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## Carbonate sedimentation through the late Precambrian and Phanerozoic

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with 4 figures

**Abstract:** The global sediment mass-age distribution indicates large variations in the rates of carbonate sedimentation through time. The largest mass of carbonate deposited during the entire history of the earth was produced during the Cambrian, possibly following on an episode of phosphogenesis in the Late Precambrian. A second major episode occurred during the Late Devonian, probably reflecting the invasion of land by plants that altered the rock-weathering and soil-forming regimes. Other lesser pulses of carbonate deposition occurred in the Late Permian, Triassic, and Cretaceous. A shift in the locus of carbonate deposition from shallow waters to the deep sea occurred during the Cretaceous.

**Zusammenfassung:** Die globale Massen-Zeitverteilung von Sedimenten deutet auf große Variationen der Sedimentationsrate von Karbonaten in der geologischen Vergangenheit hin. Dabei wurde die größte Karbonatmenge der Erdgeschichte während des Kambriums produziert, was wahrscheinlich mit einer Episode von erhöhter Phosphogenese im späten Präkambrium zusammenhängt. Zu einer zweiten Phase verstärkter Karbonatproduktion kam es im späten Devon. Diese spiegelt wahrscheinlich die Besiedlung des Landes durch Pflanzen wider, in dessen Folge es zu verstärkter Gesteinsverwitterung und somit auch zu erhöhter Bodenbildung kam. Auch im späten Perm, der Trias und der Kreide kam es zu Phasen erhöhter Karbonatablagerung, die jedoch nicht die Ausmaße der zuvor erwähnten Zeitscheiben erreicht haben. In der Kreide kam es zu einer Verschiebung des karbonatischen Sedimentationsmilieus vom Flachwasser hin zur Tiefsee.

### Introduction

BUDYKO et al. (1985, 1987) presented a global synthesis of the volumes and masses of Phanerozoic sediments and volcanic rocks. They demonstrated that there is a close relation between volcanism and the accumulation of CO<sub>2</sub> in carbonate and other rocks, as shown in Fig. 1. The data on that had been gathered at the Vernadsky Institute in Moscow were reviewed, revised, and presented in a comprehensive work on the evolution of sedimentary rocks by RONOVA (1993). His Table 20 listed areas, volumes, masses of sediments by age for the continental platforms, geosynclines, and orogenic zones along with the proportions of different types of sediment in each of these regions, but the new compilations do not include the Antarctic or Quaternary. The masses of Quaternary sediments have

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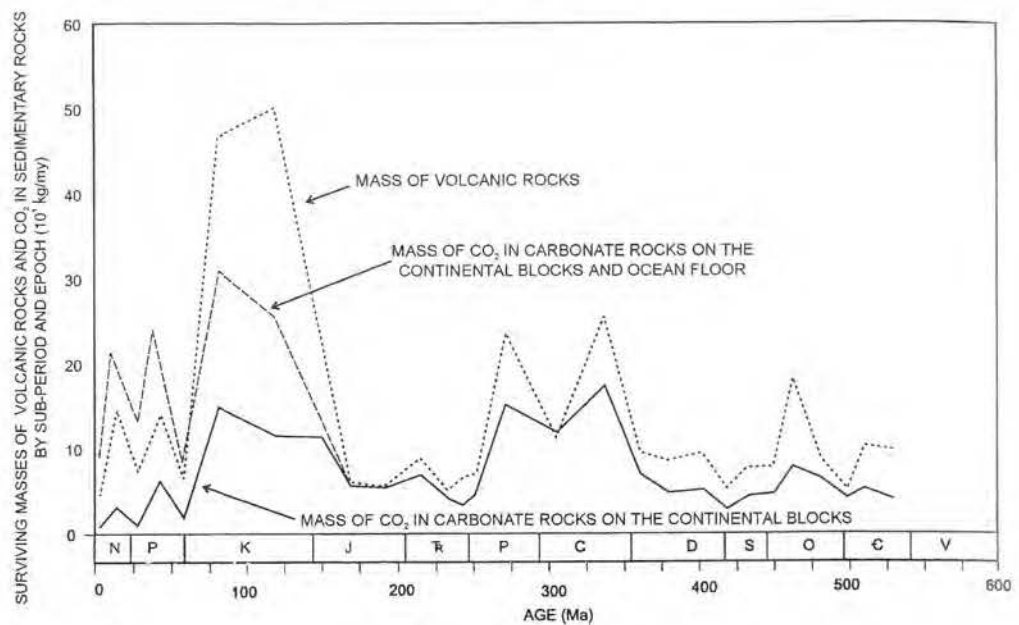


Fig. 1. The correlation between masses of volcanic rocks (dotted line) and  $\text{CO}_2$  in sedimentary rocks (dashed and solid lines) after data in BUDYKO et al. (1987).

been estimated by HAY (1994). Exclusion of the Antarctic means that estimates of the volumes and masses of sediment on the continent are about 9.5% less than they should be. The RONOV (1993) data sets have been used for the analyses of the sedimentary system presented here because they are internally consistent, thorough, and (except for Antarctica) global compilations. To account for the missing data from Antarctica, which is 10.5% of the global continental area, I assumed that the sediments on it have the average continental distribution, and multiplied the masses of continental sediments of each age by 1.105 to obtain new global totals. The data, originally gathered for geologic subperiods and epochs of unequal length, were normalized to 10 million year intervals to simplify the reconstruction of changing rates.

### Reconstructing ancient fluxes

The reconstruction of the masses of sediment that existed in the past and of ancient sediment fluxes rests on the assumption that their mass-age distribution reflects an exponential decay. VEIZER & JANSEN (1979, 1985) showed that the exponential decay with age relationship holds for: 1) the age/area distribution of continental basement; 2) the thicknesses of both sedimentary and volcanogenic units; 3) the thickness, area and volume of sedimentary rocks; and 4) the cumulative reserves of most mineral commodities.

The mass-age distribution of sediment existing today is not smooth, but shows sharp fluctuations (Fig. 2), which must reflect changes in the erosion/deposition rates through time. To reconstruct the changes in rates, WOLD & HAY (1990) proposed starting with an exponential decay having the form

$$y = A e^{-bt} \quad (1)$$

fitted to the distribution. This decay curve represents the long term average sedimentary cycle of erosion of older sediment to form younger sediment. Here  $y$  is the remnant of the original sediment deposited at time  $t$ , after  $t$  my of cycling at a constant rate of erosion  $b$  (decay constant, or "average recycling proportionality parameter" of VEIZER & JANSEN 1985), and a constant depositional rate,  $A$  (the average rate at which sediment was deposited). The RONOV (1993) data on sediment masses and the exponential decay curve fit to them ( $A = 5.985 \times 10^{18}$  kg/my;  $b = 0.00280$ /my) are shown in Fig. 2. The decay constant ( $b$ , 0.0028) is intermediate between that estimated for platform deposits by WILKINSON & WALKER (1989, 0.0025) and for slope and rise deposits by VEIZER & JANSEN (1985, 0.0030). The anomalously large masses of young (< 140 Ma) sediment are largely an expression of the sediment masses on the present ocean floor. Since the Archaean ancient mass-age distributions would always have had the same general form as that shown in Fig. 2, with anomalously large amounts of "young" sediment always present on the moving, ephemeral ocean floor.

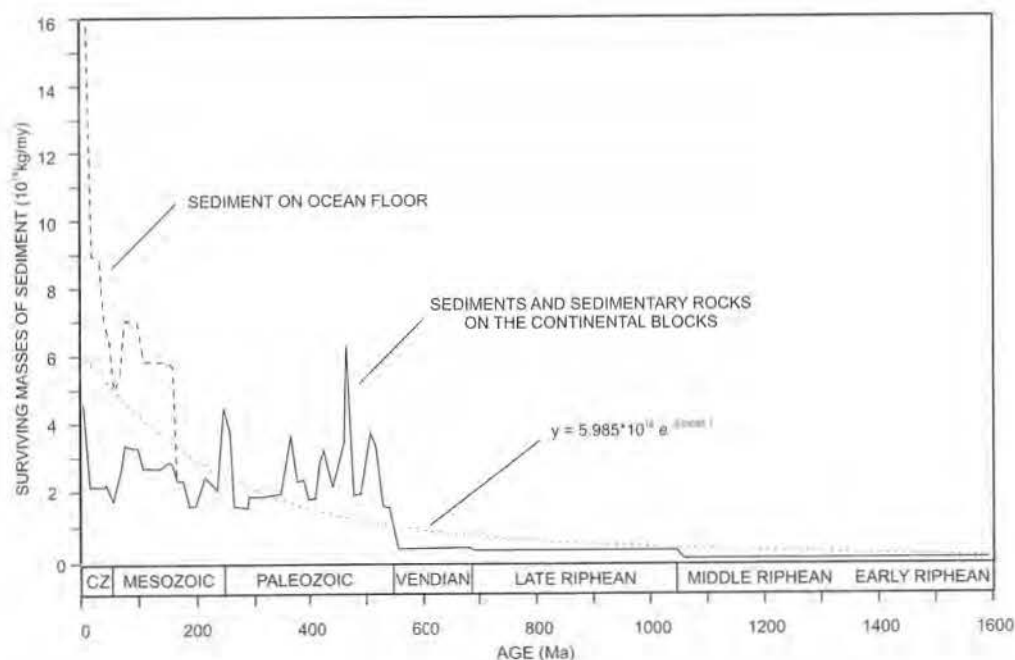


Fig. 2. Mass-age distribution of sediments, sedimentary rocks, and metasediments on the continental blocks and the additional sediment that lies on the ocean floor. The exponential regression fit to the total sediment mass is shown as a dotted curve.

WOLD & HAY (1990) proposed that the temporal variations in the rates of erosion and deposition could be estimated from the proportional deviations of the surviving sedimentary mass from the decay curve. They believed that the original flux at any moment in time could be reconstructed by multiplying the long term average rate of sediment deposition,  $A$ , by the proportional deviation for that time.

WOLD & HAY (1993) noted that the mass represented by the area under the curve is not exactly equal to the mass of sediment observed, and successive reconstructions based on this method yield a (slightly) varying total mass of sediment. They proposed that variations from the average rate of erosion and deposition require linked variations of both the rate of deposition  $A$ , and the decay constant  $b$ , with time. If the total sedimentary mass (TSM) is held constant, these fluctuations of rate can be incorporated into the reconstruction. Over the length of the Phanerozoic, Vendian, and Riphean (1600 my)  $A$  and  $b$  are related to TSM by the definite integral

$$\text{TSM} = \int_0^{1600} A e^{bt} dt \quad (2)$$

where time ( $t$ ) is given in millions of years. The solution to eq (3) is

$$\text{TSM} = \frac{A}{b} (e^{b \cdot 1600} - 1) \quad (3)$$

$A$  and  $b$  are dependent on a constant total global sediment mass (TSM) and on each other, so that

$$A = \frac{b \text{ TSM}}{e^{b \cdot 1600} - 1} \quad (4)$$

Every change in the flux in the past implies a change in the erosion rate at which older materials were attacked. When the deposition rate per unit time increases, the erosion rate increases, but not only is all preexisting sediment more rapidly destroyed, the younger sediment is destroyed more rapidly than the older sediment. We used this technique to produce two models of the fluxes of sediment with time, shown in Fig. 3, assuming the total sedimentary mass to be  $2638.8 \times 10^{18}$  kg (the total of existing Phanerozoic and Proterozoic sediment based on RONO, 1993). The solid line in Fig. 3 is based on the assumption that the total sedimentary mass has remained constant since 1600 Ma. The dotted line is based on the assumption of linear growth of the total sedimentary mass since the time of formation of the oldest preserved sediments, 3800 Ma. These two assumptions are extremes, and the real answer probably lies between the two curves. However, it is apparent that making either of these assumptions the Phanerozoic sedimentary mass is almost constant. The apparent "exponential growth" of sediment fluxes with age in the Vendian and Riphean are an artifact of the method. There is no information on variation of rate during these long periods of time; the average fluxes during these times would be the mean of the lowest and highest reconstructed values, shown in Fig. 3 as dashed horizontal lines.

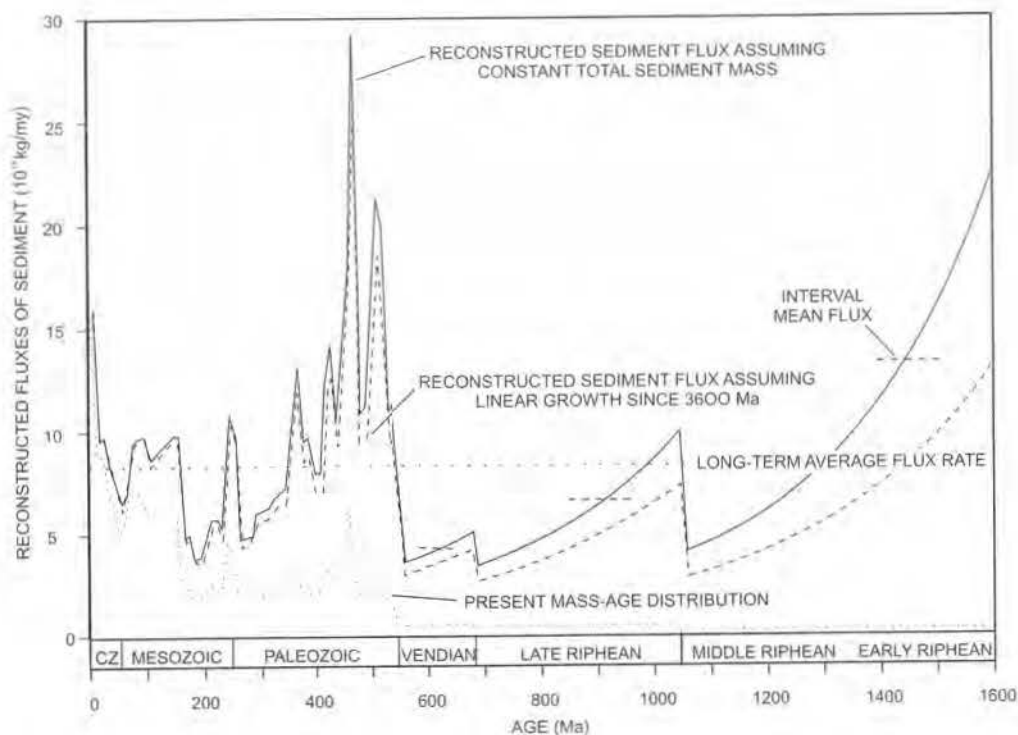


Fig. 3. Reconstructed fluxes of sediment during the Late Proterozoic and Phanerozoic. The solid line is the reconstruction based on the assumption that the total sedimentary mass has remained a constant  $2640 \times 10^{18}$  kg. The dashed line is the reconstruction based on the assumption that the total sedimentary mass has grown linearly since 3600 Ma. The thin dotted curve represents the present mass-age distribution of sediment. The straight dotted line is the average flux rate of sediment over the past 1600 Ma assuming a constant sedimentary mass.

HAY et al. (1988) estimated the long-term (last 180 my) global rate of sediment subduction to be of the order of  $1 \times 10^{18}$  kg/my. If this rate has remained constant an equivalent of the entire existing sedimentary mass, about  $2640 \times 10^{18}$  kg, has been subducted since the Archaean. This also implies that if the total sedimentary mass is essentially constant during the Phanerozoic, the long-term weathering of silicate igneous rocks to form sediment proceeds at rate of  $1 \times 10^{18}$  kg/my, or about 1/9 the long-term average sediment flux rate of  $8.6 \times 10^{18}$  kg/my. VON HUENE & SCHOLL (1991), on the basis of estimates of material presently entering subduction zones, estimated the global rate of subduction of sediment over the past 30 my to be  $0.7 \text{ km}^3$  (solid) per year. This is about  $1.9 \times 10^{18}$  kg/my, almost 2 times higher than the long term average proposed by HAY et al (1988). However, Late Cenozoic erosion-deposition rates are generally about twice as high as those of the Early Cenozoic and Mesozoic (HAY 1994).

GARRELS & MACKENZIE (1971) had suggested that different lithologies might have different erosion rates and hence cycling rates might be lithology-dependent.

WOLD & HAY (1993) demonstrated that this cannot be true on regional or global scales. Although some sedimentary rocks are more resistant to erosion than others, superposition requires that erosion must attack sedimentary layers sequentially. This means that it is possible to reconstruct not only the mass-age distributions of sedimentary materials for past ages, but also the masses of rocks of different lithology that have existed in the past. This technique has been applied here to carbonate occurring as sediments and rocks (limestone, dolostone, chalk, etc.).

VEIZER & JANSEN (1985) noted that rocks recycle at different rates in different kinds of tectonic province, such as cratons, orogenic belts, etc. Differential recycling has been neglected in the reconstructions given here.

The existing masses of carbonate sediment and rock on the continental blocks and ocean floor are shown in Fig. 4. This is based on the proportions of carbonate as part of the total sediment mass determined by RONOV (1993). The reconstructed flux of carbonate onto the continental blocks and the reconstructed total carbonate fluxes are also shown in Fig. 4.

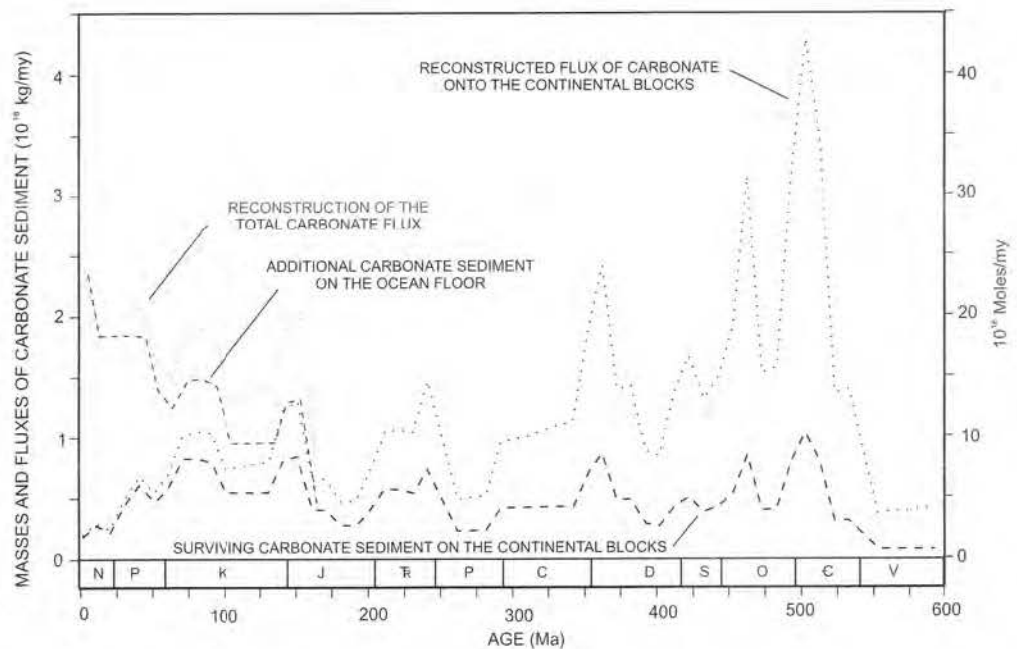


Fig. 4. Reconstructed global fluxes of carbonate sediment and rock (limestone, dolostone, chalk, etc.) during the Phanerozoic. The solid line is the present mass-age distribution of carbonate rocks on the continental blocks. The dashed line is the carbonate sediment on the ocean floor. The heavy dotted line is the reconstructed flux of carbonate on the continental blocks, the light dotted line is the reconstructed global flux taking into account the carbonate on the ocean floor.

## Discussion

WOLD & HAY (1990) concluded that the fluctuations of erosion-deposition rates reflected changes in elevation as a result of orogenic processes, and to a lesser extent climate change. They based this conclusion on the fact that most of the sediments are detrital, and that the major factor affecting rates of mechanical erosion in a drainage basin is elevation. Since then it has become apparent that at least some of the fluctuations in rate reflect stages in the evolution of life.

From the present mass-age distribution of sedimentary materials, shown in Fig. 2, it might be concluded that rates of erosion and deposition in the Phanerozoic were much greater than those during the Proterozoic. Preserved masses of Precambrian sediment are much lower than expected from the decay curve. However, when recycling is taken into account and original fluxes compared, it appears that rates of erosion and deposition during the Middle and Early Riphean were similar to those of the Early Paleozoic and Cenozoic, whereas those of the Late Riphean and Vendian were similar to those of the Late Paleozoic and Early Mesozoic.

Both the mass age distribution of existing sediment (Fig. 2) and the reconstruction of sediment fluxes (Fig. 3) indicate that something very significant happened at the beginning of the Cambrian. The paucity of Vendian sediments contrasts with the abundance of Cambrian sediment. The Cambrian sediments, deposited at rates up to  $14 \times 10^{18}$  kg/my must be largely eroded-redeposited Precambrian sedimentary material. The Cambrian was a time of transgression, after the very low sea-levels of the terminal Precambrian (MCMENAMIN & MCMENAMIN 1990), but the reason why Cambrian rocks are so much more abundant than those of the Late Precambrian remains unclear.

Peaks of sediment flux occur in the Late Cambrian, the Late Ordovician, Late Silurian, Late Devonian, Late Permian, Late Jurassic, Late Cretaceous, and Late Cenozoic. The increase in erosion and deposition in the Late Ordovician may be associated with the initial invasion of the land by larger plants, although they did not become widespread until the Devonian. They are thought to have greatly modified the weathering system (BERNER 1997). With rootlets secreting humic acids and litter increasing soil  $\text{CO}_2$  and allowing retention of water, they would have accelerated erosion. However, as the plant cover spread over the land, and root penetration deepened, it had the effect of retarding erosion, with leaves protecting the soil surface from the impact of raindrops, and the root systems acting to bind soil in place. The generally low erosion-deposition rates of the Late Paleozoic and Early Mesozoic probably reflect the spread of forests and herbaceous shrubs. The Late Permian-Middle Triassic peak can be associated with the fusion of Gondwana and Laurussia which resulted in highly arid conditions and a great reduction in plant cover. The Jurassic and Cretaceous peaks appear to be associated with major steps in the breakup of Pangaea and probably reflect regional uplift associated with rifting (HAY 1981, HAY et al. 1987). The Late Cenozoic peak remains controversial, either reflecting uplift that was the cause of climatic changes or reflecting the climate change itself (MOLNAR & ENGLAND 1990). Alternatively, the

Late Cenozoic peak may reflect the increasing global aridity as a result of the spread of water-conserving C4 plants (HAY et al. 1997).

The mass-age distribution of carbonate using data of RONO (1993) is shown in Fig. 4. The carbonate sediment existing on the continental blocks does not show an appreciable decline with age. It is necessary to take the carbonate sediment on the ocean floor into account before the exponential decay with age becomes apparent. The carbonate on the ocean floor reflects the mass on the continental blocks from 180 Ma to 100 Ma. This may suggest that the Jurassic and Early Cretaceous carbonates in the deep sea have a mostly littoral origin, similar to the aragonite accumulations on the deep sea floor surrounding modern carbonate banks. The accumulation of carbonate on the deep sea floor increases greatly after 100 Ma, while at the same time the deposition of carbonate on the continental blocks rapidly declines.

The reconstructed fluxes of carbonate during the Phanerozoic, shown in Fig. 4, indicate that the carbonate fluxes onto the continental blocks reached a maximum in the Cambrian and, although fluctuating greatly, have decreased since. The proportions of carbonate rock to total sediment average about 18% during the Phanerozoic, 13% during the Vendian, and only 8% during the Riphean.

The most striking feature of the reconstructed fluxes of carbonate is the jump from relatively low levels during the Precambrian to very high levels during the Cambrian. Cambrian carbonates are most abundant in Eurasia and Australia, but large amounts of carbonate also occur interbedded with clastics in North America and Africa. This is not a direct result of the appearance of shelly faunas, because shells make up only a small part of the limestones and dolostones that formed then. Something very dramatic happened at the beginning of the Cambrian, and it appears that the ocean geochemical system went through a transition to a new state. KEMPE & DEGENS (1985) suggested that the chemistry of the early Precambrian ocean was dominated by sodium carbonate. Because of the great solubility of  $\text{Na}_2\text{CO}_3$  in water, up to half of the present global inventory of carbonate and organic carbon could have been held in solution in such an ocean. With time the steady addition of outgassed hydrogen chloride converted the soda ocean into a halite ocean and eventually forced the precipitation of limestone and dolostone. This hypothesis was further developed by KEMPE et al. (1987) and treated at greater length by DEGENS (1989); they believe that the conversion from soda ocean to halite ocean occurred gradually during the Proterozoic, but at the end of the Precambrian a major change in the system occurred. As the level of  $\text{Cl}^-$  rose, the amount of the  $\text{HCO}_3^-$  that could be balanced by  $\text{Na}^+$  decreased, but deposition of  $\text{CaCO}_3$  was probably inhibited by the presence of large amounts of  $\text{PO}_4^{3-}$ . At the end of the Proterozoic there was a global phosphogenic event (COOK & SHERGOLD 1984), possibly as a result of overturning following a long period of ocean anoxia. At the same time, the  $\text{Ca}^{2+}$  concentration in the ocean had steadily increased from Archaean levels of  $10^{-7}$  moles/ltr, through the  $10^{-4}$  threshold required for cell aggregation (KAZMIERCZAK & DEGENS 1986; KEMPE & KAZMIERCZAK 1994) to a molarity of about  $10^{-2}$  at the end of the Precambrian. At this concentration it became a threat to the operations of living cells, and organisms began to expel it as calci-



um phosphate and then as calcium carbonate skeletal materials. The great pulse of carbonate deposition in the Cambrian must reflect a major step in evolution of ocean chemistry mediated by living organisms. The carbonate could have come from both the dissolution of pre-existing carbonates and possibly a dissolved reservoir of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  larger than that in the ocean today.

The relation between volcanism and carbonate rock accumulation, shown in Fig. 1, does not directly reflect weathering of silicate rocks. The masses of carbonate rock are of the same order of magnitude as the masses of volcanic rocks, whereas the  $\text{CO}_2$  content of volcanic emissions is only a fraction of a percent of the mass of volcanic rock. The large masses of carbonate rock reflect the "catalytic" activity of  $\text{CO}_2$  in the dissolution and transport of pre-existing carbonate rock. Water and  $\text{CO}_2$  form carbonic acid, which dissolves carbonate rock; the ions are then transported as  $\text{Ca}^{2+}$  (and  $\text{Mg}^{2+}$ ) balanced by  $2 \text{HCO}_3^-$ . In the sea, the ions are recombined as  $\text{CaCO}_3$  water and  $\text{CO}_2$  returns to the atmosphere. Some of the  $\text{CO}_2$  is consumed in the weathering of silicate rocks to form new carbonates.

The second major feature of the reconstructed fluxes of carbonate is the general decline in the masses of carbonate rocks deposited on the continental blocks during the Phanerozoic. During the Late Mesozoic and Cenozoic there has been a major shift in the site of fixation of carbonate from shallow water regions to the open ocean (SOUTHAM & HAY 1981, HAY 1985). OPDYKE & WILKINSON (1988) interpreted the shift as a response to loss of accommodation space in shallow water regions as a result of the changing paleogeography associated with general decline of sea level since the mid-Cretaceous. WILKINSON & WALKER (1989) discussed this transfer as being a response to either the "biogenic pull" of the developing open ocean calcareous plankton, or the "physicochemical push" of loss of accommodation space. SOUTHAM & HAY (1981) had suggested that the development of the calcareous plankton might be a result of the lowering of the global ocean salinity as the deposition of the North Atlantic, Gulf of Mexico, and South Atlantic evaporites occurred. The reconstructions of flux presented here suggest that a moderate loss of carbonate to the deep sea was going on throughout most of the Phanerozoic, but accelerated sharply during the Cretaceous and Cenozoic. Carbonate rocks are rare in mountain chains associated with subduction zones, suggesting that carbonate deposited on the deep sea floor tends to be subducted.

### Summary and Conclusions

The geologic record of carbonate rocks and sediments suggests that widespread deposition of carbonates coincided with the development and diversification of animals at the beginning of the Cambrian, but that since then there has been a gradual loss of carbonate to the deep sea. During most of the Phanerozoic the loss to the deep sea was probably as fine grained carbonate shed from platforms and shelves, but during the Late Mesozoic and Cenozoic the site of fixation of carbonate has shifted from shallow water regions to the open ocean. The calcareous plankton responsible for this shift may have diversified and become widespread in re-

sponse to a lowering of the salinity as a result of the deposition of evaporites in the opening Atlantic and Gulf of Mexico.

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