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SEA LEVEL, SEDIMENTS AND THE COMPOSITION OF SEAWATER

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Dedicated to Manfred Schidlowski with thanks for 33 years of friendship.

ABSTRACT. The composition of seawater changed significantly during the course of the Phanerozoic in concert with long-term changes in sea level, which were largely the result of changes in the volume of mid-ocean ridges. These reflect changes in the rate of seafloor spreading and determine the rate of seawater cycling through mid-ocean ridges. Spencer and Hardie (1990) and Hardie (1996) proposed that the changes in the cycling rate of seawater through mid-ocean ridges have been responsible for the changes in the composition of seawater during the Phanerozoic. This explanation cannot account for the major changes in the composition of seawater during the Cenozoic, which was a time of nearly constant seafloor spreading rate. However, changes in the rate of deposition of shallow water carbonates and their penecontemporaneous dolomitization can explain the Cenozoic changes in seawater composition. This indicates that sedimentologic parameters have played a major role in the chemical evolution of seawater.

The more rapid cycling of seawater through MORs during the Mesozoic can explain semiquantitatively the fairly minor differences between the composition of seawater in the Eocene and in the Jurassic. Changes in the composition of seawater during the Paleozoic were probably determined both by changes in the rate of dolomite and gypsum/anhydrite deposition and by changes in the rate of seawater cycling through mid-ocean ridges. If the causes of these compositional changes are the same as those during the Cenozoic and Mesozoic, then sedimentologic factors have been significantly more important than the rate of cycling of seawater through MORs in shaping the chemical evolution of seawater during the Phanerozoic.

INTRODUCTION

It is now virtually certain that the composition of seawater has varied significantly during the Phanerozoic (see figs. 1, 2 and 3). The data in these figures, which are derived from the composition of fluid inclusions in halite from marine evaporites, are supported by evidence from several other lines of inquiry (for a recent summary see Holland, 2003 and Berner, 2004). However, the proposed changes in the concentration of the major cations and anions are still somewhat uncertain, and will probably need to be modified as additional data for the composition of seawater during the Phanerozoic become available.

An explanation for the observed changes in the Ca^{2+}, Mg^{2+}, and SO_4^{2-} concentration of seawater was offered by Spencer and Hardie (1990) and Hardie (1996). These authors proposed that the major changes in sea level during the Phanerozoic were caused by changes in the rate of seafloor spreading. Times of rapid seafloor spreading are times of large mid-ocean ridge volumes, and hence times of high stands of sea level. During periods of rapid seafloor spreading the rate of seawater cycling is expected to be faster than during periods of slow seafloor spreading. Hardie (1996) proposed that the Mg^{2+} and SO_4^{2-} concentration in seawater would therefore be abnormally low and the concentration of Ca^{2+} and K^+ abnormally high during periods of rapid spreading. These predictions agree with the available data for the concentration of Ca^{2+}, Mg^{2+}, and SO_4^{2-} in seawater during periods of high sea level stands, but they do not agree with the near-constancy of the concentration of K^+ in seawater during the Phanerozoic.

A serious objection to the Spencer-Hardie (1990) model was raised by the observation that the composition of seawater changed considerably during the last 40

Ma (Zimmermann, 2000), a period during which changes in the rate of seafloor spreading were almost certainly very small (Kominz, 1984; Lithgow-Bertelloni and others, 1993; Gaina and Mueller, 2004). This constancy could also have pertained for the entire last 180 Ma. Rowley (2002) pointed out that the observed variation of seafloor area with time since 180 Ma can be explained if the rate of seafloor spreading has been essentially constant. If this is correct, the variations in sea level and in the composition of seawater during the last 180 Ma must be due to causes other than variations in the rate of seafloor spreading.

However, Demicco (2004) has shown that there are alternative extensions of the available data, which allow for the non-steady state production of ocean crust during the Mesozoic, and the analyses of plate motions by Kominz (1984, 2004), Lithgow-Bertelloni and others (1993) and Gaina and Mueller (2004) indicate that the rate of seafloor spreading was considerably faster during the Cretaceous than during the Cenozoic. Gaina and Mueller's (2004) preliminary results show that the mean spreading rate decreased from approximately 145mm/yr in the Barremian to 85 mm/yr in the Maastrichtian, and that the spreading rate has been almost constant during the last 75 Ma. The issue is currently unresolved. It is proposed in this paper that, even if the rate of seafloor spreading during the Cretaceous was twice as fast as today, variations in the ratio of dolomite to limestone deposition and in the rate of gypsum/anhydrite deposition were more important than changes in the seafloor spreading rate as causes of the observed changes in the concentration of Ca^{2+}, Mg^{2+}, and SO_4^{2-} in seawater.

THE CENOZOIC

The Ca^{2+}, Mg^{2+}, and SO_4^{2-} concentration of seawater changed considerably during the Tertiary (see figs. 1, 2 and 3). It is proposed here that these changes were caused by the shift in the deposition of $CaCO_3$ from shallow to deep parts of the oceans. Hay (1994) summarized the available data for the apparent accumulation rate of deep water carbonates and estimated that today ca. 85 percent of marine $CaCO_3$ are deposited in the deep oceans. If we assume that the total rate of $CaCO_3$ deposition has remained roughly constant during the Tertiary, it follows from Hay's (1994) data that at the end of the Cretaceous only ca. 30 percent of marine $CaCO_3$ were deposited in the deep ocean (see fig. 4). Since deep water $CaCO_3$ is dolomitized only very slightly except in areas where organic matter is abundant, the amount of dolomite formed during the Tertiary has decreased progressively, even though shallow water carbonate platforms continued to be thoroughly dolomitized (see Holland and Zimmermann, 2000). A rather simplified model was developed on this basis to explain the increase in the Mg^{2+} concentration of seawater during the Tertiary (Holland and Zimmermann, 2000). It is repeated here in abbreviated form as a prelude to an analogous treatment of changes in the Ca^{2+} and SO_4^{2-} concentration of the other major constituents of seawater.

The Mg^{2+} Balance

The loss of the majority of Mg^{2+} from seawater is the sum of three terms:

$$J = A + B + C \ \frac{\text{mol}}{\text{yr}} \tag{1}$$

where A is the loss of Mg^{2+} to dolomite, B the loss to ocean-floor basalts, and C the loss to a variety of clay minerals in a variety of settings. The loss to dolomite can be parameterized approximately in the form

$$A \approx k_A f(G) \mathrm{R}_{SWC} m_{\mathrm{Mg}^{2+}} \ \frac{mol}{yr} \tag{2}$$

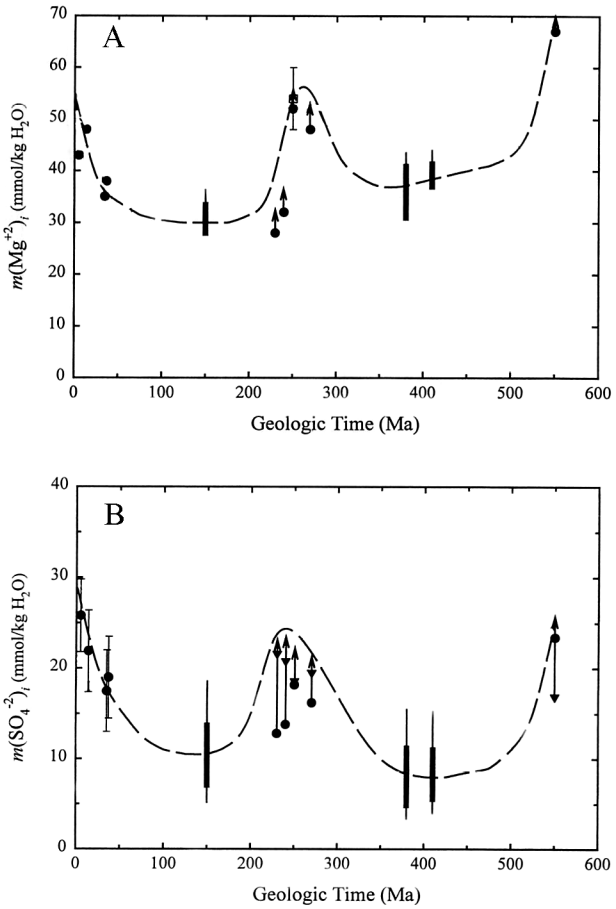

Fig. 1. (A) Concentration of Mg^{2+} in seawater during the Phanerozoic based on analyses of fluid inclusions in marine halite. Thick and thin vertical bars are based on the assumption of different values for $m_{Ca^{2+}} \cdot m_{SO_4^{2-}}$ (Horita and others, 2002). (B) Concentration of SO_4^{2-} in seawater during the Phanerozoic based on analyses of fluid inclusions in marine halite (solid symbols); circles, triangles, and thick-thin vertical bars are based on the assumption of different values for $m_{Ca^{2+}} \cdot m_{SO_4^{2-}}$ (Horita and others, 2002).

where $m_{Mg^{2+}}$ is the Mg^{2+} concentration in seawater, R_{SWC} is the rate of shallow-water carbonate deposition, $f(G)$ is a function that depends on a variety of geographic variables, as well as on temperature and relative humidity, and k_A is a constant.

The loss of Mg^{2+} to ocean-floor basalts can be parameterized approximately to the form:

$$B \approx k_B R_{SFS} m_{Mg^{2+}} \frac{mol}{yr} \tag{3}$$

where R_{SFS} is the rate of seafloor spreading, and k_B is a constant.

The loss to clays can be parameterized approximately to the form:

$$C \approx k_C m_{Mg^{2+}} \frac{mol}{yr} \tag{4}$$

where k_C is a constant (see for instance Sayles and Mangelsdorf, 1977).

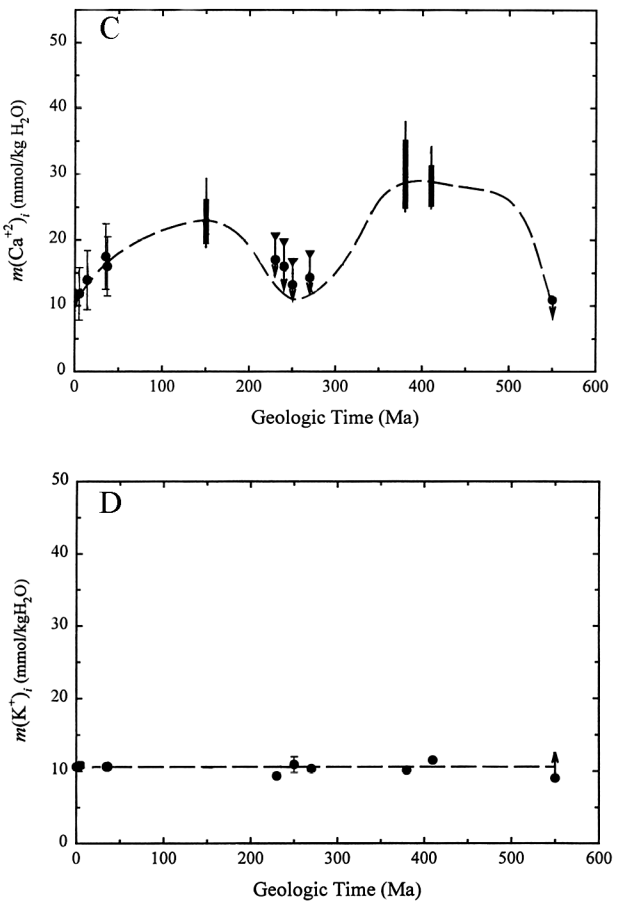

Fig. 1 (continued). (C) Concentration of Ca^{2+} in seawater during the Phanerozoic based on analyses of fluid inclusions in marine halite (solid symbols): circles, triangles, and thick-thin vertical bars are based on the assumption of different values for $m_{Ca^{2+}} \cdot m_{SO_4^{2-}}$ (Horita and others, 2002). (D) Concentration of K^+ in seawater during the Phanerozoic based on analyses of fluid inclusions in marine halite. (Horita and others, 2002).

In this simplified formulation the output of Mg^{2+} from the oceans is therefore:

$$J = [k_A f(G)\mathrm{R}_{SWC} + k_B \mathrm{R}_{SFS} + k_C] m_{\mathrm{Mg}^{2+}} = a m_{\mathrm{Mg}^{2+}} \frac{mol}{yr} \tag{5}$$

The rate of change of the Mg^{2+} content of seawater is given by the expression:

$$W_{SW} \frac{dm_{Mg^{2+}}}{dt} = I - J \frac{mol}{yr} \tag{6}$$

where W_{SW} is the mass of seawater, and I is the rate of the river input of Mg^{2+} to the oceans in mol/yr. Inserting equation 5 into equation 6 and rearranging, one obtains:

$$a = \frac{I - W_{SW} \dfrac{dm_{Mg^{2+}}}{dt}}{m_{\mathrm{Mg}^{2+}}} \frac{kg}{yr} \tag{7}$$

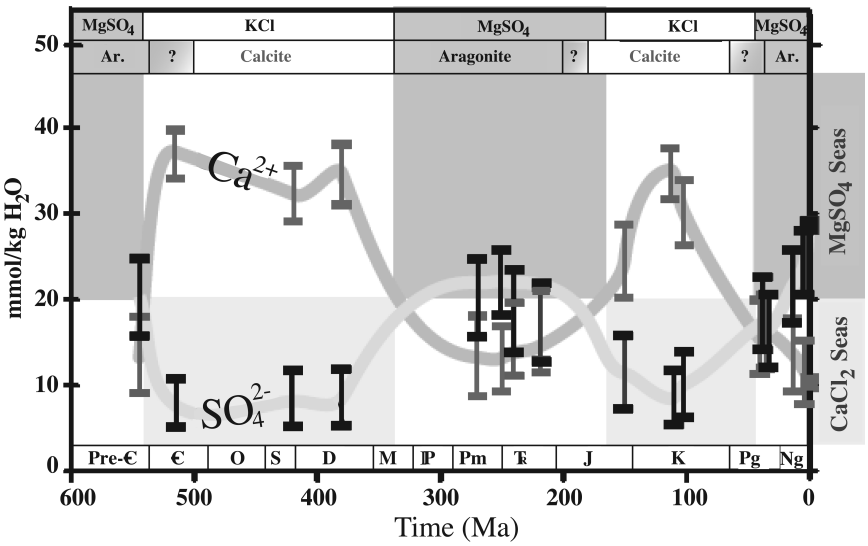

Fig. 2. Secular variation in Ca^{2+} and Ca^{2+} and SO_4^{2-} concentrations of seawater during Phanerozoic time, estimated from fluid inclusions in marine halites (Lowenstein and others, 2003).

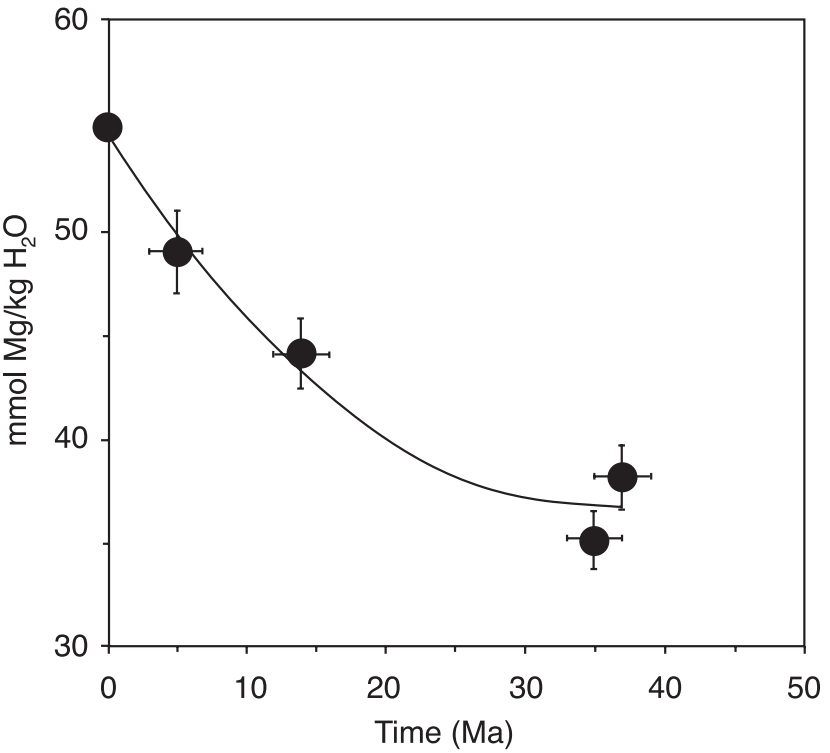

Fig. 3. The concentration of Mg^{2+} in seawater during the last 40 Ma as inferred from the composition of fluid inclusions in halite from marine evaporites (Zimmermann, 2000).

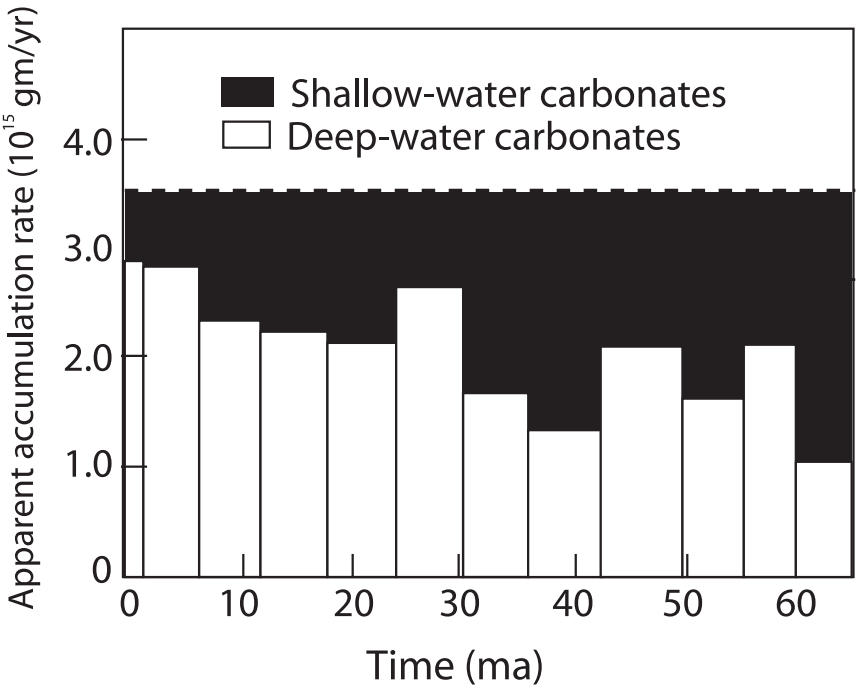

Fig. 4. The concentration of Mg^{2+} in seawater during the last 40 Ma as inferred from the composition of fluid inclusions in halite from marine evaporites (Zimmermann, 2000).

The value of the parameter "*a*" during the past 40 Ma can be calculated from the data in figure 3, assuming that the river input of Mg^{2+} to the oceans has been equal to the present-day value of ca. 6.1×10^{12} mol/yr (see table 1). The value of the parameter "*a*" has been plotted in figure 5 as a function of the R_{SWC}, the apparent accumulation rate of marine carbonates deposited in shallow water settings. The linear relationship between the parameter "*a*" and the rate of shallow water carbonate deposition tends to confirm the first order model for the output of Mg^{2+} from the oceans.

The apparent rate of carbonate accumulation in figure 4 is twice the rate calculated in tables 2 and 3 on the basis of the river input of Ca^{2+} and Mg^{2+} that accumulates as carbonates. The reason for this is not clear. If the apparent accumulation rates in figure 4 are reduced by a factor of two, the correlation of "*a*" with R_{SWC} in figure 5 is maintained; the slope of the line is increased by a factor of 2, but the intercept at $R_{SWC} = 0$ remains the same.

There is a good deal of evidence that the river input of Mg^{2+} has not been constant during the past 40 Ma. In their table 10 Gibbs and others (1999) have listed the estimated total bicarbonate flux from rivers to the oceans during the past 237 Ma. The ratio of their averaged bicarbonate flux at 20 Ma to the present flux is ca. 1.35. The ratio of their averaged bicarbonate flux at 40 Ma to the present flux is ca. 1.56. These numbers are somewhat uncertain, but they are clearly significantly in excess of 1.0. If, as seems likely, the ratio of the concentration Mg^{2+} to that of HCO_3^- in average river water did not change significantly during the past 40 Ma, I, the flux of Mg^{2+} to the oceans was ca. 8.1×10^{12} mol/yr at 20 Ma and ca. 9.6×10^{12} mol/yr at 40 Ma. Similarly, if the ratio of the concentration of Ca^{2+} to that of HCO_3^- in average river water did not change significantly during the past 40 Ma, the rate of $CaCO_3$ accumulation in the oceans was ca. 4.7×10^{12} gm/yr at 20 Ma and ca. 5.5×10^{12} gm/yr at 40 Ma. With these

numbers and using the data for the rate of accumulation of $CaCO_3$ in the deep oceans (Hay, 1994), one can calculate the value of the parameters "*a*" and R_{SWC} at 20 and 40 Ma. These are shown in figure 5 together with the values calculated with the assumption of a constant river input of solutes. Perhaps somewhat surprisingly, all of the data points fall close to a single straight line, which defines the relationship between the parameter "*a*" and the rate of shallow water $CaCO_3$ deposition. The insensitivity of the slope and the intercept of the line to the magnitude of the river inputs to the oceans probably explains, at least in part, the success of the very simplified model proposed here for the Mg^{2+} output from the oceans.

The value of the terms in equation 5 can be determined quite readily. From figure 3 the increment of Mg^{2+} to the oceans today is 1.7×10^{12} mol/yr. Hence the output, J, of Mg^{2+} to the three sinks in equation 6 is 4.4×10^{12} mol/yr. The loss of Mg^{2+} to ocean-floor basalts during the hydrothermal cycling of seawater is the product of the mass of seawater cycled through ocean crust per year times the loss of Mg^{2+} during this cycling. The most recent estimate of the rate of seawater cycling is $(3.7 \pm 0.5) \times 10^{13}$ kg/yr (Mottl, 2003). This value is similar to the axial flow rate of $(3 \pm 1.5) \times 10^{13}$ kg/yr proposed by Elderfield and Schultz (1996). Since Mg^{2+} in seawater is lost almost entirely to the oceanic crust during high-temperature hydrothermal cycling, 55 mmol of Mg^{2+} are lost per kg of cycled seawater.

The second and third terms in equation 5 can be deconvolved by extrapolating the line in figure 5 to a zero value of the rate of shallow water carbonate deposition. At this point the value of "*a*" is 5.0×10^{13} kg/yr. From equation 5 it follows that

$$k_B R_{SFS} + k_C = 5.0 \times 10^{13} \frac{kg}{yr} \tag{8}$$

since $R_{SWC} = 0$. As $k_B R_{SFS} = 3.7 \times 10^{13}$ kg/yr, the value of k_C is 1.3×10^{13} kg/yr. This implies that the present day loss of Mg^{2+} to "clays" is ca.

$$1.3 \times 10^{13} \frac{kg}{yr} \times 55 \times 10^{-3} \frac{mol}{kg} = 0.7 \times 10^{12} \frac{mol}{yr}.$$

Approximately 0.3×10^{12} mol/yr of this loss is due to cation exchange on clays (Drever and others, 1988). The remaining 0.4×10^{12} mol/yr are probably lost by reverse weathering reactions and during the low temperature alteration of seafloor basalt. The loss of Mg^{2+} to dolomite in table 1 is then, by difference, equal to 1.7×10^{12} mol/yr.

As shown in figure 3, the rate of change of the Mg^{2+} concentration in seawater at 35 Ma was considerably smaller than today. The increment of Mg^{2+} to the oceans at that time derived from the data in this figure was 0.4×10^{12} mol/yr. If the rate of seawater cycling through MORs was the same then as now, the output of Mg^{2+} to the MORs was

$$3.7 \times 10^{13} \frac{kg}{yr} \times 39 \times 10^{-3} \frac{mol}{kg} = 1.4 \times 10^{12} \frac{mol}{yr}$$

and the loss to dolomites was 3.8×10^{12} mol/yr, that is somewhat more than twice the present rate. It should be noted that these output figures should not be regarded as anything but approximate, because both the inputs and the parameterization of the outputs are somewhat uncertain.

A reasonably useful crosscheck can be obtained with Hay's (1994) estimates of the rate of shallow water deposition and the observed dolomite content of Tertiary shallow water carbonates. According to Hay (1994) ca. 0.6×10^{15} gm/yr of the carbonates deposited during the last 5 Ma were shallow water in origin. In the 35 to 40 Ma age range the rate of shallow water carbonates was ca. 1.9×10^{15} gm/yr. The estimated rate

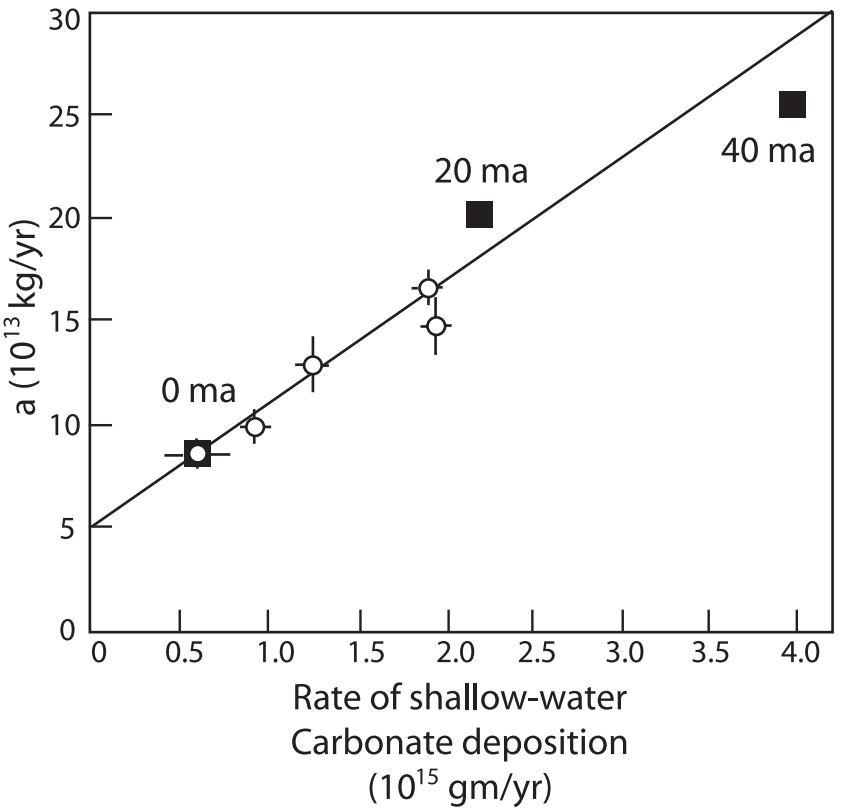

Fig. 5. The value of the parameter "*a*" in equation 6 during the past 40 Ma, plotted against the rate of shallow water carbonate accumulation (Holland and Zimmermann, 2000). Circles were calculated assuming a constant rate of $CaCO_3$ precipitation. Squares were calculated using the variable rate of $CaCO_3$ precipitation of Gibbs and others (1999).

TABLE 1

The approximate marine inputs and outputs of Mg^{2+} today and at 35 Ma. (The uncertainties are estimated to be ca. ± 20%.)

	Today (10^{12} mol/yr)	At 35 Ma (10^{12} mol/yr)
INPUTS		
river input	6.1	6.1
OUTPUTS		
to MORs	2.0	1.4
to cation exchange	0.3	0.2
*other	0.4	0.3
to dolomite	1.7	3.8
increment to oceans	1.7	0.4
total:	6.1	6.1

*Low temperature alteration of oceanic crust and reverse weathering

of dolomite deposition in table 1 during these time periods was 0.3×10^{15} gm/yr and 0.7×10^{15} gm/yr respectively. This corresponds to ca. 50 percent and 40 percent of the total quantity of shallow water carbonates deposited during the two time periods. These percentages are perhaps somewhat lower than estimates based on drill core and exposure information (see Holland and Zimmermann, 2000). The differences, if they are real, may be due in part to differences in the estimated rates of total carbonate deposition (see above).

The SO_4^{2-} Balance

The data for the riverine input of sulfate have been reviewed recently by Meybeck (2003). His figures do not differ significantly from previous estimates (see for instance Holland, 1978). The marine outputs are somewhat uncertain, but they are consistent with an estimated river input of 4.2×10^{12} mol/yr. During high temperature cycling of seawater through the oceanic crust SO_4^{2-} is lost nearly completely. The output of SO_4^{2-} to MORs is therefore the product of the concentration of SO_4^{2-} in seawater and the annual flux of seawater through MORs.

$$28 \times 10^{-3} \frac{mol}{kg} \times 3.7 \times 10^{13} \frac{kg}{yr} = 1.0 \times 10^{12} \frac{mol}{yr}$$

This figure must be reduced by the quantity of H_2S which is returned to the oceans in hydrothermal vent fluids (see for instance Elderfield and Schultz, 1996) and by the later resolution of $CaSO_4$. The isotopic composition of sulfur in seawater sulfate indicates that the output of marine sulfur to pyrite is roughly half of the river input. The current increment of SO_4^{2-} to seawater, calculated in the same manner as the increment of Mg^{2+}, is ca. 1.0×10^{12} mol/yr.

The output of SO_4^{2-} to evaporites can be estimated, but only very roughly, by comparison with the estimated rate of dolomite formation. Most penecontemporaneous dolomite forms in sabkha-like settings. Kinsman (1966) showed that in these settings the precipitation of calcite and/or aragonite during evaporation is followed by the precipitation of gypsum and/or anhydrite. During this process the Ca^{2+} concentration drops rapidly, and the Mg^{2+}/Ca^{2+} ratio rises rapidly. Dolomitization of $CaCO_3$ then releases Ca^{2+}, which is used to precipitate the remaining quantity of SO_4^{2-}. After the concentration of SO_4^{2-} has approached very low values, the concentration of Ca^{2+} in the brines rises due to continued dolomitization, and the Mg^{2+}/Ca^{2+} ratio gradually decreases to values between 1 and 2. If the Mg^{2+}/Ca^{2+} ratio reaches 1, then 37 mmol Mg^{2+} are lost per kg of present day seawater. If the Mg^{2+}/Ca^{2+} ratio reaches only 2, then 31 mmol Mg^{2+} are lost per kg of modern seawater. In that case, the loss of Mg^{2+} from seawater is nearly the same as that of SO_4^{2-}. The minimum mass of seawater required to generate a quantity of dolomite containing 1.7×10^{12} mol Mg^{2+} (see table 1) is therefore 4.6×10^{13} kg. The quantity of $CaSO_4$ that can be deposited from this amount of seawater is 1.3×10^{12} mol. This is considerably greater than the estimated quantity of $CaSO_4$ precipitated annually with evaporites (see table 2). The difference is probably due to the resolution of gypsum and anhydrite by rainwater and by seawater that has not been evaporated or was evaporated only slightly.

The figures in table 2 for the estimated marine SO_4^{2-} budget at 35 Ma differ significantly from those for the present. The river input has been kept the same, perhaps unreasonably so; the quantity of SO_4^{2-} that disappeared into MORs was smaller, because the concentration of SO_4^{2-} in the oceans was only18 mmol/kg. The S output to FeS_2 was taken to be approximately the same as today, because the value of $\delta^{34}S$ of ocean SO_4^{2-} was essentially the same as today (Paytan and others, 1998). The increment to the oceans was smaller, because the curve of $m_{SO_4^{2-}}$ versus time has a gentler slope at 35 Ma than at present (see figs. 1, 2 and 3). The estimated output of

TABLE 2

The approximate marine inputs and outputs of SO_4^{2-} today and at 35 Ma. (The uncertainties are estimated to be ca. ± 20%.)

	Today (10^{12} mol/yr)	At 35 Ma (10^{12} mol/yr)
INPUTS		
river input	4.2	4.2
OUTPUTS		
to MORs	1.0	0.7
to evaporites	0.2	1.3
to FeS_2	2.0	2.0
increment to oceans	1.0	0.2
total:	4.2	4.2

SO_4^{2-} with evaporites was significantly greater than today, reflecting the greater rate of dolomitization during the Oligocene.

The Ca^{2+} Balance

Approximate figures for the input and output of Ca^{2+} to and from the oceans are summarized in table 3. The river input is based on the estimate by Meybeck (2003). The Ca^{2+} input rate due to cation exchange on clays is taken from Drever and others (1998). The calcium flux from MORs is somewhat uncertain. von Damm (1990) proposed an average of 20 mmol/kg for the Ca^{2+} concentration in black smoker fluids. On the basis of a more extensive data set Mottl (personal communication, 2004) has suggested that the figure of 20 mmol/kg is too low. This conclusion is consistent with figure 4 in von Damm's (1995) summary. An average of 35 mmol/kg is more likely. This implies that the input of Ca^{2+} from MORs is currently ca.

$$(35 - 10) \times 10^{-3} \frac{mol}{kg} \times 3.7 \times 10^{13} \frac{kg}{yr} = 0.9 \times 10^{12} \frac{mol}{yr}.$$

TABLE 3

The approximate marine inputs and outputs of Ca^{2+} today and at 35 Ma. (The uncertainties are estimated to be ± 20%.)

	Today (10^{12} mol/yr)	At 35 Ma (10^{12} mol/yr)
INPUTS		
river input	15.0	15.0
cation exchange on "clays"	1.0	1.0
from MORs	0.9	0.7
decrement from oceans	0.7	0.5
total:	17.6	17.2
OUTPUTS		
to evaporites	0.2	1.3
to $CaCO_3$	15.7	12.1
to $CaMg(CO_3)_2$	1.7	3.8
total:	17.6	17.2

TABLE 4

The approximate marine inputs and outputs of Na^+ today and at 35 Ma. (The uncertainties are estimated to be ± 20%.)

	Today (10^{12} mol/yr)	At 35 Ma (10^{12} mol/yr)
INPUTS		
river input	2.4	2.4
total:	2.4	2.4
OUTPUTS		
to MORs	1.1	1.1
to cation exchange	1.5	1.5
total:	2.6	2.6

The output to evaporites is based on the $CaSO_4$ output in table 2. The increment to the oceans was calculated like those for Mg^{2+} and SO_4^{2-}. The output of Ca^{2+} as a constituent of dolomite is derived from table 1. The output of $CaCO_3$ was determined by difference. It should be noted that the total output of $CaCO_3$ and $CaMg(CO_3)_2$ is only half of the value estimated by Hay (1994).

Since black smoker fluids are rather well buffered by the mineralogy of hydrothermally altered oceanic crust (Berndt and others, 1989; Seyfried and others, 2002), their composition was probably not affected seriously by the changes in the composition of seawater that have occurred during the last 35 Ma. The figures in table 3 at 35 Ma were estimated on this basis.

The Na+ Balance

Tables 4 and 5 approximate the major marine inputs and outputs of Na^+ and K^+. The Na^+ input from rivers was taken to be the difference between the average Na^+ and the average Cl^- content of river waters (Meybeck, 2003), because so much of the Cl^- in river water is due to marine aerosols. The output of Na^+ to MORs is difficult to estimate with any degree of precision. The negative correlation of the Na^+/Cl^- ratio with the Ca^{2+}/Cl^- ratio in hydrothermal fluids (fig. 4 in von Damm, 1995) is quite striking. For

TABLE 5

The approximate marine inputs and outputs of K^+ today and at 35 Ma. (The uncertainties are estimated to be ± 20%.)

	Today (10^{12} mol/yr)	At 35 Ma (10^{12} mol/yr)
INPUTS		
river input	1.4	1.4
from MORs	0.6	0.6
total:	2.0	2.0
OUTPUTS		
to cation exchange	0.3	0.3
to reverse weathering	0.8	0.8
to low temperature alteration of oceanic crust	0.4	0.4
total:	1.5	1.5

TABLE 6

The approximate marine inputs and outputs of HCO_3^- today and at 35 Ma. (The uncertainties are estimated to be ± 20%.)

	Today (10^{12} mol/yr)	At 35 Ma (10^{12} mol/yr)
INPUTS		
river input	37.6	37.6
from generation of SO_4^{2-} reduction	4.0	4.0
total:	41.6	41.6
OUTPUTS		
to $CaCO_3$ deposition	31.4	24.2
to $CaMg(CO_3)_2$ deposition	6.8	15.2
to MORs	0.1	0.1
total:	38.3	39.5

values of 35 mmol/kg for the average Ca^{2+} concentration in hydrothermal fluids, the Na^+ concentration is ca. 440 mmol/kg. Hence the loss of Na^+ during passage through MORs is close to 30 mmol/kg, and the annual loss rate of Na^+ is 1.1×10^{12} mol. The other major loss of Na^+ is due to cation exchange on clays. Drever and others (1998) have suggested that this occurs at a rate of ca. 1.5×10^{12} mol/yr. The sum of the two loss rates is the same, within the uncertainty of the measurements, as the estimated rate of the river input of Na^+ (see Berner and Berner, 1996).

The K^+ Balance

The river input of K^+ in table 5 was based on Meybeck's (2003) data. The input from MORs is based on von Damm (1990), Elderfield and Schultz (1996), and Mottl (2003). The loss of K^+ due to cation exchange on clays was taken from Drever and others (1988). The figure of 0.4×10^{12} mol/yr for the loss of K^+ by reverse weathering is the best estimate of R. C. Aller (personal communication, 2004). The loss of K^+ by low-temperature alteration of oceanic crust is the average proposed by Elderfield and Schultz (1996, table 15). The process of reverse weathering, which was first proposed by Mackenzie and Garrels (1966), plays a significant role in the geochemistry of K^+, as pointed out recently by Michalopaulos and Aller (1995, 2004) and by Mackenzie and Kump (1995). However K^+ exchange for other interlayer cations in smectite-rich clay and weathered illite also provides a substantial sink for K^+ in the marine environment (Hover and others, 2002). The K^+ inputs currently do not balance the estimated K^+ outputs, probably because one or more of the output rates have been underestimated. The figures for K^+ inputs and outputs at 35 Ma were taken to be equal to those for the present.

The HCO_3^- Balance

As shown in table 6, rivers are the major source of HCO_3^- to the oceans. The major output is the precipitation of $CaCO_3$ and $CaMg(CO_3)_2$. The loss of HCO_3^- to the MORs is a minor but potentially important part of the HCO_3^- geochemistry of the oceans. The figures for $CaCO_3$ deposition in table 6 are based in part on the assumption that the removal of Mg^{2+}, K^+, and Na^+ from seawater with clays takes place entirely by cation exchange with Ca^{2+}. Since the removal of these cations with clays takes place in part by reverse weathering reactions, the loss of HCO_3^- by the precipitation of $CaCO_3$ and $CaMg(CO_3)_2$ is slightly less than that shown in table 6, and the resulting imbalance in

TABLE 7

The approximate marine inputs and outputs of H_4SiO_4 today and at 35 Ma. (The uncertainties are estimated to be ± 20%.)

	Today and at 35 Ma (10^{12} mol/yr)
INPUTS	
river input	7.0
from MORs	0.5
total:	7.5
OUTPUTS	
to siliceous organisms	6.0
to reverse weathering reactions	1.5
total:	7.5

the HCO_3^- budget is eliminated by the loss of HCO_3^- during reverse weathering reactions such as:

$$3\underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} + 2K^+ + 2HCO_3^- \rightarrow 2\underset{\text{muscovite}}{KAl_3Si_3O_{10}(OH)_2} + 5H_2O + 2CO_2 \qquad (9)$$

HCO_3^- is generated during the reduction of SO_4^{2-} and the precipitation of FeS_2 via reactions such as:

$$2\text{“}FeO\text{”} + 4SO_4^{2-} + 7C^\circ + CO_2 + 4H_2O \rightarrow 2FeS_2 + 8HCO_3^- \qquad (10)$$

Ca. 4×10^{12} mol HCO_3^- are produced in this fashion today. The figure 37.6×10^{12} mol/yr for the river input of HCO_3^- is based on the estimate by Meybeck (2003) and the requirement of electrical neutrality for the average river water composition chosen for this paper. The agreement between the estimated HCO_3^- input to and output from the oceans is reassuring.

The H_4SiO_4 Balance

Most of the H_4SiO_4 delivered to the oceans by rivers and hydrothermal solutions leaves the oceans as a constituent of amorphous SiO_2. The quantity that is removed by reverse weathering reactions is a small fraction of the total. Just how small, is currently not known, but perhaps as much as 20 to 25 percent of the river input may be removed by reverse weathering reactions (R. C. Aller, personal communication, 2004). The estimated silica output with siliceous organisms in table 7 agrees surprisingly well with the very rough estimate of 8.5×10^{12} mol/yr by Broecker and Peng (1982) for the rate of opal deposition in the oceans.

THE MESOZOIC

The progressive changes in the composition of seawater from the early Cretaceous to the present have been essentially unidirectional. The concentration of Mg^{2+} and SO_4^{2-} increased and that of Ca^{2+} decreased. Changes in the concentration of Na^+ can be inferred from variations in the Na^+/Cl^- ratio of inclusion fluids in halite from marine evaporites and by the difference between the Cl^- concentration in ancient seawater and the concentration of the sum of the major ions other than Na^+. Figure 6 (Lowenstein and others, 2001) shows that during the Early Cretaceous the concentra-

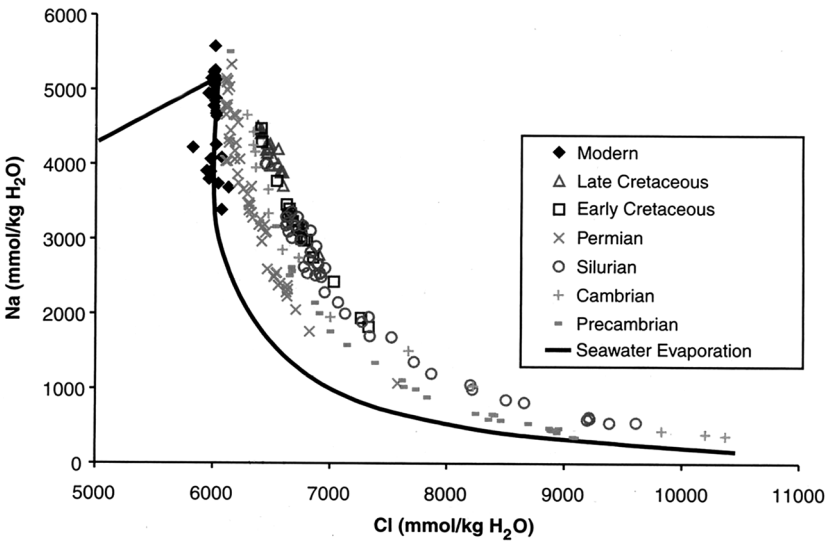

Fig. 6. The value of the parameter "*a*" in equation 6 during the past 40 Ma, plotted against the rate of shallow water carbonate accumulation (Holland and Zimmermann, 2000). Circles were calculated assuming a constant rate of $CaCO_3$ precipitation. Squares were calculated using the variable rate of $CaCO_3$ precipitation of Gibbs and others (1999).

tion of Na^+ at a given Cl^- concentration in primary fluid inclusions in halite from marine evaporites was higher than in present day, in Permian, and in latest Precambrian inclusion fluids. On evaporating present-day seawater, the brine becomes saturated with respect to halite when $m_{Na^+} \cdot m_{Cl^-} = 30.0\ (\text{mol/kg})^2$. Along an extension of the Cretaceous Na^+ - Cl^- curve in figure 5 $m_{Na^+} \cdot m_{Cl^-} = 30.0\ (\text{mol/kg})^2$ when $m_{Na^+} = 4.76$ mol/kg H_2O and $m_{Cl^-} = 6.30$ mol/kg H_2O. The m_{Na^+}/m_{Cl^-} ratio at this composition is 0.77. In seawater today, the m_{Na^+}/m_{Cl^-} ratio is 0.86. If the Cl^- concentration of Cretaceous seawater was the same as at present, m_{Na^+} was therefore approximately 425 mmol/kg H_2O.

From the data in figure 1 and assuming that $m_{HCO_3^-} = 2$ mmol/kg H_2O

$$m_{Na^+} = m_{Cl^-} + 2m_{SO_4^{2-}} - 2m_{Mg^{2+}} - 2m_{Ca^{2+}} - m_{K^+} + m_{HCO_3^-} = 453\,\frac{mmol}{kg}\,H_2O \qquad (11)$$

and $m_{Na^+}/m_{Cl^-} = 0.83$.

The difference between the two estimates of m_{Na^+} is probably within the uncertainties of the data which were used to calculate the ratios. The decrease in the m_{Na^+}/m_{Cl^-} ratio from 0.86 to 0.80 $\pm$ 0.03 due to a change in salinity caused by halite precipitation in Tertiary and Cretaceous marine evaporites is unlikely. The decrease is much more likely to be due to an increase in the rate of Na^+ removal from seawater by cation exchange with clays. At 150 Ma the concentration of Mg^{2+} in seawater was approximately half its present value (see fig. 1). If the Mg^{2+} removal rate by cation exchange at that time was approximately half of the present rate, and if the difference was compensated by an uptake of Na^+, an additional 0.3×10^{12} mol/yr of Na^+ was taken up by cation exchange at that time. This could have been compensated by a decrease in the Na^+ uptake by MORs if the loss of Na^+ during the passage of seawater through MORs at high temperatures was only ca. 20 mmol/kg. This, in turn, could have been accomplished by dropping the Na^+ concentration of seawater by ca. 10 mmol/kg, that

is to ca. 455 mmol/kg. The agreement with the available data for the Na^+ concentration in Jurassic seawater is encouraging. However, the above calculation is based on too many assumptions to claim that this is the reason for the progressively lower Na^+/Cl^- ratio from the present to the early Cretaceous.

The course of the concentration of Mg^{2+} in seawater during the Mesozoic was probably influenced both by changes in the rate of seawater cycling through MORs and by the flooding of the continents during the high stand of sea level. The effect of changes in the cycling of seawater through MORs can be estimated, at least roughly. Kominz (1984), Lithgow-Bertelloni and others (1993), and Gaina and Mueller (2004) have suggested that the rate of seafloor spreading during the Cretaceous may have been up to twice the present rate. If so, the value of R_{SFS} in equation 5 would have been ca. 3.7×10^{12} kg/yr higher than during the Cenozoic. If we simply take the best estimates for the value of "*a*" at 35 Ma, we can readily estimate the effect of a doubling of the rate of seafloor spreading under the prevailing conditions. At steady state and at the present rate of Mg^{2+} river input

$$m_{Mg^{2+}} = \frac{6.1 \times 10^{12} \dfrac{mol}{yr}}{(15.0 + 3.7) \times 10^{13} \dfrac{kg}{yr}} = 32\ mmol/kg.$$

At steady state and at a Mg^{2+} river input rate of 9.6×10^{12} mol/yr the estimated Mg^{2+} concentration in seawater becomes

$$m_{Mg^{2+}} = \frac{9.6 \times 10^{12} \dfrac{mol}{yr}}{(25.0 + 3.7) \times 10^{13} \dfrac{kg}{yr}} = 33\ mmol/kg.$$

The estimated Mg^{2+} concentration in seawater at a doubled rate of seawater cycling is therefore rather insensitive to variations in the river input of Mg^{2+}. The calculated Mg^{2+} concentration of ca. 33 mmol/kg is surprisingly similar to the estimated concentration in Jurassic seawater in figure 1. A simple doubling of the rate of seawater cycling through MORs can therefore account for the difference between the Mg^{2+} concentration in Eocene and Jurassic seawater.

This similarity suggests that the output of Mg to dolomite was comparable at 35 Ma and 150 Ma. An increase in the rate of dolomite formation due to flooding of the continents was therefore either minor or, if it was major, the increase in dolomite formation in the warm, shallow continental seas was balanced by a decrease in the rate of dolomite formation in areas where dolomite formation was intense at 35 Ma. The field evidence regarding the quantity of dolomite deposited in continental seas is still equivocal (see fig. 7). Given and Wilkinson (1987) reported that dolomites accounted for 50 and 70 percent of the Mesozoic carbonates which they studied. On the other hand Vinogradov and Ronov (1956), Schmoker and others (1985), and Daly (1909) reported generally less than 20 percent dolomite in the Mesozoic carbonates which they analyzed. If this analysis is correct, the difference between the composition of Mesozoic and Eocene seawater was largely due to a change in the rate of seafloor spreading and the cycling of seawater through MORs; the difference between Eocene and present day seawater was largely due to a decrease in the rate of dolomite formation.

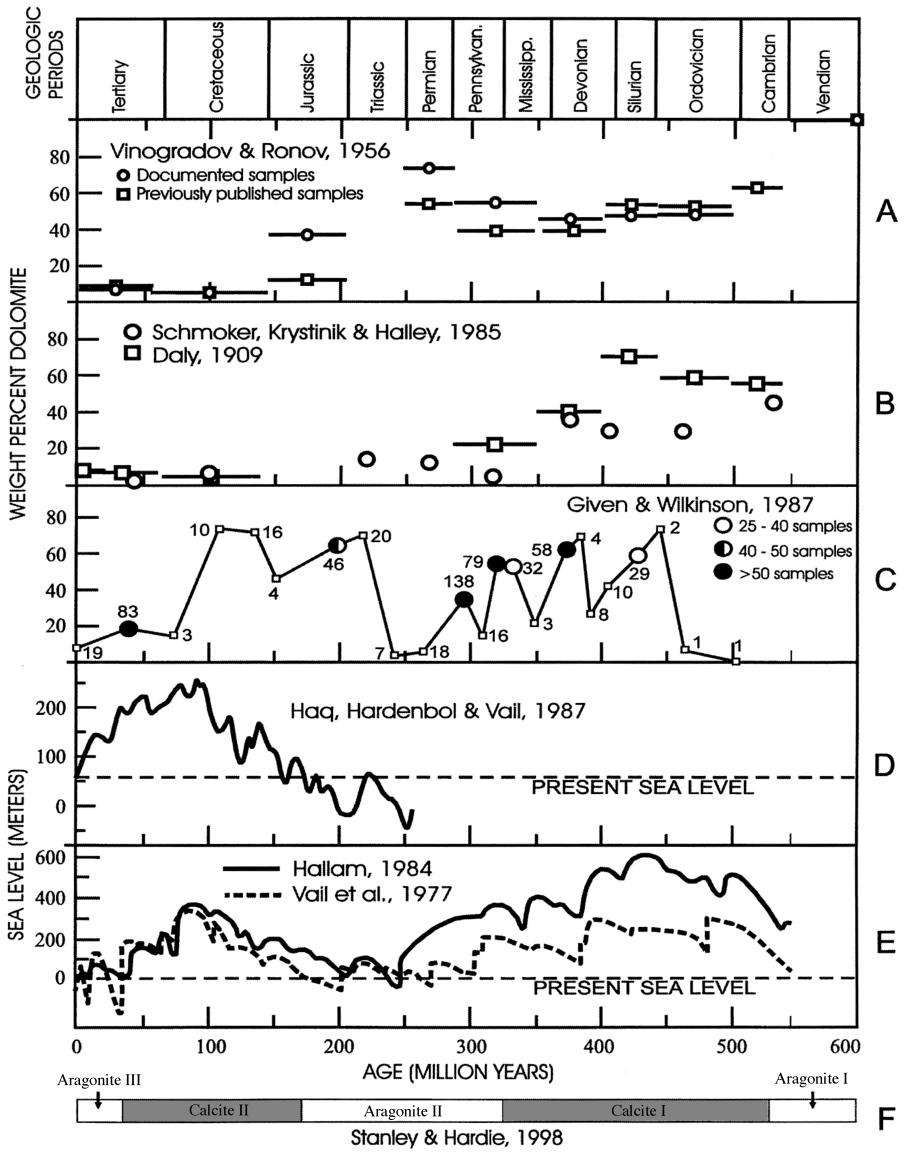

Fig. 7. (A.) The percentage of dolomite in Phanerozoic carbonate sediments of the Russian Platform (Vinogradov and Ronov, 1956), based on 8351 previously published analyses and 8847 specimens in their analyses of documented samples. (B.) The percentage of dolomite in Phanerozoic carbonate sediments of the North American Platform in the compilation of 900 analyses by Daly (1909) and the compilation of Schmoker and others (1985) based on 1290 limestone and dolomite formations. (C.) Percentage of dolomite in Phanerozoic carbonate sediments (Given and Wilkinson, 1987). The numbers indicate the number of analyses for each data point. (D.) Mean sea level during the Mesozoic and Cenozoic (Haq and others, 1987). (E.) Mean sea level during the Phanerozoic (Vail and others, 1977; Hallam, 1984). (F.) Secular variation in the mineralogy of Phanerozoic nonskeletal marine carbonates (Stanley and Hardie, 1998).

THE PALEOZOIC

The composition of seawater during the Permian was similar to that of today's seawater (see fig. 1). The stand of sea level was low, roughly comparable to that of the present day. This suggests that the rate of seafloor spreading was similar to the current

rate. A part of the difference between the composition of Jurassic and Permian seawater is therefore probably due to the lower seafloor spreading rate during the Permian. By analogy to the proposed explanation of the difference between the composition of Eocene and Jurassic seawater, the change in seafloor spreading rate between the Permian and the Jurassic probably accounts for only a part of the difference between the composition of Jurassic and Permian seawater. The remainder is probably due to a change in the rate of dolomite formation. At the low stand of sea level during the Permian the rate of $CaCO_3$ deposition in inland seas was probably minor. Planktonic foraminifera and coccoliths had not yet appeared. The major biological factors that drive the deposition of $CaCO_3$ in the deeper parts of the oceans today were therefore absent. Most of the marine deposition of $CaCO_3$ must therefore have occurred in shallow water on the shelves. It is fair to ask why the composition of Permian seawater differed from that during the Eocene.

Grotzinger and Knoll (1995) have pointed out that late Permian reef complexes contain anomalously large volumes of aragonite and calcite marine cements and seafloor crusts, as well as abundant microbial precipitates. Their textures and genesis are best understood by comparison with the older rock record, particularly that of the early Precambrian. The anomalous late Permian seafloor precipitates are probably the product of reduced shelf space for carbonate precipitation and a relatively high flux of Ca^{2+} to the oceans during high rates of continental erosion occasioned by the low stand of sea level (see for instance Walker, Wilkinson, and Ivany, 2002). The smaller shelf space during the Permian reduced the area available for shallow water $CaCO_3$ deposition and reduced the amount of dolomite deposition in shallow water settings; but this observation leaves unanswered the question why the total amount of dolomite deposition in the late Permian appears to have been no greater than today. Apparently, a large fraction of the carbonates that were deposited rapidly in shallow water settings was transported into deep, cold water where dolomitization was minor (see for instance chapter 5 in Cook and others, 1983). Newell and others (1972) have pointed out that the time equivalent carbonates of many of the near-shore dolomitic beds of the Permian Reef complex of the Guadalupe Mountain Region of Texas and New Mexico are limestones in the deeper parts of the basin. Similar observations have been made by McIlreath (1977) for the Middle Cambrian boundary limestone adjacent to the Cathedral escarpment in the Main Ranges of the Southern Canadian Rocky Mountains, and by Enos (1977) for the Tamabra limestone of the Poza Ricca trend in Mexico. The process seems to be quite general. Its effect on the overall limestone/dolomite ratio of carbonates was probably particularly pronounced during the late Permian, a time when the stand of sea level was very low and the area of continental shelves available for shallow water carbonate deposition was unusually small. This explanation for the similarity of present day and late Permian seawater is reasonable, but there are as yet too few quantitative data to make it compelling.

The composition of seawater during the earlier part of the Paleozoic follows the changes in sea level much as in the Mesozoic. The explanation that was advanced for this correlation in the Mesozoic also fits the pattern in the Paleozoic. However, some differences are demanded by the absence of $CaCO_3$ secreting plankton. There was no deep sea $CaCO_3$ deposition due to the accumulation of their tests. $CaCO_3$ deposition in shallow continental seas probably replaced the earlier deep water accumulations. These seem to be more dolomitic than their Mesozoic equivalents (see fig. 7). If much of this dolomite is syndepositional or penecontemporaneous, its formation contributed to the low Mg^{2+} and SO_4^{2-} concentration in seawater during mid-Paleozoic time.

THE PRECAMBRIAN

The only Precambrian halite-containing marine evaporite studied to date is the 550 Ma Ara formation in Oman. The composition of fluid inclusions in halite from this

formation indicates that the composition of seawater at that time was similar to that of the late Permian (see fig. 1), as expected for seawater during a time of low sea level stand. The evidence needed to define the major ion composition of seawater before 550 Ma is still very scant (see Holland, 2003), although it is likely that the SO_4^{2-} concentration of seawater was much lower before the Neoproterozoic (Canfield and Raiswell, 1999). It remains to be seen whether the effects of changes in sea level on the composition of seawater during the Precambrian were similar to those during the Phanerozoic.

summary and conclusions

This paper proposes that the changes in the composition of seawater during the last 550 Ma are due in large part to changes in the degree of dolomitization of marine calcite and aragonite, to related changes in the precipitation of gypsum and anhydrite, to gains and losses due to cation exchange on clays, and to reverse weathering reactions. During the Cenozoic these changes were driven largely by a shift of $CaCO_3$ deposition from shallow to deeper water. During the Mesozoic and Paleozoic the changes were largely driven by variations in sea level.

The effect of changes in the rate of seawater cycling through MORs due to changes in the rate of seafloor spreading during the past 180 Ma seems to have been minor. Even if the higher Cretaceous spreading rates proposed by Kominz (1984), Lithgow-Bertelloni and others (1993), and Gaina and Mueller (2004) are correct, the increase in spreading rates seems to be too small to account for the observed changes in the Mg^{2+}, SO_4^{2-}, and Ca^{2+} concentration of seawater during the Cenozoic and Mesozoic.

The variation in the composition of seawater during the Paleozoic follows a pattern similar to that during the Mesozoic. It was almost certainly determined in large part by the same processes as in more recent times. However, the response of seawater composition to the stand of sea level was apparently modified and modulated by the width of shallow water marine shelves and by the absence of calcareous plankton.

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