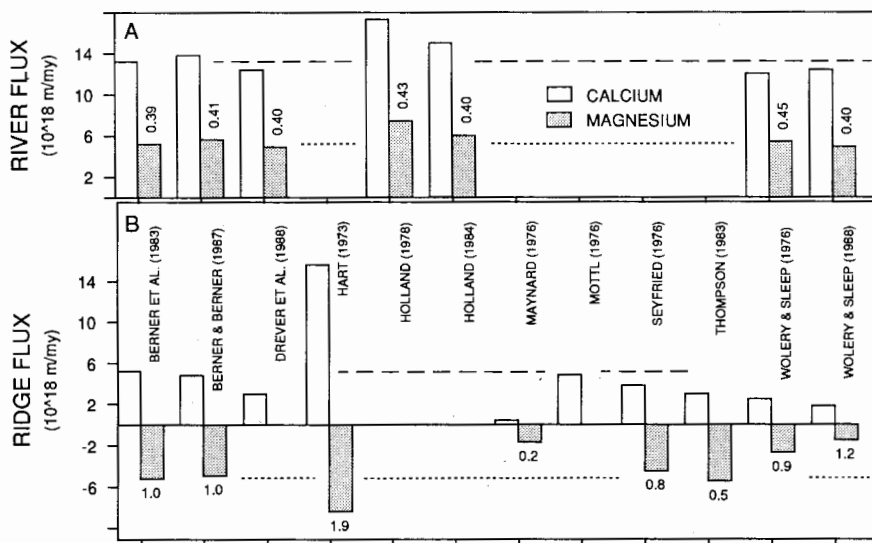


Fig. 2. Estimates of rates of Ca and Mg transfer via rivers and ridges. (A) River Ca (open bars) and Mg (shaded) fluxes. Global Mg/Ca ratio indicated above shaded bar; horizontal dashed line at 13.2×10^{18} m/my and dotted line at 5.2×10^{18} m/my are Ca and Mg fluxes used herein. (B) Ridge Ca (open) and Mg (shaded bars) fluxes. Ca-Mg exchange ratios indicated below each shaded bar; horizontal dashed and dotted lines at 5.1×10^{18} m/my are Ca and Mg flux values used herein.

and 1.0 moles of Ca (Drever, Li, and Maynard, 1988) which is ultimately removed during carbonate precipitation.

Berner, Lasaga, and Garrels (1963) estimate the magnitude of hydrothermal Ca-Mg exchange at about 5.2×10^{18} m/my, an amount equivalent to the flux of river Mg determined by Meybeck (1979). Differences between river Mg supply and Holocene carbonate Mg content in Milliman (1974) are in agreement with this value, suggesting that about 98 percent (5.1×10^{18} m/my) of river Mg is removed at ridges and about 2 percent (0.1×10^{18} m/my) is incorporated into magnesian calcite and dolomite (fig. 3).

Based on limestone-dolomite mass-age data (discussed below), the present Ca flux to carbonate sediment is about 23.7×10^{18} m/my, roughly half of which is delivered by rivers (13.2×10^{18} m/my) and 20 percent of which is derived from ridges (5.1×10^{18} m/my). Sources of the remaining 30 percent (5.4×10^{18} m/my) are less well constrained but include contribution via submarine infiltration of groundwater (Nace, 1969), submarine dissolution of cratonic carbonate rock (Walter and Burton, 1987), and/or the dissolution of pelagic ooze at subducting plate margins. Chaudhuri and Clauer (1986) suggest that groundwater seepage accounts for between 5 and 10 percent of river discharge volume, whereas data in Kharaka, Callender, and Carothers (1978),

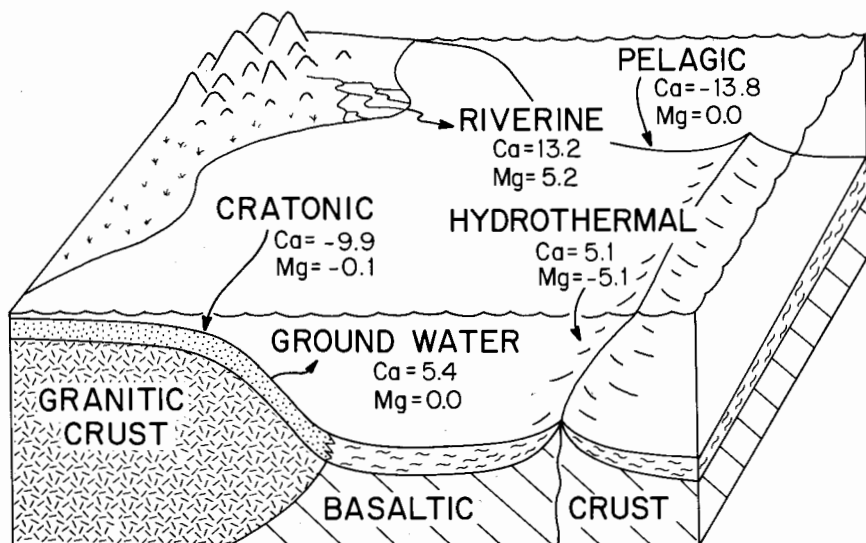


Fig. 3. Present rates of river, groundwater, and ridge Ca-Mg transfer through global oceans. All units as 10^{18} m/my. Modified from Drever, Li, and Maynard (1988). River fluxes from Livingstone (1963) and Meybeck (1979); ridge fluxes modified from Berner, Lasaga, and Garrels (1983); cratonic and pelagic fluxes from mass-age data. Groundwater seepage Ca value determined by summing all other fluxes and is in close agreement with a "sediment-seawater" exchange rate of 4.5×10^{18} m/my determined by Drever, Li, and Maynard (1988).

Magaritz and Luzier (1985), and Sass and Starinsky (1979) indicate that even shallow groundwaters may be an order of magnitude more concentrated in Ca than typical river water. This amount alone may largely balance Ca fluxes requisite for carbonate accumulation.

If seafloor carbonate dissolution is also a significant source of Ca ions, it is important that carbonate units be older than sediment deposited in the time-frame under consideration. Dissolution of pelagic ooze below lysoclines, while important in the cycling of Ca and CO_3^{2-} ions through seawater, results in no long term net contribution to carbonate reservoirs. Non-fluvial supply of Ca probably involves dissolution of Pleistocene and older Tertiary cratonic limestones along continental margins or deep-sea pelagic carbonates along subduction zones. Fresh water flow through carbonate aquifers of peninsular Florida (Kohout, 1967) and expulsion of Ca-rich fluid at convergent plate margins may serve as prime examples of such transfer processes. In the following, this 5.4×10^{18} m/my Ca contribution is collectively considered as undifferentiated groundwater seepage which, with 13.2×10^{18} m/my delivered by rivers, yields a Mg/Ca ratio of weathering products of global oceans of 0.28, about 75 percent that of rivers alone (fig. 3).

Summation of Ca-Mg transfer rates yields cycling parameters wherein sources and sinks are balanced (table 1). However, such a system is clearly not in equilibrium. As noted above, the present river flux of Mg to seafloor basalt is on the order of 5.1×10^{18} m/my, approx 42 percent of which is derived from the subaerial weathering of dolomitic carbonate (Meybeck, 1987). This represents a flux of 2.1×10^{18} m/my of Mg from carbonate to silicate reservoirs, a rate equivalent to the transfer of 1200×10^{18} moles over Phanerozoic time. Data on dolomite abundances indicate that sedimentary carbonate Mg mass is on the order of 1000×10^{18} moles (Berner, Lasaga, and Garrels, 1983), requiring an average Mg flux to dolomite of 1.8×10^{18} m/my. These values indicate that current magnitudes of seawater Mg removal by

TABLE 1

Present Ca-Mg fluxes through global oceans as 10^{18} m/my. Riverine-ridge data modified from Berner, Lasaga, and Garrels (1983); carbonate values from y-intercepts of mass-age data (fig. 4)

	Ca	Mg
Weathering		
Rivers	13.2	5.2
Groundwater/dissolution	5.4	0.0
Hydrothermal alteration	5.1	-5.1
Carbonate deposition		
Continental	-1.7	-0.1
Slope-rise	-8.2	-0.0
Pelagic	-13.8	0.0

hydrothermal alteration can not be representative of average oceans, require a long term net transfer of Mg from silicate to carbonate (rather than carbonate to silicate) reservoirs, and implicate significant secular variation in modes of cation exchange over Phanerozoic time.

CARBONATE CATION FLUXES

Given estimates of present seawater Ca-Mg fluxes via river discharge, groundwater seepage, and hydrothermal alteration, what can be said about rates of transfer through ancient oceans?

Carbonate Accumulation Rate

Cation removal rate during carbonate accumulation is obtained from mass-age data on pelagic, slope-rise, and continental sequences. Like many rock reservoirs (Veizer and Jansen, 1979), global limestone/dolostone sequences generally exhibit exponentially decreasing mass/volume with increasing age (fig. 4A), a trend that reflects long term destruction and accumulation in direct proportion to reservoir size. At this scale of resolution, accumulation rate can be determined from estimates of present reservoir mass and cycling rate typical of tectonic settings in which carbonate is deposited.

Mass-age relations for global sediments have been discussed by Garrels and Mackenzie (1971), Gregor (1985), and Ronov (1964), and cycling parameters for individual carbonate reservoirs have been quantified by Wilkinson and Walker (1989). Cycling of continental sequences (fig. 4B) proceeds by subaerial exposure and erosion, whereas most pelagic carbonate (fig. 4D) is removed from the Earth's surface during the subduction of oceanic lithosphere. Destruction of slope-rise carbonate (fig. 4C) reflects some combination of these processes, depending on relative amounts of subduction and obduction along continental margins. Because rate of subduction is much greater than rate of weathering, pelagic carbonate is largely Cenozoic in age (fig. 4D) whereas continental limestone/dolostone sequences extend well back into the Precambrian.

Available mass-age data suggest generally constant global carbonate mass over Phanerozoic time and exponential decay of component slope-rise and pelagic reservoirs. However, extant continental mass linearly increases back to the Mesozoic (fig. 4B), a trend that must record transfer from shallow to deep marine settings over about the past 150 my. Such a pattern has been noted by Hay and Southam (1976), Kuenen (1950), Milliman (1974), and Sibley and Vogel (1976) who suggested that Mesozoic diversification of planktonic calcifiers had a profound influence on patterns of carbonate sedimentation.

Quantification of best-fit trends for these reservoirs (fig. 4) yields characteristic cycling parameters. Accumulation rate for global, continental, slope-rise, and pelagic settings are 23.7, 1.7, 8.2, and 13.8×10^{18} m/my, respectively, and characteristic decay constants for continental, slope-rise and pelagic sequences are 0.002, 0.005, and 0.019 /my,

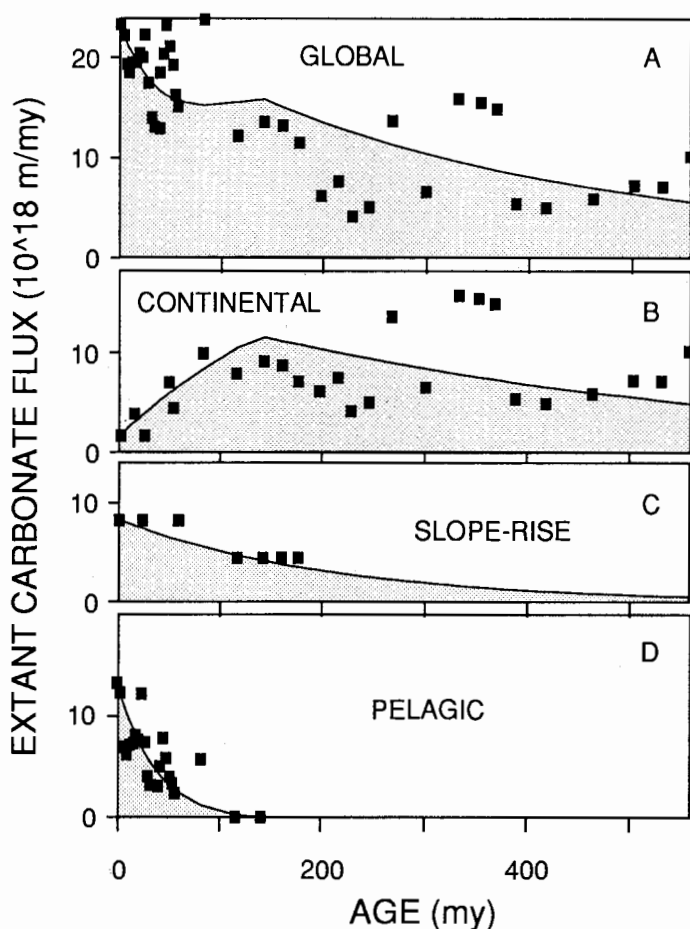


Fig. 4. Mass-age data and model trends for global, continental, slope-rise, and pelagic carbonate reservoirs expressed as apparent mass accumulation rates using the time scale of Harland and others (1982). Model trends constrained to intercept most recent flux values.

(A) Global data (rectangles) and best-fit model trend (shaded) calculated as the sum of continental, slope-rise, and pelagic values. Global reservoir modeled as a constant mass-flux system cycling at 23.7×10^{18} m/my.

(B) Continental carbonate data from Khain and Balukhovskiy (1979), Khain, Ronov, and Balukhovskiy (1975), Khain and Seslavinskiy (1977), Ronov and Khain (1954, 1955, 1956, 1961, 1962), Ronov, Kain, and Balukhovskiy (1978), Ronov, Khain, and Seslavinskiy (1976), and Ronov, Seslavinskiy, and Khain (1974). Best-fit trend calculated assuming a Mesozoic-Cenozoic flux decline of 0.1×10^{18} m/my and a decay constant of 0.002 /my.

(C) Slope-rise data from Hay (1985). Model trend calculated assuming a constant flux of 8.2×10^{18} m/my and a decay constant of 0.005 /my.

(D) Pelagic masses from data in Davies and Worsley (1981). Model trend calculated assuming a Mesozoic-Cenozoic flux increase of 0.1×10^{18} m/my and a decay constant of 0.019 /my.

TABLE 2

Phanerozoic carbonate masses and cycling parameters. Mass as 10^{18} m; flux and growth values as 10^{18} m/my

	Present mass	Flux	Decay constant	Growth rate
Continental	4514	1.7	0.002	-0.1
Slope-rise	1626	8.2	0.005	0.0
Pelagic	477	13.8	0.019	0.1
Global	6617	23.7	—	0.0

respectively (table 2). Furthermore, the apparent rate of continental carbonate mass decrease indicates a Mesozoic-Cenozoic increase in pelagic accumulation of about 0.1×10^{18} m/my. On the basis of these parameters, long term values of extant carbonate mass in agreement with actual mass-age data (fig. 5A, B) can be calculated.

It is important to point out, however, that mass-age data for all reservoirs exhibit a considerable amount of short term secular variation from long term trends (fig. 4). These differences reflect some combination of three possible explanations: (1) rate of carbonate accumulation has changed little over Phanerozoic time, and short term variation reflects preferential preservation of different portions of each reservoir; (2) rate of carbonate accumulation has varied considerably over Phanerozoic time, and short term variation accurately records changes in cation flux to global oceans; (3) rate of carbonate accumulation has varied little over Phanerozoic time, and short-term variation in mass-age data reflects inherent imprecision in estimates of extant carbonate mass in continental, slope-rise, and pelagic settings.

In a context of determining rates of seawater cation removal, two scenarios span this range of possibilities. Because exponential decay schemes relate extant mass (M_r) to deposition rate (M_o) by $M_r = M_o * e^{-kt}$, carbonate fluxes can be determined by each sedimentary setting either assuming that mass-age data (fig. 5C) or long term trends (fig. 5D) more faithfully record rates of carbonate accumulation. In determining rates of Ca-Mg removal by carbonate deposition, both scenarios of carbonate accumulation are considered herein.

Carbonate Composition

Data on sequence composition is also necessary to determine seawater cation fluxes because transfer rates of Ca and Mg determine amounts of aragonite, magnesian calcite, and/or dolomite in each reservoir. With the exception of a few reported occurrences of dolomite in distal slope settings (Baker and Burns, 1985), pelagic carbonate is largely calcitic (Lumsden, 1985). With respect to the amount of dolomite in continental and slope-rise carbonates, one of several time-honored truisms is that dolomite abundance generally increases with stratigraphic age (fig. 6). This conclusion is largely based on dolostone/

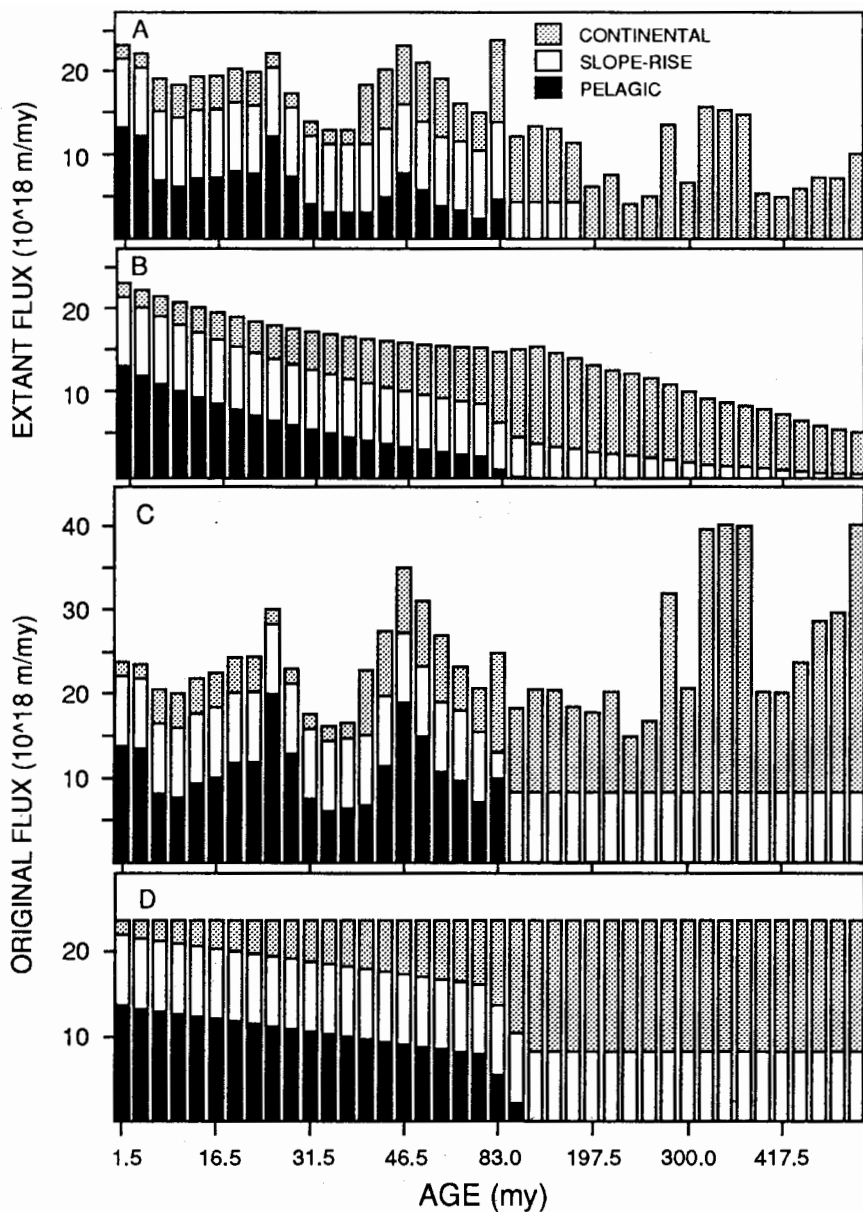


Fig. 5. Remaining (A, B) and original (C, D) rates of shallow continental, slope-rise, and deep pelagic carbonate accumulation. Horizontal axes nonuniform.

(A) Mass-age data for principal global carbonate reservoirs from data as in figure 4. (B) Long term mass-age trends calculated assuming global cycling at 23.7×10^{18} m/my, that flux to the pelagic reservoir has grown (to a present value of 13.8×10^{18} m/my) at expense of continental flux (presently 1.7×10^{18} m/my), and decay constants as in figure 4.

(C) Short term accumulation rates calculated from extant masses (M_r) of principal rock reservoirs (A) from $M_r = M_o * e^{-kt}$ employing values of k as in figure 4.

(D) Long term carbonate accumulation rates calculated from long term mass-age trends (B) assuming global cycling at a rate of 23.7×10^{18} m/my, pelagic reservoir growth of 0.1×10^{18} m/my, and decay constants as in figure 4.

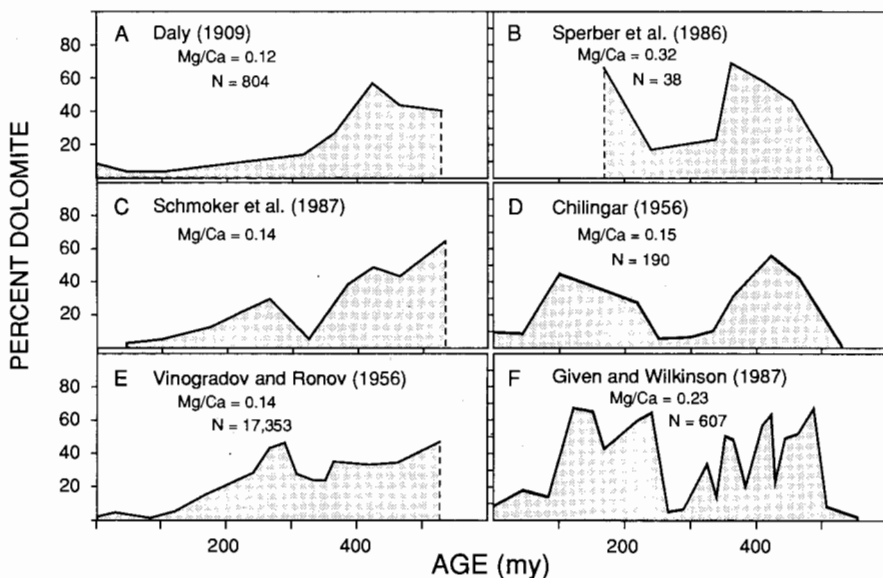


Fig. 6. Published estimates of dolomite abundance in cratonic carbonate rocks versus stratigraphic age. Data in Daly (1909), Schmoker, Krystink, and Halley (1987), and Sperber, Wilkinson, and Peacor (1984) represent North American sequences. Vinogradov and Ronov (1956) data from the Russian platform. Abundances in Chilingar (1956) are global in distribution but largely from North America and Europe, as are those from Given and Wilkinson (1987) as calculated from data in Baum, Harris, and Drez (1985), Langbein, Landgraf, and Milbrodt (1984), Lumsden and Chimahusky (1980), and Marschner (1968). Note that the Daly (1909), Schmoker, Krystink, and Halley (1987), and Vinogradov and Ronov (1956) tabulations suggest increasing dolomite with age whereas data in Sperber, Wilkinson, and Peacor (1984), Chilingar (1956), and Given and Wilkinson (1987) suggest greater dolomite abundances during intervals of sealevel highstand and continental flooding.

limestone compilations by Daly (1909), Schmoker, Krystink, and Halley (1985), and Vinogradov and Ronov (1956) and is in accord with one (or a combination) of two possible patterns of dolomite formation: (1) dolomitization occurs slowly at depth during the entire diagenetic history of a carbonate sequence, or (2) some aspect of atmospheric-hydrospheric chemistry was sufficiently different that dolomitization occurred rapidly in early Phanerozoic marine settings (fig. 6A, C, E).

Land (1985), Morrow (1982), and Machel and Mountjoy (1986) suggested that seawater is the only fluid capable of significant dolomite precipitation, an argument based on the fact that all dolomitization must involve the massive transfer of Mg from some source reservoir to some precursor calcium carbonate sequence, and that the only Mg-rich fluid in/on the crust of the Earth is marine or modified marine water. Such a suggestion is in accord with limestone/dolostone ratios in Chilingar (1956), Given and Wilkinson (1987), and Sperber, Wilkinson, and Peacor (1984) which suggest that dolomite abundance bears little

relation to sequence age and may increase during periods of continental submergence (fig. 6B, D, and F).

At present, there is little agreement as to which endmember pattern of dolomite abundance (increasing with age or continental flooding) is more accurate, or if dolomite is predominantly a syndimentary marine or burial diagenetic precipitate. If dolomitization is largely a syndepositional process, then dolomite/calcite ratios serve as a direct record of Mg flux from oceans to continental and slope-rise carbonate. If, on the other hand, most dolomite forms in the presence of deep meteoric/connate fluids, then actual process of dolomite formation has little direct influence on the seawater cycling of Mg ions.

Like contrasting interpretations of carbonate accumulation rate, uncertainties relative to dolomite abundance and setting of dolomite formation can be evaluated by considering alternate scenarios. Herein, abundance data from both Vinogradov and Ronov (1956) and Given and Wilkinson (1987) are considered as two patterns representative of dolomite abundance increasing with age and eustasy, respectively. Assigning equal proportions of dolomite to continental and slope-rise sequences, long and short term fluxes of Ca and Mg ions to carbonate reservoirs can be determined (fig. 7). Contemplation of dolomite as a marine or burial precipitate involves additional consideration of cation mass-balances.

EARTH-SURFACE CATION FLUXES

Owing to small masses of Ca (14×10^{18} m) and Mg (75×10^{18} m) in seawater, cation cycling between oceans and rock reservoirs can be described as a series of mass-conservative equations. These relate source fluxes of Ca from hydrothermal alteration at ridges (RdCa), river discharge (RvCa), and groundwater seepage (GwCa), with Ca removal fluxes as sedimentary carbonate (CbCa), and equate Mg from rivers (RvMg) to Mg sinks as dolomitic carbonate (CbMg) and altered ridge basalt (RdMg). The two cation systems are further linked by the stoichiometry of Ca-Mg exchange at ocean ridges (fig. 8).

General Considerations

Depending on diagenetic setting of dolomitization, two mass-balance schemes are plausible (fig. 8). If most dolomite is a syndimentary phase, RvMg is variably partitioned between CbMg and RdMg. In this case:

$$RvCa + CbCa + RdCa + GwCa = 0$$

$$RvMg + CbMg + RdMg = 0$$

$$RdCa/RdMg = -X$$

where X represents the stoichiometry of Ca for Mg exchange during hydrothermal alteration. If, on the other hand, the bulk of dolomite has

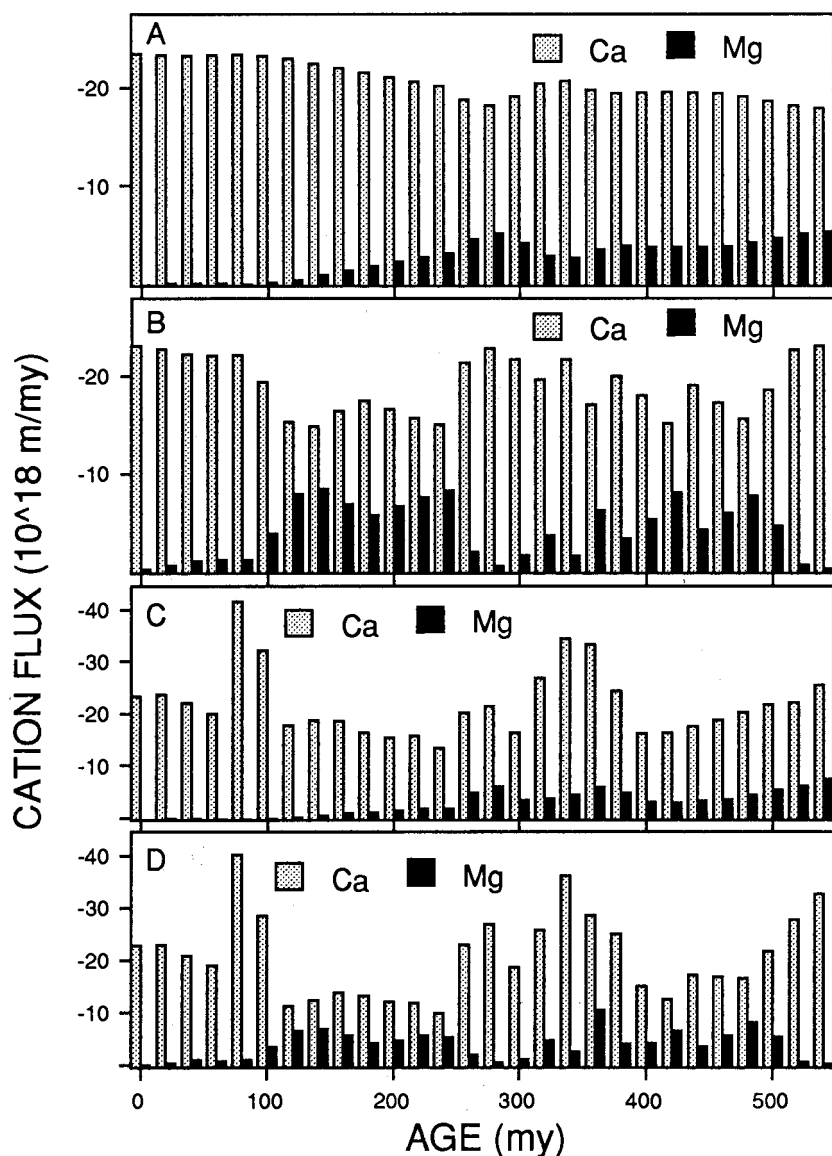


Fig. 7. Phanerozoic Ca (shaded) and Mg (solid) fluxes to carbonate sediment determined from long term (A and B) and short term (C and D) accumulation rates and dolostone/limestone ratios from Vinogradov and Ronov (1956, A and C) and Given and Wilkinson (1987, B and D). Cation fluxes calculated assuming equal proportions of dolomite in continental and slope-rise sequences, and that pelagic carbonate is entirely calcite.

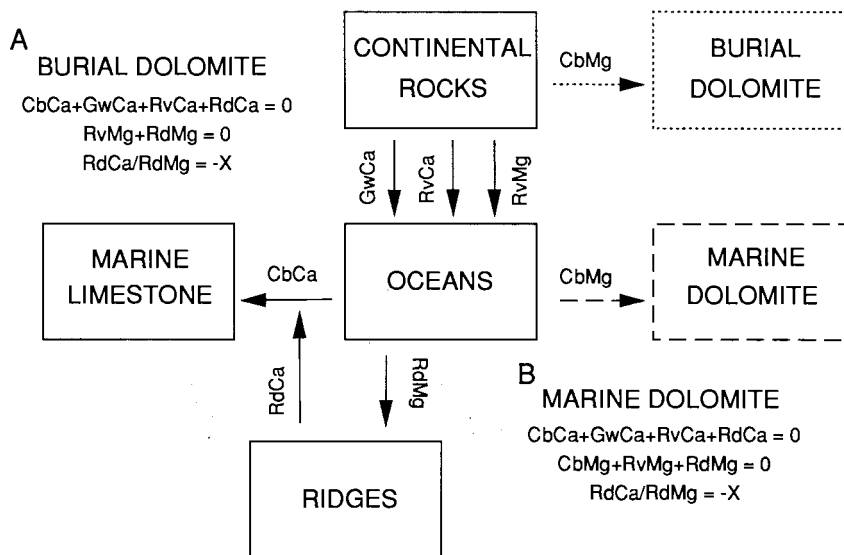


Fig. 8. Primary reservoirs and paths of Ca and Mg transfer at the Earth's surface. RvCa and RvMg are river fluxes; CbCa and CbMg are fluxes to carbonate reservoirs; RdCa and RdMg are fluxes through oceanic ridges; GwCa is a groundwater seepage and/or carbonate dissolution flux. Mass-balances for two endmember dolomitization scenarios are shown to the upper left (A) and lower right (B). If dolomite is a burial precipitate, all river Mg is removed at ridges ($\text{RvMg} = -\text{RdMg}$). If dolomite is a marine precipitate, river Mg is partitioned between ridges and dolomitic carbonate ($\text{CbMg} = -\text{RvMg} - \text{RdMg}$).

formed as a burial precipitate, hydrothermal alteration is the only important sink for river Mg, and the system is described as:

$$\begin{aligned}\text{RvCa} + \text{CbCa} + \text{RdCa} + \text{GwCa} &= 0 \\ \text{RvMg} + \text{RdMg} &= 0 \\ \text{RdCa}/\text{RdMg} &= -X\end{aligned}$$

In order to evaluate past rates of Ca-Mg transfer, permissible ranges of RvCa, GwCa, RdCa, RvMg, and RdMg were calculated employing alternate assumptions of: (1) short versus long term carbonate accumulation rates; (2) increasing dolomite abundance with age or continental flooding; (3) precipitation of dolomite from burial versus marine fluids; (4) average Mg/Ca ratio; and (5) average ridge Ca-Mg exchange.

In each case, RvCa, RdCa, GwCa, RvMg, and RdMg were calculated from input values of CbCa and CbMg determined by choice of dolomite abundance and carbonate accumulation rate, while constraining the system by choice among the three remaining scenarios. Because either set of mass-balance equations (fig. 8) contains five residual unknown entities (RvCa, RdCa, GwCa, RvMg, and RdMg), two addi-

tional relations are needed to resolve the system. The first of these was to assume some average value of river Mg/Ca. The other was to assume that the contribution of river Ca relative to the total weathering flux (river discharge plus groundwater seepage) has remained constant at 0.71, the ratio from current values of RvCa and GwCa. In other words, the present weathering Mg/Ca ratio (Wr Mg/Ca, 0.28) is presently 71 percent of the river Mg/Ca ratio (Rv Mg/Ca, 0.39), and this proportion was taken as a Phanerozoic constant. Such an assumption merely considers the net contribution of Ca from the weathering of continental rocks as a singular entity, roughly two thirds of which represent transport via rivers and one third via groundwater infiltration.

Functionally, some average value of Rv Mg/Ca was first assumed, and Wr Mg/Ca calculated as 0.71 Rv Mg/Ca. Appropriate values of CbCa and CbMg were then chosen depending on hypothetical scenarios of dolomite abundance and carbonate accumulation rate (fig. 7). If dolomite was considered a burial phase, values of CbMg were set at 0.0 (no seawater Mg to carbonate reservoirs), and values of CbCa then increased proportionally. The reason for incrementing CbCa by values of CbMg is that both were initially determined from carbonate accumulation rate and limestone/dolostone data. If dolomitization significantly postdates carbonate accumulation, original limestone accumulation rate (CbCa) would be higher in proportion to present dolomite content. Next, river Mg fluxes were calculated as:

$$RvMg = (CbCa + CbMg)/(1 + (1/(Wr Mg/Ca))),$$

a relation readily derived from either set of mass-balance equations. Finally, RdMg, RdCa, RvCa, and GwCa were determined from:

$$RdMg = -(CbMg + RvMg)$$

$$RdCa = -X * RdMg$$

$$RvCa = RvMg * 1/(Rv Mg/Ca)$$

$$GwCa = -(CbCa + RvCa + RdCa).$$

Output uniquely assesses secular variation in RvCa, RdCa, GwCa, RvMg, and RdMg over the past 560 my relative to assumptions about dolomite abundance and formation, carbonate accumulation, river Mg/Ca, and ridge Ca-Mg exchange (fig. 9).

Three general approaches can be taken in applying this methodology to determine Phanerozoic seawater fluxes: (1) the sensitivity or degree of uncertainty in flux estimates resulting from alternate assumptions of infrastructure variables can be evaluated by alternate choice of individual cycling parameters; (2) allowable ranges of river, groundwater, and ridge Ca-Mg fluxes can be evaluated by solutions incorporating all possible limiting assumptions; and (3) actual Phanerozoic seawater fluxes can be estimated by incorporating dolomite abundance and formation, carbonate accumulation, river Mg/Ca, and ridge Ca-Mg

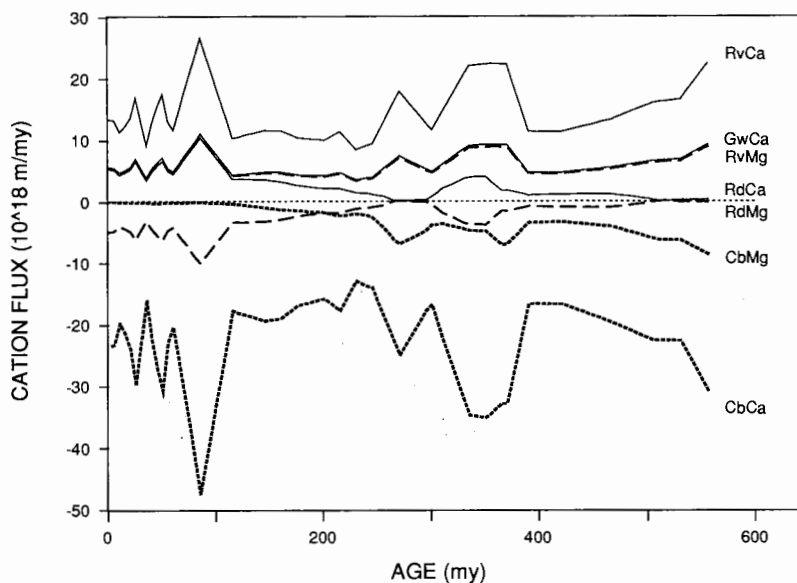


Fig. 9 Model seawater Ca-Mg fluxes, in this case calculated from mass-balance equations employing: (1) short term carbonate accumulation values, (2) dolomite/calcite ratios from Vinogradov and Ronov (1956), (3) a river Mg/Ca ratio of 0.4, (4) a hydrothermal Ca-Mg exchange ratio of 1.0, and (5) assuming that dolomite is a marine precipitate. Carbonate calcium (CbCa) and magnesium (CbMg) fluxes as heavy dotted lines, river (RvCa), groundwater (GwCa) and ridge (RdCa) calcium fluxes as solid lines, and river (RvMg) and ridge (RdMg) magnesium fluxes as dashed lines.

values that seem most reasonable in light of plausible ranges of system parameters.

System Sensitivity

The sensitivity of different flux estimates to choices of dolomite abundance, carbonate accumulation rate, dolomitization setting, river Mg/Ca ratio, and ridge Ca-Mg exchange may be evaluated by incorporating alternative choices of any one variable and solving appropriate mass-balances while holding all others constant (fig. 10).

Dolomite abundance.—Choice of dolomite abundance trends, either correlative with temporal or eustatic variation, introduces uncertainty with respect to calculated rates of ridge Ca-Mg replacement (fig. 10D, E); river and groundwater flux values are not dependent on the abundance of dolomite in the stratigraphic record. The reason for this is that regardless of diagenetic setting, dolomitization must occur either up-stream (burial) or down-stream (marine) of river systems and is not related to cation delivery from weathering-dissolution processes. With respect to ridge fluxes, greater rates of dolomite formation lead to lower rates of Ca-Mg exchange, because all river Mg is ultimately partitioned

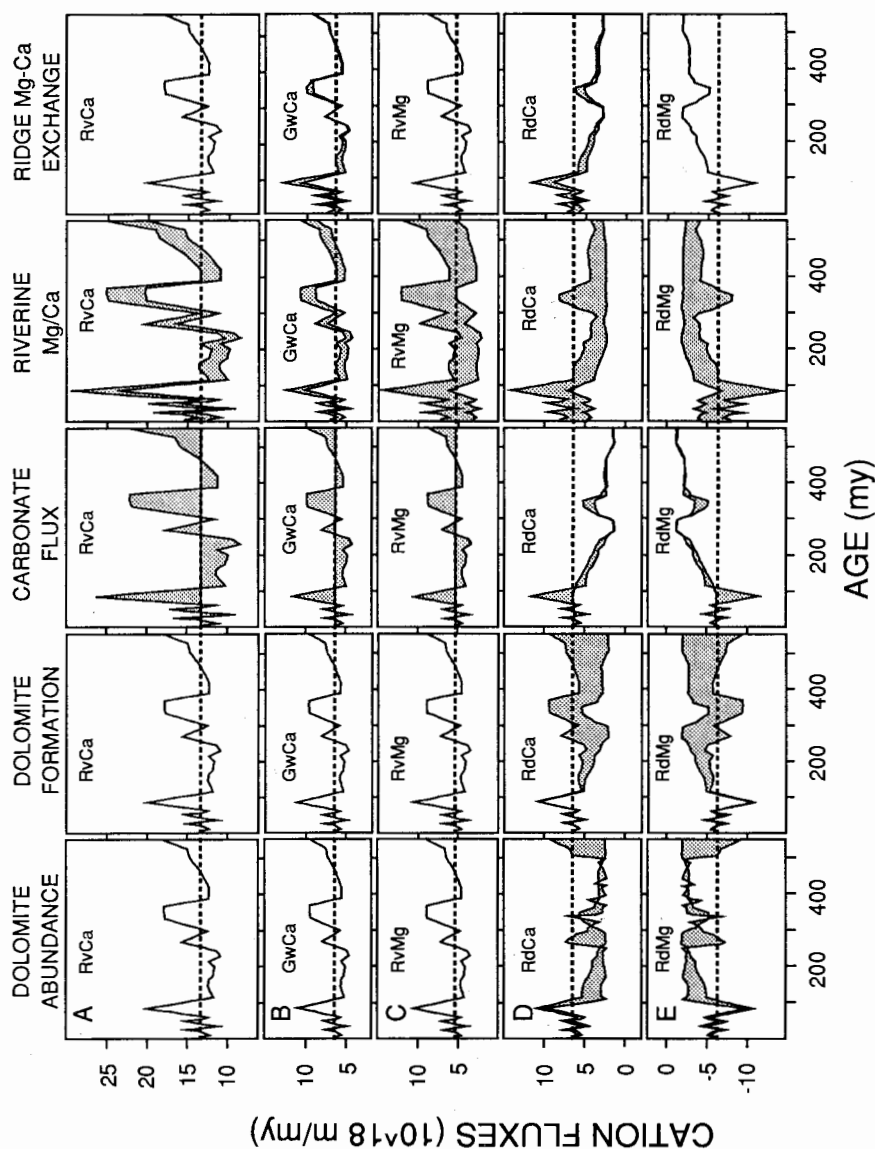


Fig. 10. Sensitivity analysis of cation cycling rates derived by repeated solution of mass-balance equations for a standard system as in figure 9. Each column delineates the range of values for all seawater fluxes resulting from the alternate choices of one assumption. Each row shows the range of values for one flux that results from the alternate choice of five assumptions. Note that dolomite abundance variation (secular/eustatic) or setting of dolomite formation (marine/burial) only affects ridge fluxes, that carbonate accumulation rate (long/short term) and river Mg/Ca ratio (0.2/0.6) affects all fluxes, and that ridge Ca-Mg stoichiometry (0.7/1.0) only affects groundwater and ridge Ca fluxes. Dashed lines are present fluxes.

between carbonate and basalt reservoirs, and seawater Mg removal by marine dolomitization is inversely proportional to Mg removal by hydrothermal alteration. Average difference in values of RdCa and RdMg calculated employing dolomite abundance data of Vinogradov and Ronov (1956) and Given and Wilkinson (1987) is 2.0×10^{18} m/my (table 3).

Dolomite formation.—Like choice of dolomite abundance, considering dolomite as a marine or burial precipitate only introduces uncertainty with respect to rates of ridge Ca-Mg replacement (fig. 10D, E). Values of RvCa, GwCa, and RvMg are not dependent on dolomite formation in different diagenetic settings. Burial dolomitization requires higher model values of CbCa and, as a result, higher fluxes of RdCa in order to balance mass-conservation equations. For example, if dolomitization of some body of carbonate occurs in the marine environment, then both Ca and Mg ions are removed from seawater. Conversely, if dolomitization of the same limestone occurs in the burial environment, original accumulation of marine carbonate only represents the

TABLE 3

Uncertainties in calculated Phanerozoic seawater cation fluxes stemming from alternate choices of different cycling scenarios. Values as 10^{18} m/my; average percent variation relative to present fluxes (present flux/average range)

Parameter	Alternate choices	Seawater flux	Max range	Min range	Avg range	Avg pcnt
Dolomite abundance	Temporal versus eustatic	RvCa	0.0	0.0	0.0	0
		GwCa	0.0	0.0	0.0	0
		RvMg	0.0	0.0	0.0	0
		RdCa	8.2	0.1	2.0	40
		RdMg	8.2	0.1	2.0	40
Dolomite formation	Marine versus burial	RvCa	0.0	0.0	0.0	0
		GwCa	0.0	0.0	0.0	0
		RvMg	0.0	0.0	0.0	0
		RdCa	8.6	0.1	3.2	63
		RdMg	8.6	0.1	3.2	63
Carbonate flux	Short term versus long term	RvCa	12.5	0.1	4.4	33
		GwCa	5.1	0.3	1.8	33
		RvMg	4.9	0.0	1.7	33
		RdCa	5.2	0.1	2.3	45
		RdMg	5.2	0.1	2.3	45
River Mg/Ca Ratio	0.2 versus 0.6	RvCa	5.9	1.9	3.2	24
		GwCa	2.4	0.8	1.3	24
		RvMg	2.4	0.8	1.3	25
		RdCa	8.3	1.2	3.5	69
		RdMg	8.3	1.2	3.5	69
Ridge Ca-Mg exchange	0.7 versus 1.0	RvCa	0.0	0.0	0.0	0
		GwCa	3.1	0.0	0.7	13
		RvMg	0.0	0.0	0.0	0
		RdCa	3.1	0.0	0.7	14
		RdMg	0.0	0.0	0.0	0

removal of Ca ions and, thus, a higher initial value of CbCa. The mean difference in values of RdCa and RdMg calculated assuming dolomite forms in marine versus burial settings is 3.2×10^{18} m/my (table 3).

Carbonate flux.—Choice of long versus short term carbonate accumulation scenarios has a significant influence on all calculated fluxes (fig. 10). The reason for this is that assumed rate of carbonate accumulation directly affects calculated values of both CbCa and CbMg. Because RvCa, GwCa, RvMg, RdCa, and RdMg are determined from CbCa and CbMg, these must change in direct proportion to inferred sediment accumulation rate. Average disparity in values of RvCa, GwCa, RvMg, RdCa, and RdMg calculated from long versus short term carbonate flux estimates are 4.4, 1.8, 1.7, 2.3, and 2.3×10^{18} m/my, respectively (table 3).

River Mg/Ca ratio.—Choice of river Mg/Ca ratio also affects all flux values (fig. 10) as all are calculated from estimates of CbCa, CbMg, and Wr Mg/Ca, and the latter varies in direct proportion to river Mg/Ca. All seawater fluxes, therefore, are dependent on proportions of exposed crustal lithologies. Values of RvCa, GwCa, and RdMg increase and values of RvMg and RdCa decrease, with increasing river Mg/Ca ratio. The average difference in RvCa, GwCa, RvMg, RdCa, and RdMg fluxes calculated assuming global Rv Mg/Ca values ranging from 0.2 to 0.6 are 3.2, 1.3, 1.3, 3.5, and 3.5×10^{18} m/my, respectively (table 3).

Ridge Ca-Mg exchange.—Finally, some small range in cation fluxes results from uncertainties in the stoichiometry of Ca-Mg exchange during hydrothermal alteration. Based on current estimates, one mole of seawater Mg incorporated into ridge basalt and associated sediment is accompanied by the liberation of between 0.7 (Drever, Li, and Maynard, 1988) and 1.0 (Owne and Rea, 1985) moles of Ca, the difference largely being balanced by output of hydrogen ions. This range only affects estimates of GwCa and RdCa (fig. 10B, D) because the only cycling processes down-stream of river discharge are carbonate accumulation, ground-water seepage, and ridge alteration, and flux rate in the first case is constrained by mass-composition data on sedimentary carbonates. All values of GwCa and RdCa increase with decreasing Ca-Mg exchange. Incorporation of Ca-Mg replacement values of 0.7 and 1.0 results in an average difference in GwCa and RdCa of 0.7×10^{18} m/my (table 3).

In essence, different inferences about dolomite abundance, dolomite formation, carbonate accumulation, river Mg/Ca, and ridge Ca-Mg replacement, individually impart up to 4.4×10^{18} m/my uncertainty in calculated seawater fluxes, ambiguities that correspond to as much as 69 percent of present values (table 3). This assessment serves to identify those portions of the system most sensitive to imprecision in estimates of carbonate rock mass and composition and provides a context in which to evaluate interdependence between different transfer pathways.

Relative to individual fluxes, rates of Ca delivery via hydrothermal alteration are potentially the least-well constrained because all cycling

assumptions influence RdCa, and several of these (dolomite abundance, setting of dolomite formation, river Mg/Ca ratio) result in significant differences in calculated values. Relative to alternate cycling parameters, choice of values of ridge Ca-Mg substitution have the least potential effect on calculated flux rates. Values of RvCa, RvMg, and RdMg are independent of ridge Ca-Mg ratio, and only a small variance in GwCa and RdCa results from a plausible range of exchange values.

Permissible Flux Variation

While consideration of alternate inferences about Ca-Mg transfer individually suggests that ambiguity in input data and cycling pathways imparts no more than about 70 percent uncertainty in calculated fluxes, the important remaining question is: To what degree does the carbonate rock record constrain allowable limits of variation in past rates of Ca-Mg transfer among the principal reservoirs?

Permissible ranges of transfer rate resulting from the simultaneous consideration of all cycling scenarios indicate that each of the five principal fluxes under consideration has varied by no more than about 120 percent relative to present rates (table 4). Since even this amount corresponds to only a few time intervals, mass-composition estimates of the sedimentary carbonate rock record suggest a relative constancy of Earth-surface cation cycling (fig. 11). Rates of chemical denudation of continental crustal rocks have evidently changed little over the past 560 my.

Phanerozoic Seawater Fluxes

What then can be said about the actual history of Earth-surface cation cycling? In order to derive unique solutions to mass-balance equations, it is first necessary to choose among alternate scenarios that define permissible flux ranges. With respect to dolomite abundance and carbonate accumulation rate, a reasonable approximation of actual secular variation may be obtained by determining mean values from endmember alternatives. Because short term carbonate accumulation rates discount any difference resulting from selective preservation

TABLE 4

Permissible ranges in seawater fluxes based on masses and compositions of Phanerozoic carbonate rocks. Values as 10^{18} m/my; range of variation relative to present flux (maximum-minimum)/(present)

Flux	Maximum flux	Minimum flux	Average flux	Present flux	Percent variation
RvCa	19.7	10.5	13.8	13.2	70
GwCa	8.8	4.5	5.9	5.4	80
RvMg	7.9	4.3	5.5	5.2	70
RdCa	6.5	0.4	2.0	5.1	120
RdMg	-0.5	-7.2	-2.3	-5.1	120

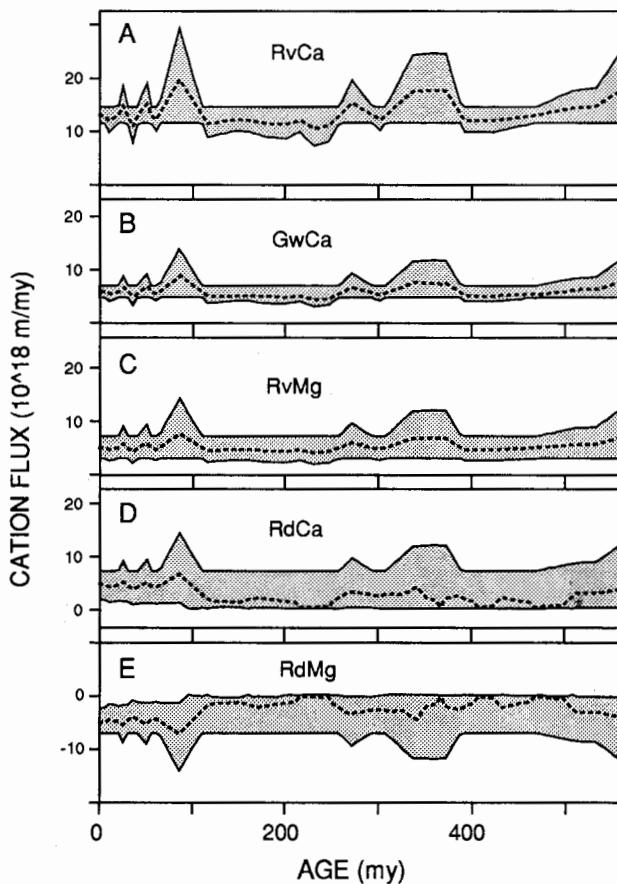


Fig. 11. Permissible ranges of seawater Ca-Mg fluxes (shaded) determined by the solution of mass-balance equations resulting from all possible choices of five assumptions about cation cycling. Dashed lines are transfer rates calculated from epoch-interval averages of long and short term carbonate accumulation rates, average dolomite abundances from Vinogradov and Ronov (1956) and Given and Wilkinson (1987), and assuming a river Mg/Ca ratio of 0.4, a ridge Ca-Mg exchange ratio of 0.9, and that 90 percent of Phanerozoic dolomite is a marine precipitate. Note that river and groundwater Ca and Mg fluxes (A, B, C) fall about in the middle of allowable ranges, but rates of ridge Ca-Mg exchange (D, E) are lower during periods of enhanced dolomite formation.

and/or imprecision in mass-age data, these undoubtedly over estimate variation in seafloor carbonate cation flux. Conversely, long term accumulation rates by definition preclude assessment of any real short term change in carbonate accumulation. Averaging long and short term rates, while not unequivocally accurate, does serve to diminish obvious inadequacies in either short or long term accumulation rate estimates. Similarly, employing dolomite abundances determined by averaging

data in Vinogradov and Ronov (1956) and Given and Wilkinson (1987) serves to take the middle ground insofar as apparent correlation between secular versus eustatic variation. In addition, the Vinogradov and Ronov (1956) data are exclusively from the Russian platform whereas the Given and Wilkinson (1987) tabulation largely represents North American and European analyses. Averaging these may in fact result in a better estimate of global dolomite abundances than either compilation taken individually.

Choice of appropriate values of river Mg/Ca ratio and hydrothermal Ca-Mg exchange are less equivocal. Contemporary rivers have a Mg/Ca ratio of 0.39 (Meybeck, 1979), and the Mg/Ca ratio of common continental lithologies only ranges from 1.12 for shale to about 0.26 for carbonate (Turekian and Wedepohl, 1961). Given that global river fluxes result from the weathering of a mixture of common rock types, Phanerozoic river Mg/Ca ratios have probably varied little from the present value. Similarly, suggested ranges in hydrothermal Ca-Mg replacement only vary from about 0.7 to 1.0, and the former value largely stems from theoretical consideration of high-temperature seawater-basalt interactions (Edmond and others, 1979). Moreover, Berner, Lasaga, and Garrels (1983) point out that both laboratory and field measurements of net acidities of hydrothermal fluids indicate most Mg loss from seawater does not involve replacement by hydrogen ions. As a result, Ca-Mg exchange ratios are probably much closer to 1.0 than to 0.7; a value of 0.9 as suggested by data in Humphries and Thompson (1978) may be an appropriate exchange rate for hydrothermal alteration.

The question of settings of dolomite formation is more complex, but mass-balance considerations strongly suggest that most dolomite precipitation occurs in the presence of marine or marine-derived fluids. In a context of cation cycling, the principal difference between alternate interpretations of dolomite formation involves where dolomitization occurs relative to river discharge. Hardie (1987) has put forth the most refined argument for the potential importance of calcite replacement by dolomite in burial settings, pointing out that molar Mg/Ca ratios of fluids in equilibrium with calcite and dolomite decrease with increasing temperature. Given sufficient rates of fluid Mg mass-transfer (Garvin, 1985; Garvin and Freeze, 1984) even meteoric groundwaters could give rise to the vast volumes of dolomite now in Phanerozoic carbonate sequences. Regardless of starting fluid composition, however, burial dolomitization must involve the transport of thousands of fluid pore volumes through basinal limestones undergoing replacement, and this fluid must ultimately be carried to oceans via riverine discharge. Moreover, like marine dolomite, sources of Mg requisite for burial dolomitization must ultimately be derived from the weathering of crustal rocks but in this case presumably somewhere adjacent to basin margins. The critical difference between burial and marine dolomitization then is whether rivers transport a Mg mass that is residual from

crustal rock weathering and burial dolomitization or a Mg mass that will in part replace an equivalent mass of Ca during marine dolomite formation.

The relative importance of marine versus burial dolomitization processes can be assessed by considering river mass-balances and Mg/Ca ratios of common continental rocks. Specifically, Berner and Berner (1987), Berner, Lasaga, and Garrels (1983), Garrels (1976), Holland (1978, 1984), Meybeck (1979), Stallard (1980), and Wollast and Mackenzie (1983) have now offered estimates of the relative importance of different lithologies in contributing various ions to present rivers. Moreover, Meybeck (1987) has recently shown that combination of data on river water compositions with data on the relative proportion of lithologies exposed the Earth's surface leads to a theoretical average composition of global river water in close agreement with actual measured values. Collectively, these studies allow for calculation of the net contribution of different rock types to current Ca and Mg river fluxes (fig. 12). At present, silicates, evaporites, dolostones, and limestones

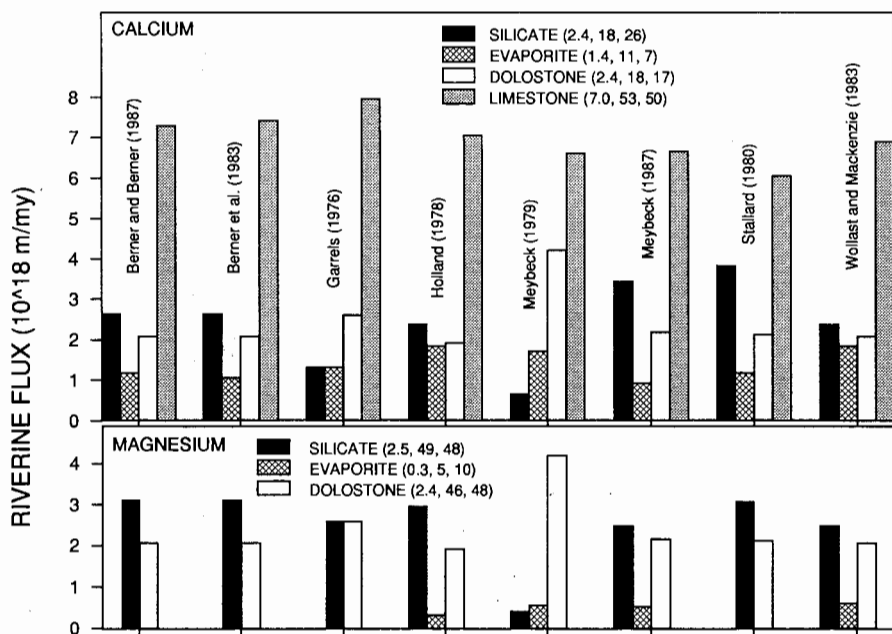


Fig. 12. Estimates of the relative Ca and Mg contribution of silicates, evaporites, dolostones, and limestones to present rivers. Numbers in parentheses following each rock type indicate mean cation contribution (10^{18} m/my) from these eight references, average percent contribution from each rock type, and percent contribution values from Meybeck (1987) used in determination of mass-balances for marine versus burial dolomitization in figure 13. River Ca is chiefly derived from the weathering of limestone, whereas Mg is derived in roughly equal proportions from silicates and dolostones.

contribute about 26, 7, 17, and 50 percent of the global river Ca flux and 48, 10, 42, and 0 percent of the river Mg flux, respectively (table 5).

Mass-age and dolomite abundance data in Vinogradov and Ronov (1956) and Given and Wilkinson (1987) indicate a net Mg mass in the global dolomite reservoir of 833 and 1254×10^{18} moles, respectively. If a value of 1000×10^{18} moles is taken as a representative estimate of Phanerozoic dolomite Mg mass (Berner, Lasaga, and Garrels, 1983), this corresponds to a net Mg flux to the dolomite reservoir of 1.8×10^{18} m/my. Given these assessments of relative river Ca-Mg contribution and dolomite Mg flux, refined cation mass-balances can be constructed by assuming that present river fluxes are representative of average Phanerozoic streams, a stability suggested by permissible ranges of riverine flux variation (fig. 11).

If the relative contribution of Mg from different crustal lithologies to basinal fluids is the same as their relative donation to river systems, provenance Mg/Ca ratios requisite for average rates of dolomitization are readily determined. In the case of dolomite as a burial precipitate and using data from Meybeck (1987) on river water compositions, the Mg/Ca ratio calculated for non-carbonate rocks is 1.22 and for carbonate rocks is 0.36 (fig. 13). These values are much higher than those for common crustal lithologies and require an average silicate rock composition more mafic than basalt and an average carbonate composition more Mg-enriched than suggested by any compilation of dolostone/limestone ratios for Phanerozoic carbonate sequences (fig. 6). At a global scale and regardless of specifics of the relative ionic contribution of different lithologies to global rivers, burial dolomitization cannot be a significant diagenetic process, because requisite Mg for such a process to be volumetrically important requires far greater concentrations in crustal rocks than presently exist at the Earth's surface (fig. 14).

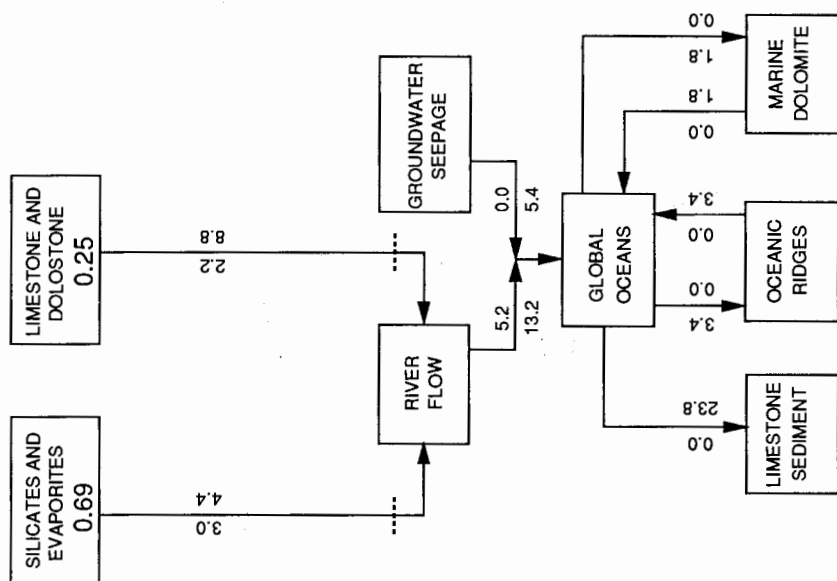
In the case of dolomite as a marine precipitate, analogous mass-balance calculations yield an average non-carbonate rock Mg/Ca ratio of 0.69 and an average carbonate rock Mg/Ca ratio of 0.25 (fig. 13), values well within the range of those determined for common crustal lithologies. In short, most dolomitization must proceed down-stream of

TABLE 5

Relative contribution of Ca and Mg ions to global rivers by different crustal lithologies from Meybeck (1987). Values as 10^{18} m/my; percent of total river flux in parentheses

River Ca = 13.2 (100)	River Mg = 5.2 (100)
Evaporites = 0.92 (7)	Evaporites = 0.52 (10)
Silicates = 3.43 (26)	Silicates = 2.49 (48)
Carbonates = 8.84 (67)	Carbonates = 2.18 (42)
Dolostone = 2.18 (16.5)	Dolostone = 2.18 (42)
Limestone = 6.66 (50.5)	Limestone = 0.00 (0)

MARINE DOLOMITE



BURIAL DOLOMITE

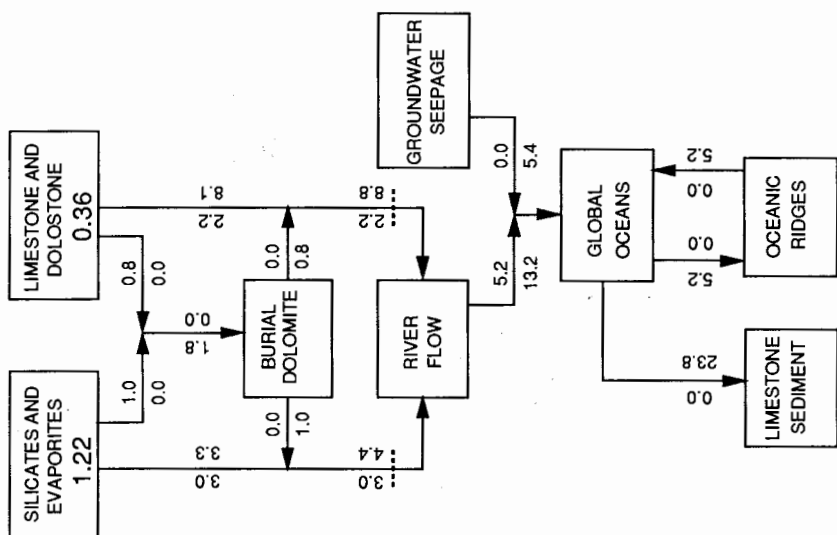


Fig. 13. Average Phanerozoic fluxes of Ca and Mg if dolomite is a burial versus a marine precipitate, assuming river Ca and Mg fluxes of 13.2×10^{18} and 5.2×10^{18} m/m.y., a carbonate Mg flux of 1.8×10^{18} m/m.y. mole-for-mole Ca-Mg exchange during dolomitization, and that the relative contribution of Mg to basinal fluids by silicate-evaporite (58 percent) and limestone-dolomite (42 percent) source rocks is the same as their relative contribution to modern rivers (table 5). Fluxes for all reservoirs expressed as Mg over Ca. Short dashed lines represent the junction of major rivers and global oceans. Note that for dolomite to be a burial phase, Mg/Ca ratios of non-carbonate (1.22) and carbonate (0.36) source lithologies would have to be in excess of average values for rocks now exposed at the Earth's surface. Conversely, if dolomite is a marine precipitate, requisite Mg/Ca ratios of non-carbonate (0.69) and carbonate (0.25) provenance lithologies are similar to average values for such rocks.

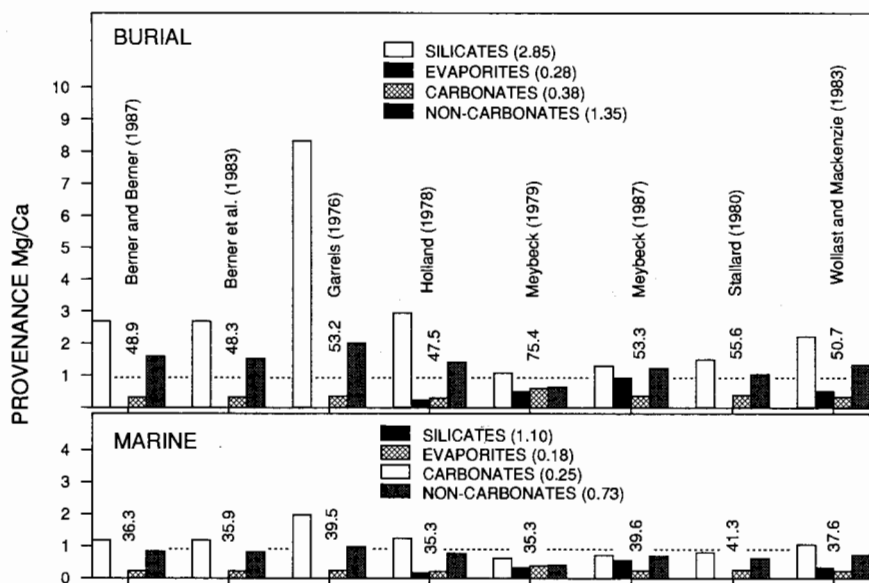


Fig. 14. Source rock Mg/Ca ratios necessary for an average 1.8×10^{18} m/my Mg flux to the Phanerozoic dolostone reservoir based on eight published estimates of source rock contribution to river Ca and Mg.

(A) Provenance Mg/Ca ratios necessary for burial dolomitization. Average requisite Mg/Ca in parentheses, carbonate percent dolomite above values from each study. The horizontal dotted line at 0.9 is the Mg/Ca ratio of average igneous rocks from Drever, Li and Maynard (1988). Note that, in all cases, requisite silicate and carbonate Mg contents are in excess of those of common crustal lithologies.

(B) Provenance Mg/Ca ratios needed for marine dolomitization. Average Mg/Ca in parentheses, carbonate percent dolomite above values from each study. In this case, both carbonate and silicate Mg/Ca ratios are in close agreement with actual source rock values, suggesting that most dolomite forms in marine settings.

river discharge and, therefore, must proceed via the replacement of calcium carbonate sediment or limestone rock in the presence of marine fluids.

Returning to discussion of a best-estimate of Phanerozoic seawater fluxes. Consideration of dolomite as a largely (90 percent) marine precipitate and using average carbonate accumulation rates, average dolomite abundances, a river Mg/Ca ratio of 0.4 and a ridge Ca-Mg exchange value of 0.9 allow for the calculation of "most-probable" mass-balances and the determination of river, groundwater, and hydrothermal Ca and Mg fluxes (fig. 11). By definition, these lie within the allowable range of fluxes determined by considering all cation transfer scenarios. As would be anticipated from using average carbonate accumulation and dolomite abundance values, calculated $RvCa$, $GwCa$, and $RvMg$ lie near the middle of permissible ranges (fig. 11A, B, C), vary by no more than about 80 percent relative to current estimates, and suggest relative constancy of river-groundwater cation delivery to global oceans

TABLE 6

Best-approximation estimate of past variation in seawater cation fluxes based on masses and compositions of Phanerozoic carbonate rocks.

Values as 10^{18} m/my

Flux	Maximum	Minimum	Average	Present
RvCa	19.8	10.8	13.8	13.2
GwCa	8.6	4.5	5.8	5.4
RvMg	7.8	4.2	5.4	5.2
RdCa	6.6	0.4	2.1	5.1
RdMg	-0.5	-7.1	-2.2	-5.1

(table 6). Two periods of elevated weathering flux occur at about 85 and 355 my and correspond to upper Cretaceous and upper Devonian-Mississippian time. The significance of these apparent flux increases is unknown, but they generally correspond to periods of large ridge volume and eustatic highstand as defined by Mackenzie and Pigott (1981). If, as suggested by Berner, Lasaga, and Garrels (1983), intervals of higher sealevel correspond to periods of higher atmospheric $p\text{CO}_2$ and higher rates of crustal weathering, such correspondence may be manifest in river and groundwater fluxes.

Values of RdCa and RdMg, on the other hand, exhibit significant deviation from permissible range averages, being lower throughout much of the Phanerozoic than at present (fig. 11D, E). The reason for this is that all limestone/dolostone tabulations suggest relatively low Tertiary-Quaternary dolomite abundance (fig. 6). Accepting the premise that dolomite is a marine precipitate and given that dolomite abundance is generally higher in Paleozoic-Mesozoic sequences, therefore requires lower rates of Ca-Mg exchange at oceanic ridges during much of the past 560 my. On average, Phanerozoic rates of hydrothermal Mg removal have been about 45 percent of present rates; only during periods of enhanced river Mg delivery (that is, upper Cretaceous, upper Devonian, and Mississippian) do rates of hydrothermal Ca-Mg exchange approach present values.

DISCUSSION

The carbonate record of Ca-Mg cycling through global oceans suggests relative constancy of rates of cation transfer among the principal reservoirs, particularly with respect to weathering fluxes from continental rocks. In retrospect, such a conclusion is perhaps not unexpected in that, at the epoch-interval time scale under consideration, rates of continental denudation should approximate rates of tectonism and uplift (Holland, 1978) which, over Phanerozoic time, probably vary within a limited range. Although apparent epoch-interval increases in weathering flux may record global response to orogeny and/or change in continental freeboard, carbonate rock masses and compositions generally define limited secular variation in river-groundwater Ca and Mg delivery to global oceans.

Long term Mg fluxes to the cratonic dolomite reservoir, in conjunction with estimates of riverine Ca-Mg contribution by different rock types, suggest that most dolomite is a synsedimentary marine precipitate. If so, past rates of dolomite formation have had a profound influence on rates of seawater Mg removal during hydrothermal alteration, with net Ca for Mg exchange decreasing with increased rates of dolomite precipitation. Because dolomitic carbonate and ridge basalt serve as the only important sinks of seawater Mg, removal of marine Mg can be perceived conceptually as proceeding via the differential partitioning of this ion between silicate and carbonate reservoirs. Best-estimate calculation of seawater fluxes allows for determination of the importance of these two Mg sinks over the past 560 my (fig. 15). At present, hydrothermal circulation accounts for about 98 percent of seawater Mg removal, and only about 2 percent becomes incorporated into magnesian carbonate in shallow cratonic sequences. During periods of enhanced dolomite formation, on the other hand, ridge removal processes accounted for no more than about 10 percent of the river Mg flux. Even though hydrothermal alteration is presently a highly efficient mechanism of Mg fixation, literally removing all Mg from seawater that comes into contact with hot basalt, the absolute mass of magnesian carbonate in the rock record simply requires that hydrothermal removal has been a subordinate process over much of Phanerozoic time.

The most important question relative to such a change in Mg partitioning relates to driving mechanisms of dolomite formation in ancient seas. In this context, it is important to remember that most dolostone originates during the replacement of calcium carbonate

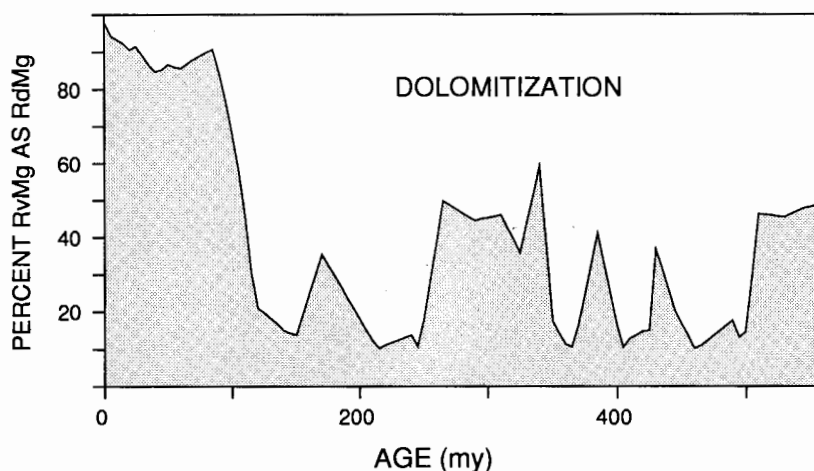


Fig. 15 Percent of river Mg removed during hydrothermal alteration versus marine dolomitization. Note that while 98 percent of river Mg is presently lost at ridges, this amount falls to about 10 percent during periods of enhanced dolomitization.

sediment and must proceed via the dissolution of some precursor phase in the presence of Mg-enriched fluids. Dolomitization by marine fluids therefore requires that $k(\text{precursor carbonate}) > \text{IAP}(\text{seawater}) > k(\text{dolomite})$. If dolomite is rare in modern marine sediment, what processes might give rise to sufficient rates of dolomite precipitation such that largely the whole of river Mg was required for the formation of this carbonate phase?

One possible explanation for enhanced dolomite formation in the presence of marine fluids undersaturated with aragonite and magnesian calcite but supersaturated with dolomite is that seawater IAP has varied inversely with atmospheric $p\text{CO}_2$ such that marine fluid saturation decreases with increasing sealevel and decreasing continental freeboard. While past variation in saturation is also dependent on seawater alkalinity, elevated $p\text{CO}_2$ has long been correlated with periods of continental flooding (Fischer, 1983) and the precipitation of less soluble calcium carbonate phases (Sandberg, 1985). Either alone or in conjunction with mixed meteoric fluids (Badiozamani, 1973), higher values of atmospheric $p\text{CO}_2$ and lower seawater CO_3^{2-} concentrations may, as suggested by Mackenzie and Pigott (1981), enhance the dissolution of precursor carbonate minerals in the presence of Mg-enriched fluids, processes that favor the formation of syndepositional dolomite in sedimentary carbonate sequences.

Mass-age and dolomite abundance data also allow for calculation of seawater Ca and Mg concentrations. Relations between cation mass (Ms) and flux (Fl) are defined by residence time (Rt) where $R_t = M_s/Fl$. In a context of marine Ca and Mg:

$$R_v\text{Mg} = (\text{CcRdMg} * \text{VolSw}/\text{RtRdMg}) + (\text{CcCbMg} * \text{VolSw}/\text{RtCbMg}) = M_s\text{SwMg}/\text{RtSwMg}$$

and:

$$\text{FlRvCa} + \text{FlGwCa} + \text{FlRdCa} = \text{CcCbCa} * \text{VolSw}/\text{RtCbCa} = M_s\text{SwCa}/\text{RtSwCa}$$

where Cc = concentration (m/l), Fl = flux (m/my), Rt = residence time (my), and Ms = mass (m) for cations transferred among river (Rv), groundwater (Gw), ridge (Rd), carbonate (Cb), and seawater (Sw) reservoirs, and where VolSw = ocean volume (l).

In order to derive concentration from seawater flux, it is necessary to constrain estimates of Ca and Mg residence time for each of the reservoirs under consideration. With respect to Ca, Berner, Lasaga, and Garrels (1983) point out that although virtually all marine Ca is removed during the secretion of carbonate skeletons, seawater concentration of Ca^{++} and HCO_3^- can not have varied greatly from saturation with calcium carbonate. Present oceans are approximately saturated with respect to calcite, and, given a current carbonate flux of 23.7×10^{18} m/my, the residence time of seawater Ca is about 0.59 my (table 7). In

TABLE 7
*Present seawater concentrations, masses, fluxes, and residence times of
 Ca and Mg*

	Concentration 10 ⁻² m/l	Mass 10 ¹⁸ m	Flux 10 ¹⁸ m/my	Residence Time my
CbMg	0.004	0.06	0.10	0.59
RdMg	5.305	71.62	5.10	14.04
SwMg	5.310 ¹	71.68	5.20	13.79
SwCa	1.030 ²	13.91	23.70	0.59

³Volume seawater = 13.5×10^{20} l
 Ridge seawater flux = 0.96×10^{20} l/my

1, 2 = Holland (1984); 3 = Garrels and Mackenzie (1971)

order to evaluate the influence of variable carbonate flux on marine Ca concentration, we have assumed an invariant Phanerozoic Ca residence time of 0.6 my. Although secular variation in atmospheric pCO₂ and seawater alkalinity surely induces some change in Ca residence time independent of flux, such variation is small compared to that for Mg.

Unlike Ca, Mg residence time is determined by rates of transfer to marine carbonate and ridge silicate rock reservoirs and, in the latter case, depends both on seawater Mg concentration and on rate of hydrothermal circulation through ocean ridges. Conceptually, net seawater residence time for any ion is dependent on masses and fluxes of that ion relative to each reservoir in the marine system. With respect to Mg, it is important therefore to differentiate those ions incorporated as dolomitic carbonate and those destined for ridge basalt. Specifically, the residence time for all seawater Mg is described by:

$$\begin{aligned} \text{RtSwMg} &= (\text{MsCbMg} + \text{MsRdMg})/(\text{FlCbMg} + \text{FlRdMg}) \\ &= ((\text{RtCbMg} * \text{CbMg}) + (\text{RtRdMg} * \text{RdMg})) / (\text{FlCbMg} + \text{FlRdMg}) \end{aligned}$$

where residence time (Rt) and mass (Ms) refer to the seawater reservoir.

Calculation of seawater Mg concentration from marine carbonate and ridge silicate fluxes requires estimates of residence times for Mg relative to dolostone formation and hydrothermal alteration. In the first instance, we presume that the residence time of dolomite Mg is the same as that for carbonate Ca, about 0.6 my. Given that virtually all seawater Mg and Ca is derived from the weathering of crustal rocks and that the composition of dolomite requires nearly identical Ca-Mg fluxes to dolostone reservoirs, such an assumption must be largely correct if dolomite is a syndimentary marine phase.

With respect to the residence time for Mg removed at ridges, we have taken an approach similar to that proposed by Berner, Lasaga, and Garrels (1983) who detailed the interdependence between residence time, concentration, and removal rate of seawater Mg during hydro-

thermal alteration. They suggested that values of $RdMg$ are best described by the first-order relation:

$$FlRdMg = MsRdMg / RtRdMg$$

and:

$$RtRdMg = RtRdMg(o) * SR(t) / SR(o)$$

where SR = rate of seafloor area generation, and (o) and (t) designate present and past time, respectively. In determining residence times of ridge-bound Mg , we consider two alternate scenarios, one that presumes no change from a present residence time of about 14 my, and one that presumes linear and inverse correlation between residence time and seafloor generation rate (fig. 16A) based on estimates from Gaffin (1987).

Employing these relations, values of seawater concentration, mass, and residence time for carbonate Ca , carbonate Mg , and ridge Mg are readily determined for present (table 7) and Phanerozoic oceans. Concentration of marine Ca has ranged from 0.68 to 1.52×10^{-2} m/l and is independent of assumptions about spreading rate (fig. 16B). Compared to a present concentration of 1.03×10^{-2} m/l, seawater Ca mass has evidently varied little over Phanerozoic time. Concentration of seawater Mg , on the other hand, has varied considerably. Assuming no relation between seafloor spreading rate and ridge-bound Mg residence time (constant at 14 my, table 7), marine Mg concentration has ranged from 0.67 to 5.31×10^{-2} m/l (fig. 16C). Assumption of linear correlation between spreading rate and residence time, on the other hand, yields Mg concentration from 0.56 to 5.31×10^{-2} m/l (fig. 16D). Regardless of relations between spreading rate and seawater flux through ridges, the present mass of oceanic Mg is as large as at any time during the Phanerozoic eon. Not unexpectedly, either conjecture yields seawater Mg concentration that exhibits an inverse correlation with carbonate Mg flux (fig. 17). Moreover, at equivalent values of $CbMg$, greater rates of ridge spreading result in somewhat lower seawater Mg concentration (fig. 16C, D).

Somewhat surprisingly, greater rates of seafloor accretion, presumed greater rates of seawater flow through hot ridge basalt, and lower residence times of ridge-bound Mg only result in small decreases in marine mass. When considering both constant and variable ridge residence times, average Phanerozoic Mg mass differs by only about 7.5×10^{18} m, about 10 percent of the present seawater Mg mass. Moreover, extrapolation of model $CbMg$ - $MsSwMg$ relations allows for the derivation of hypothetical global oceans in which all river Mg is removed either during hydrothermal alteration or dolomite precipitation (fig. 17). In an ocean devoid of dolomite, increased seafloor accretion only lowers Mg mass by about 15×10^{18} m (table 7), variation in ridge spreading potentially induces only about 20 percent reduction in ambi-

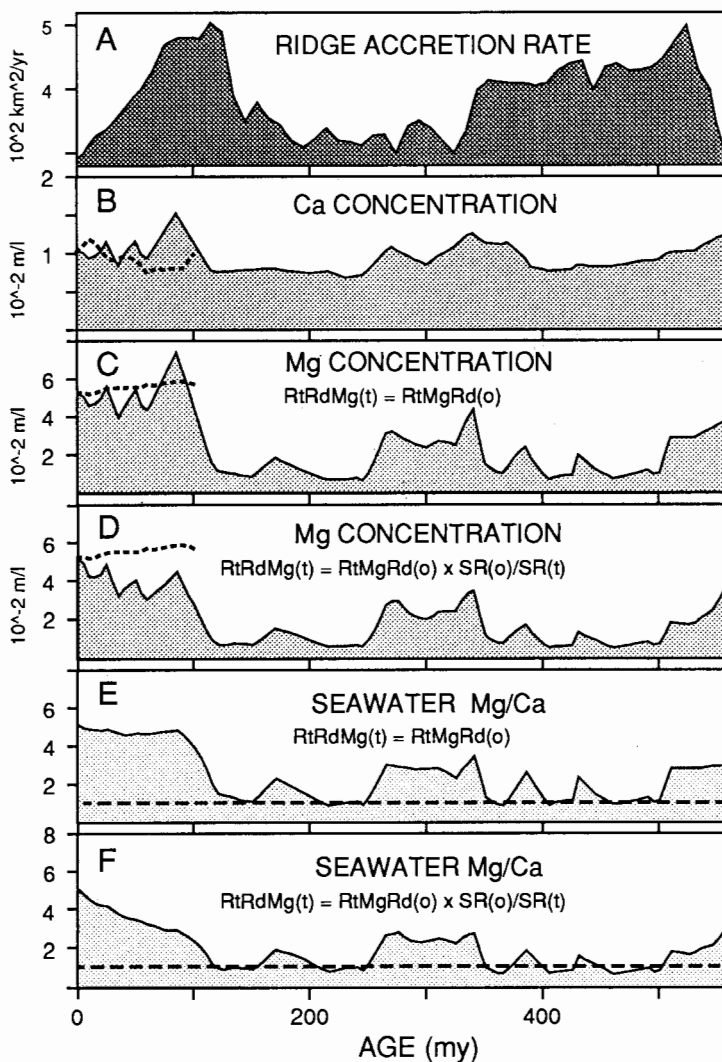


Fig. 16. Phanerozoic seawater compositions.

(A) Rates of ridge spreading and seafloor accretion from Gaffin (1987). Time intervals of more rapid spreading correspond to periods of continental submergence. Note crude inverse relation between seafloor accretion rate and dolomitization rate in figure 15.

(B) Marine Ca concentrations calculated from carbonate Ca fluxes ($RvCa + GwCa + RdCa$; fig. 11) assuming a seawater Ca residence time of 0.6 my. Dotted line is seawater Ca content for the past 100 my from Lasaga, Berner, and Garrels (1985).

(C) Marine Mg concentrations calculated from river Mg fluxes (fig. 11) assuming a ridge-bound Mg residence time of 14 my and a seawater dolomite Mg residence time equal to that for seawater Ca (0.6 my). Dotted line is seawater Mg content from Lasaga, Berner, and Garrels (1985).

(D) Seawater Mg concentrations as in (C) but assuming seawater-ridge Mg residence times proportional to ridge accretion rate where $RtRdMg(t) = RtRdMg(o) \times SR(o)/SR(t)$. Dotted line as in (C).

(E) Marine Mg/Ca ratios from concentrations in (B and C). Horizontal dashed line at $Mg/Ca = 1.0$. Note that Mg/Ca values are inversely proportional to rates of seawater Mg removal by dolomitization (fig. 15). Minimum Mg/Ca values are about 0.9.

(F) Marine molar Mg/Ca from concentrations in (B and D). Horizontal dashed line at $Mg/Ca = 1.0$. Minimum values approach 0.7.

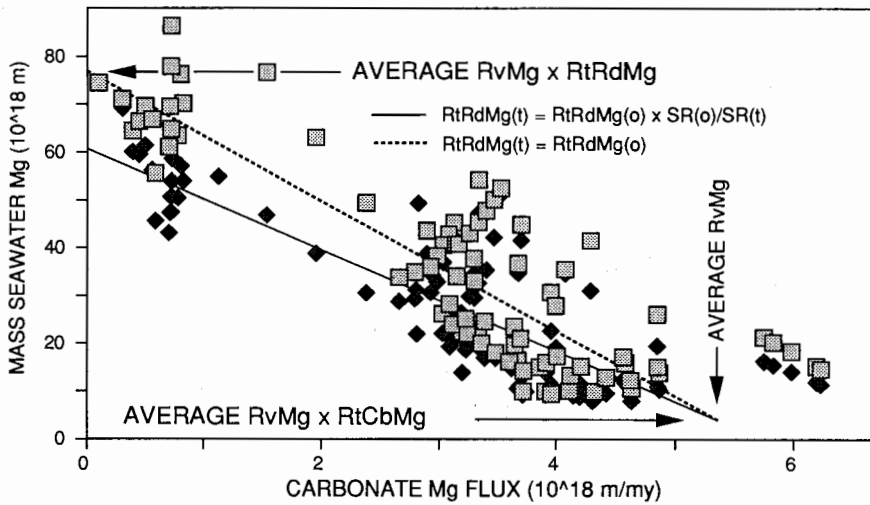


Fig. 17. Model relations between rates of marine Mg removal by dolomitization (horizontal axis) and seawater Mg masses (vertical axis). Dotted squares and regression line calculated assuming an invariant ridge-seawater Mg residence time of 14 my and carbonate-bound Ca and Mg residence times of 0.6 my. Note maximum average mass of 76.4×10^{18} m for complete Mg removal at ridges and a minimum mass of 3.2×10^{18} m for complete Mg removal by dolomite formation relative to a Phanerozoic average river Mg flux of 5.4×10^{18} m/my. Diamonds and solid regression line calculated assuming ridge-seawater Mg residence times inversely proportional to ridge spreading rates from Gaffin (1987) and carbonate-bound Ca and Mg residence times of 0.6 my. Note that alternate assumptions about seafloor accretion and hydrothermal seawater flux have little effect on marine Mg concentration relative to variable partitioning of Mg between silicate and carbonate reservoirs.

ent seawater Mg concentration. Conversely, seawater Mg mass would fall to 3.2×10^{18} m in an ocean devoid of Mg removal via hydrothermal alteration or about 4 percent of the present concentration (fig. 17). In short, small differences in marine dolomite accumulation rate have had a profound influence on marine Mg mass and concentration, whereas change over the full range of Phanerozoic seafloor spreading and inferred hydrothermal flow rates is relatively unimportant.

The reason for this difference is that seafloor accretion as determined by Gaffin (1987) has ranged from a (present) minimum rate of 2.92×10^2 km²/yr to a maximum value of 5.05×10^2 km²/yr, an increase of about 73 percent. Rates of Mg removal by dolomitization, on the other hand, have ranged from a (present) minimum of about 0.1×10^{18} m/my to a Phanerozoic maximum of 6.23×10^{18} m/my, an increase of over 6000 percent. Even more importantly, at different times over the past 560 my, virtually the entire river Mg contribution to global oceans has alternately been transferred to marine carbonate or ridge silicate reservoirs. Given that the residence time for dolomite-bound Mg is only a small fraction of that of ridge-bound Mg (presently

about 4 percent, table 7) at any specified seawater Mg flux, increasing dolomitization must have a proportionally greater effect on seawater Mg concentration.

Finally, calculated marine Mg/Ca ratios largely mimic inferred Mg concentrations, suggest that the present value of 5.16 is probably a Phanerozoic maximum, and demonstrate that marine dolomitization serves to depress Mg/Ca ratios toward unity (figs. 16E, F). Seawater Mg/Ca ratios have probably ranged from about 1.0 to about 5.2 over most of the past 560 my, decreasing markedly with increasing dolomite precipitation and decreasing slightly with increased seafloor spreading. The correspondence between minimum molar Mg/Ca ratios and unity may reflect the central importance of inherent thermodynamic requirements for dolomite formation. Data on surficial groundwaters in Hsu (1963) and Jacobson (1973) and extrapolation of high-temperature data in Rosenberg, Burt, and Holland (1967) indicate that the Mg/Ca ratio of fluids in equilibrium with calcite and dolomite at the Earth's surface is between about 0.8 and 1.0 (Carpenter, 1980; Hardie, 1987). As a result, seawater Mg removal by dolomite formation can not lower Mg/Ca activities much below this range of values. Concentrations of Ca and Mg ions inferred from mass-age data and dolomite abundances for Phanerozoic carbonate sequences are largely in agreement with these geochemical considerations.

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