PHANEROZOIC CYCLING OF SEDIMENTARY CARBONATE

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ABSTRACT. Mass-age relationships among Phanerozoic sedimentary carbonates define different patterns of exponential decay for continental and oceanic reservoirs. Global carbonates comprise about $3500 \times 10^{20}$ g of Ca with a cycling rate of $8.6 \times 10^{20}$ g/my and a decay constant of 0.0025 /my. Epoch-interval deviations indicate relatively constant rates of limestone-dolostone deposition and destruction. Best-fit curves through data on oceanic carbonate oozes require a reservoir Ca mass of about $285 \times 10^{20}$ g with a cycling rate of $5.4 \times 10^{20}$ g/my and a decay constant of 0.020 /my. Deep-water oozes comprise 7 percent of all sedimentary carbonate but presently account for over 60 percent of the total mass flux. Data on continental carbonates only define a negative exponential slope ($k = 0.0025$/my) for units older than Cretaceous. Shallow water limestone formation has been decreasing at a rate of $0.04 \times 10^{20}$ g/my for the past 100 my.

Two models are in accord with this Cenozoic decline in cratonic carbonate deposition. A biologically mediated “calcite pull” model argues that with diversification of planktic marine protists since the Jurassic, oceanic calcifiers progressively replaced shallow shelly faunas as the principal sink for finite carbonate resources. Projection of Cenozoic data indicates cessation of shallow-water carbonate deposition in about 100 my. A physicochemically mediated “calcite push” model argues that cratonic-oceanic carbonate partitioning is determined by global sealevel, with accumulation in shoal-water systems proportional to continental freeboard and area of warm carbonate-saturated seas. Constraints on completeness of the deep sea stratigraphic record, the importance of pre-Jurassic carbonate deposition in deep oceanic basins, and relationships between reservoir cycling rate and tectonic setting are but three long-term manifestations of partitioning among Phanerozoic reservoirs and the ongoing transfer of carbonate from shallow continental to deep oceanic settings.

INTRODUCTION

Among truisms in the Earth sciences, one of the most basic is that commonly presented as the Geologic Cycle, a general model in which rock materials move continuously between igneous, metamorphic, and sedimentary rock reservoirs. Despite the fact that only a few geological processes (melting, cooling, metamorphism, erosion, and deposition) are important in the transfer of rock materials between the principal rock masses, general quantification of mass-age relationships among these reservoirs has received little attention.

Here, we quantify cycling in one subset of the sedimentary rock reservoir, that comprising limestone and dolostone, through examination of mass-age data on Phanerozoic carbonate rocks. These data record fluxes and residence times of the principal divalent cations within
these lithologies. Carbonate units are an attractive rock type in this regard, because limestones and dolostones are sensitive to variations in global eustasy as determined by thermal histories of the Earth's ocean basins (Heller and Angevine, 1985; Pitman, 1978; Worsley and others, 1985). Carbonate rock mass and composition may also reflect a broad range of other physical, chemical, and biological processes manifested as secular variation in atmospheric-hydrospheric chemistries (Sandberg, 1983) and patterns of biological evolution and diversification (Lipps, 1970). In addition, past rates of formation and destruction of various carbonate rock types may record the importance of crustal processes such as calcium-magnesium exchange at oceanic spreading centers (for example, Holland, 1978, 1984).

Specifically, various authors have now argued that secular variation in the extent of continental flooding has had a profound influence on Phanerozoic values of atmospheric pCO₂ (Berner, Lasaga, and Garrels, 1983; Lasaga, Berner, and Garrels, 1985), and that such variation may be recorded by the dominance of different abiotic calcium carbonate polymorphs in shallow marine carbonate sequences (Sandberg, 1985). Others (for example, Southam and Hay, 1977) have suggested that variation in the Phanerozoic diversity of different calcareous marine organisms may have a profound influence on the relative size of cratonic versus pelagic carbonate reservoirs which constrain scenarios on secular variation of CO₂ and O₂ in the atmosphere (Budyko and Ronov, 1979; Ronov, 1976). Still others (for example, Berner and Raiswell, 1983; Garrels and Lerman, 1981; Mackenzie and Pigott, 1981; Shackleton, 1987) have suggested that variation in masses of oxidized versus reduced carbon reservoirs may be recorded as secular variation in the sulfur and carbon isotopic composition of sedimentary rocks. In short, knowledge of the Phanerozoic history of component cycling through the major carbonate rock reservoirs is central to any evaluation of crustal sedimentary processes, whether biological, chemical, or physical in nature.

Assuming that long-term changes in sealevel may have resulted in variation in the dominance of different abiotic marine carbonate polymorphs, change in the importance of various pelagic and benthic marine communities, and secular variation in other sedimentary phenomena, we might first ask: Has most carbonate sediment formed during periods of continental flooding or continental emergence? As an initial response, many would favor the first choice: that greater areal extent of shallow seas gives rise to greater deposition rates and volumes of sedimentary carbonate. However, extant limestone volumes depend both on sequence age and tectonic setting.

GLOBAL CARBONATE CYCLES

As a first approximation, the limestone-dolostone system can be considered in a context of extant masses and cycling rates of cratonic, continental margin, and deeper pelagic carbonate sediment (for exam-
ple, Berner, Lasaga, and Garrels, 1983; Garrels and Mackenzie, 1971; Hay, 1985; Veizer and Jansen, 1985). In the following we first comment on the sources of mass-age data for various carbonate reservoirs, their mathematical treatment in determining reservoir masses and cycling rates, and then discuss what these data suggest about partitioning between the various global reservoirs. The important carbonate reservoirs and their ages have been discussed by several individuals (for example, Garrels and Mackenzie, 1971; Gregor, 1985; Ronov, 1964, 1980). However, mass-age relationships within and fluxes through continental and oceanic sedimentary systems have not been quantified.


Estimates of carbonate volume in craton margins are available from several sources (Gregor, 1985; Milliman, 1974; Southam and Hay, 1977). However, among the major global reservoirs, estimates of slope-rise carbonate volume are the least constrained. Data based on numerous seismic sections examined by Gregor (1985) are the most comprehensive but only include mass-age values for all combined lithofacies. Therefore, we have utilized the estimates summarized in Hay (1985) as the (currently) best estimate of mass-age trends within the craton-margin carbonate reservoir.

Data on volumes of pelagic carbonate are available from two sources. The most recent tabulation is that by Hay (1985), but these are based on a single value estimate of average pelagic sediment thickness and carbonate content from Southam and Hay (1981) and on Mesozoic-Cenozoic areas of seafloor from Sclater, Jupart, and Galson (1980). Compared to present calcium fluxes into global oceans from rivers and oceanic ridges (Livingstone, 1963; Meybeck, 1979) this estimate of carbonate mass appears to be too large.

Davies and Worsley (1981) compiled data on calcareous ooze for DSDP sites 1 to 335 (excluding the Mediterranean Sea) and tabulated vertical rates of calcite accumulation for the past 60 my employing a standard time interval of 3 my (based on biostratigraphic data). These values were then adjusted to account for decreasing accumulation rate with depth below the lysocline and extrapolated to global carbonate masses based on present hypsometries of major ocean basins (Menard
and Smith, 1966) and estimates of rates of seafloor spreading in the
different major ocean basins over the past 150 my (for example, Worsley
and Davies, 1979a).

Before mass-age data for cratonic, cratonic-margin, and pelagic
carbonate reservoirs were evaluated, several preliminary adjustments
were applied to values from these source references. First, data on
volumes of platform and geosynclinal cratonic carbonate from Ronov
and co-workers were converted to carbonate mass values, assuming a
porosity of 10 percent.

Second, data on pelagic carbonates summarized by Davies and
Worsley (1981) were not taken at face value. These authors were
apparently influenced by previous studies of oceanic sedimentation (for
example, Davies and others, 1975; Worsley and Davies, 1979b) that
show generally decreasing sediment accumulation rate with age. Fur-
thermore, Moore and Heath (1977) and Moore and Romine (1981)
suggested that this decrease is a consequence of post-depositional
destruction of sediment on the seafloor and presented quantitative
age-based survival parameters for Cenozoic pelagic sections. Following
these studies, Davies and Worsley (1981) “corrected” their initial
calculated values of global carbonate mass by multiplication with the
appropriate Moore and Heath (1977) “correction factor.” It is impor-
tant to note an apparent circularity in reasoning when employing this
approach. Because the goal of the Davies and Worsley (1981) study was
to evaluate Cenozoic rates of oceanic carbonate deposition, to presume
that lower accumulation rate with age reflects post-depositional sea-
floor sediment dissolution, by definition, negates the possibility that
lower accumulation rates in older sections may reflect an increase with
time in the accumulation rate. Here, we are interested in defining extant
carbonate sediment mass as a function of age, and “corrected” global
Cenozoic rates from Davies and Worsley (1981) were therefore “uncor-
rected” by dividing carbonate mass accumulation values with the Moore
and Heath (1977) “correction factor.”

Third, values for craton-margin carbonates from Hay (1985) were
divided between the major continental and oceanic reservoirs. This
partitioning of the marginal-cratonic reservoir between cratonic and
pelagic reservoirs was done primarily because slope-rise carbonate is
generally polygenetic, consisting of material derived from adjacent
shallow platforms (for example, Neumann and Land, 1975) with lesser
admixtures of hemipelagic ooze. In addition, some redundancy in the
definition of “geosynclinal” cratonic as used by Ronov (1980) and
“slope-rise” cratonic as used by Hay (1985) makes distinction between
the two almost meaningless. Therefore, age-interval masses of craton-
margin carbonate from Hay (1985) were divided: 80 percent was added
to cratonic carbonate masses from Ronov and co-workers yielding a
continental reservoir, and 20 percent was added to pelagic carbonate
masses from Davies and Worsley (1981) yielding an oceanic reservoir.
Such division, albeit somewhat arbitrary, has little effect on subsequent
calculations of continental, oceanic, or global reservoir masses and/or cycling rates.

Finally, all carbonate mass-age data were converted to apparent accumulation rates (extant masses per unit time) employing epoch-interval durations from the time scale of Harland and others (1982). Because the reliability of carbonate rock mass-age data can ultimately be evaluated by comparing recent global accumulation rate with present cation fluxes via rivers and oceanic ridges, mass-age values were recalculated as apparent mass accumulation rates of carbonate calcium in units of $10^{20}$ g of calcium per million years (fig. 1).

Conversion of total carbonate mass to carbonate calcium mass, by necessity, introduces a small error in that dominant divalent carbonate cations are both calcium and magnesium. Lacking adequate data on variation in the amount of dolostone in Phanerozoic sequences, it is not possible to correct for this mixture. However, the proportion of global carbonate as dolostone is about 40 percent (Given and Wilkinson, 1987), and most dolomite contains 50 mole percent magnesium (Lumsden and Chimahusky, 1980). In the context of mass-age data tabulated as $10^{20}$ g Ca/my, each 10 percent dolostone in any time-interval-rock-mass corresponds to an overestimation of component cation mass by about 2

Fig. 1. Mass-age data on continental, oceanic, and global carbonate reservoirs expressed as $10^{20}$ g of carbonate calcium per million years. All data were converted to apparent (extant) mass accumulation rates using the time scale of Harland and others (1982). Diamonds are deep oceanic oozes from data in Davies and Worsley (1981) and Hay (1985); rectangles are cratonic values from data in Hay (1985). The global reservoir is represented as open triangles when calculated from the sum of pelagic and cratonic data and as half-solid rectangles when entirely continental. Solid rectangles are cratonic values when the global reservoir consists of both continental and deep oceanic carbonate.
percent. As will be seen, this error is insignificant compared to other limitations inherent in such a data base.

*Mass age models.—* An initial step in evaluating carbonate reservoir mass-flux relationships, similar to that first recognized by Gilluly (1949) and rigorously defined by Garrels and Mackenzie (1971) and Veizer and Jansen (1979), is to determine how closely present distributions of reservoir mass approximate an exponential decay functions. Two assumptions are implicit in such an approach. The first is that past rate of mass change (rate of cycling) of any reservoir unit (defined by present age) is proportional to the mass/volume present. In other words, the rate of destruction by erosion, melting, and/or metamorphism is proportional to the amount of extant rock material, and that ‘preferential’ preservation is an insignificant process at the time scales in question. The second assumption is that rate of change for each mass-age unit is constant (regardless of age) for all portions of any particular rock reservoir. In other words, an appropriate decay constant may be employed to describe rate of cycling, and this value applies equally to any unit mass comprising the rock reservoir in question. Considering the relatively short residence times of carbonate and calcium ions in global oceans (roughly 100,000 and 800,000 yrs, respectively), for a relatively constant erosion rate, the formation and burial of sedimentary carbonate (somewhere) must also continue at a relatively constant rate.

With both assumptions in mind, let \( f(t) \) be the total mass of sedimentary carbonate at time \( t \). For a constant mass model, \( f \) is independent of time: for a linear growth model, \( f(t) = a + bt \). Veizer and Jansen (1979) consider a family of power law models:

\[
f(t) = M(t/t_0)^n
\]

where \( M \) is the carbonate mass today (time \( t_0 \)). However, the derivation that follows does not depend on the form of \( f(t) \).

The assumption that the rate of recycling is proportional to mass and independent of age may be written as \( R(t) = k f(t) \), where \( R \) is the rate at which new rocks are made from recycled old rocks, and \( k \) is the decay constant. The amount of recycled rock, deposited in a period of duration \( T \) at time \( t \), is:

\[
R(t)T = kf(t)T.
\]

To this amount must be added first-cycle new-growth material to derive the total mass of rock deposited during the period \( T \) at time \( t \). The rate of addition of first-cycle material is \( df(t)/dt \), and the amount added during period \( T \) is:

\[
T \times \frac{df(t)}{dt} = f(t + T) - f(t)
\]

provided that the relative change in \( f \) during period \( T \) is small, \( T df/dt \ll f \).
The total mass of rock deposited during period $T$ at time $t$ is:

$$m(T, t) = kf(t)T + f(t + T) - f(t) = f(t + T) - f(t)(1 - kT).$$

During subsequent Earth history, this mass undergoes exponential decay in accordance with the assumption of constant, first-order recycling. At later time $t_o$, the mass remaining of rock originally deposited during period $T$ at time $t$ is:

$$M(T, t, t_o) = m(T, t) \times \exp[-k(t_o - t)]$$

$$= [f(t + T) - f(t)(1 - kT)] \times \exp[-k(t_o - t)].$$

For $t_o$ (the present) $t_o - t$ is the age of the material deposited at time $t$.

An equivalent result was derived by Veizer and Jansen (1979) using a finite difference approach and somewhat different notation. They express $t_o$ as $P_T$ and $t$ as $pT$, where $P$ and $p$ count recycling periods of uniform duration $T$. The mass remaining at time $t_o$ of material deposited at time $t$ is $M(T, t, t_o)$ in the present notation and $A_p(P_T)$ in their notation. The results are identical provided the fraction of rock recycled during each period $T$ is small, $kT \ll 1$.

For each choice of the function $f(t)$, a different decay scheme is obtained, two of which are where $f(t) = M$, defining a constant mass model, and where $f(t) = (M/PT)t$, defining a linear growth model (for example, Garrels and Mackenzie, 1971). In this context, Veizer and Jansen (1979) considered an infinite number of models in which:

$$f(t) = M(t/PT)^n.$$  

Where:

$$n = \text{some growth parameter.}$$

In so doing, they established a continuum of growth possibilities for any reservoir; the two noted above are where $n = 0$, defining a constant mass cycling model, and where $n = 1$, defining a constant accumulation cycling model.

Before attempting evaluation of the constancy of cycling through the global, continental, and oceanic carbonate reservoirs, it is necessary to discuss general limitations of such models and mathematical approaches that may be applied to mass-age data sets. Two alternative schemes may be employed in defining the size and cycling rate of any carbonate reservoir: one that is constrained to yield the best estimate of reservoir mass (a mass-fit approximation), and one constrained to coincide with the best estimate of the present cycling rate (a flux-fit approximation).

Considering global carbonates as a whole, the best mass-fit constant mass-constant burial flux exponential decay function defines a system mass ($M$) comprising $3850 \times 10^{20}$ g Ca, with the decay constant ($k$) of
0.0020 /my, a flux (kM) of $7.7 \times 10^{20}$ g Ca/my, and half life ($T_{50}$) of about 380 my (fig. 2). Although such approximations are commonly taken at face value in describing various rock systems, inherent in such an approach is the premise that the reliability of mass-age estimates is similar, regardless of sequence age. This is probably not the case, as data precision should exhibit a direct relation to the size of the rock mass in question (decreasing in older sequences), and data accuracy should decrease with age and increasing burial depth.

Because mass-age data for younger sequences are more reliable, an alternative curve-fitting approach is to equate the accumulation rate of the youngest datum to carbonate calcium flux and then determine the best fit curve through this constrained Y-intercept. Flux-fit exponential decay of the global carbonate reservoir determined in this manner defines a carbonate system where $M = 3170 \times 10^{20}$ g Ca, $k = 0.0030$ /my, and $kM = 9.5 \times 10^{20}$ g Ca/my, with a $T_{50}$ of about 240 my (fig. 2).

A second uncertainty that arises when relating various cycling models to mass-age data is that similar curves may be defined employing different values of $M$, $k$, and $n$ (fig. 3). Regardless of the choice of either a best-fit mass or best-fit flux model, it is still not possible to derive a unique mathematical description of the system unless additional constraints on the size of the reservoir through time are available. Because it

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**Fig. 2.** Curves through global carbonate data. Both are constant mass-flux models determined by a linear least-squares interpolation through the log of mass values. The "mass fit" curve (solid) is the best statistical approximation of total reservoir mass; the "flux fit" decay curve (dashed) is the best statistical approximation of total reservoir mass constrained to intercept the youngest (Pliocene) apparent accumulation rate. Symbols as in figure 1.
is probable that the global carbonate reservoir has indeed increased over geologic time, two additional endmember models may be defined on the basis of choice of growth parameter (n) and the time period when reservoir growth began (T_i). The mass-fit constant mass-flux curve discussed above (M = 3850 x 10^{20} g Ca, k = 0.0020 /my, kM = 7.7 x 10^{20} g Ca/my) defines one endmember; linear growth (n = 1) beginning at the end of the Archean (T_i = 2500 my) is an approximation of the other (fig. 3). In the latter case, approximately the same decay curve defines a system in which M = 2500 x 10^{20} g Ca, k = 0.003 /my, and kM = 7.7 x 10^{20} g Ca/my (by definition). While larger choices of T_i yield smaller differences (as do smaller values of n), comparison of various models serves to demonstrate that these (or any other) mass-age data can not define uniquely cycling rate but merely serve to constrain values of system size and flux.

Finally, global mass-age data exhibit a significant amount of short-term secular deviation from long-term model trends (figs. 2 and 3). The nature of this variation also merits some comment. Although it is not possible unequivocally to evaluate the nature of differences between mass-age data and various decay curves, three possibilities are plausible. First, calcium supply to global oceans may have varied at short-term time scales, giving rise to differing rates of carbonate accumulation. Such an explanation has been put forward by Wold, Hay, and Wilson (1987),
who suggested that epoch-scale variation in total Phanerozoic sediment accumulation rate records the influence of global tectonism and sealevel change. Because both marine carbonate and terrigenous clastic reservoirs exhibit similar short-term variations, increased tectonic activity and/or weathering may have given rise to epoch-interval variation in rates of carbonate deposition as well. If all short-term difference in extant global carbonate mass reflected epoch-interval variation in calcium flux, values of kM have varied with a standard deviation of about 2.4 x 10^20 g Ca/my (fig. 4A).

Conversely, it is possible that preferential preservation has been important, that rate of destruction is not simply a function of rock mass, and that a single invariant decay constant may not be applied to all portions of a rock reservoir. If all short-term difference in remaining carbonate mass was only related to variation in cycling rate, then values of k have varied with a standard deviation of about 0.004 /my (fig. 4B). Furthermore, uncertainties about accumulation rate (kM) versus destruction rate (k) are not an "either-or" proposition: both could have

![Graph](image)

Fig. 4. Possible reasons for short-term deviation of mass-age data (diamonds) from long-term decay trends. Upper graph shows calculated short-term flux variation (solid line) for the "mass fit" trend in figure 2 (dashed curve) assuming a decay constant of 0.002 /my. Short-term fluxes exhibit a standard deviation of 2.4 mass-flux units about a long-term accumulation rate of 7.7 x 10^20 g Ca/my (horizontal dashed line). Short-term mass-age variation may reflect variable accumulation rate of global carbonates. Lower graph shows calculated short-term decay constant variation (solid line) assuming a constant flux of 7.7 x 10^20 g Ca/my. Short-term decay constants have a standard deviation of 0.004 k-units about a long-term value of 0.002 /my (horizontal dashed line). Short-term mass-age variation may reflect variable preservation of different carbonate units within the global reservoir.
exhibited short-term variation over Phanerozoic time. Moore and Heath (1977) have discussed both possibilities in considerable detail in an evaluation of short-term variation in the completeness of pelagic sedimentary sections. They were able to model deviation from long-term exponential decrease by varying either (or both) parameters.

One other explanation for any lack of agreement between short-term mass-age data and long-term cycling trends is an inherent inaccuracy in mass-age estimates on which decay curves are based. All principal data sets on which continental and oceanic mass-age estimates are based reflect different inherent assumptions about the size of respective reservoir units. Because data on individual reservoirs are largely from single references (Ronov, 1980; Davies and Worsley, 1981; Hay, 1985), the reliability of mass-age estimates cannot be evaluated by comparison of data from different studies. Short-term variation may reflect nonuniform rates of deposition and destruction and/or noise in the data base.

Despite these limitations, regardless of the nature of short-term variation, and acknowledging that long-term change in reservoir mass cannot be uniquely constrained, available mass-age data are sufficient to define approximate long-term masses and cycling rates for the various sedimentary carbonate systems. These make up a global reservoir with a carbonate calcium mass of about \(3500 \times 10^{20}\) g, with a decay constant of about 0.0025 /my, and a cycling rate of about \(8.6 \times 10^{20}\) g Ca/my.

Employing a similar approach, mass distributions and rates of cycling can be determined for the oceanic and continental reservoirs that comprise limestone and dolostone. These are dissimilar. The best-fit constant mass-flux exponential decay function for oceanic oozes defines a system where \(M = 290 \times 10^{20}\) g Ca, \(k = 0.016\) /my, \(kM = 4.6 \times 10^{20}\) g Ca, and \(T_{50} = 50\) my (fig. 5). Conversely, the flux-fit decay curve constrained to pass through the most recent mass-age datum defines an oceanic system where \(M = 280 \times 10^{20}\) g Ca, \(k = 0.022\) /my, \(kM = 6.2 \times 10^{20}\) g Ca/my, and \(T_{50} = 30\) my. Owing to rapid rates of seafloor consumption by subduction, all pelagic carbonate is post-Triassic in age (fig. 5). On average, the deep marine reservoir has a carbonate calcium mass of about \(285 \times 10^{20}\) g, with a decay constant of about 0.020 /my, and a cycling rate of about \(5.4 \times 10^{20}\) g Ca/my.

Compared to the global reservoir, pelagic oozes contain only 7 percent of the total carbonate mass but account for about 60 percent of the present carbonate flux. The reason for this difference is that cycling rate within the pelagic system is an order of magnitude greater than that of the average global system. Hence, respective half-lives differ by an order of magnitude as well.

Mass-age data on continental carbonates exhibit two general trends. Because all pelagic carbonate is younger than about 200 my, pre-Jurassic global carbonate is entirely continental. Mass-age values for these units define a general exponential decrease with increasing age. By definition, this trend is identical to that derived for the older portion of the global reservoir (fig. 6). In contrast, that portion of the continental
Fig. 5. Curves through pelagic carbonate data. As in figure 2, both are constant mass-flux models. The "mass fit" curve (solid) is the best statistical approximation of total extant reservoir mass. The "flux fit" decay curve (dashed) is the best statistical approximation of total extant reservoir mass constrained to intercept the youngest (Pliocene) apparent accumulation rate.

Fig. 6. Data on cratonic carbonates, as in figure 1, and two model mass-age trends. The solid line with a positive slope is a least-squares fit through cratonic values when global carbonates consist of continental and deep oceanic units; the solid curve is the "mass fit" decay trend from figure 2 when global carbonate is exclusively continental. Area between the positive-slope segment line and the dashed curve represents the extant mass of pelagic carbonate ooze.
reservoir younger than about 200 my defines a positive trend, with mass decreasing toward the present.

This is the only portion of a major sedimentary reservoir that exhibits a linear increase in size with age. It is also a trend that may record processes other than simple deposition and destruction defined by the long-term cycling of global, oceanic, and continental carbonates. In an attempt to understand these factors and to quantify these mass-age trends, a series of models were evaluated in which a finite global carbonate flux was partitioned between oceanic and continental reservoirs.

**CARBONATE PARTITIONING**

Among patterns of Phanerozoic carbonate deposition, two scenarios span a range of possibilities: (1) cycling parameters for individual reservoirs have varied little over Phanerozoic time, and these adequately describe mass-age trends of oceanic and continental systems; and (2) long-term global cycling has varied little but transfer between shallow and deep marine reservoirs has modified extant mass trends through time. If the latter is correct, then additional queries should relate to the direction, timing, and rate of transfer.

As a starting point, mass-age trends of continental carbonates can be evaluated by considering model differences between the long-term global reservoir and the long-term oceanic reservoir. Do trends in continental carbonate reflect different but temporally-invariant values of cycling parameters for oceanic and global sequences over the full range of Phanerozoic time? They do not, as no combination of constant cycling parameters yields the positive mass-age trend apparent in data on post-Jurassic cratonic sequences (fig. 7).

The positive mass-age trend exhibited by the Cenozoic portion of the continental reservoir may, therefore, record some process of transfer between shallow and deep marine settings. Because shallow sequences exhibit a more-or-less linear decrease since the Mesozoic, the direction of this transfer must be from cratonic to pelagic settings. Furthermore, because slope reversal occurs in the middle Mesozoic, this is when transfer began (fig. 6).

Shallow-to-deep water carbonate transfer has been noted by others. Poldervaart (1955), Hay and Southam (1976), and Sibley and Vogel (1976) suggested that Mesozoic diversification of planktonic calcifiers (for example, Lipps, 1970) may have had a profound influence on patterns of global carbonate sedimentation. Similarly, Berger and Wintener (1977) and Sclater, Boyle, and Edmond. (1979) noted a significant positive correlation between positions of global sealevel and the Tertiary CCD in major ocean basins and suggested that changes in the CCD may reflect variable (and inverse) carbonate accumulation rates in deep and shallow settings. What has remained unclear regarding any carbonate transfer, however, is quantification of the rate at which transfer has occurred, the underlying cause of this transfer, and the long-term
Fig. 7. Mass-age data and model trends for the oceanic (lower dashed line), continental (upper dotted line), and global (solid line) carbonates. These model trends were calculated assuming no transfer between cratonic and pelagic reservoirs; the continental trend was calculated from the difference between long-term global and oceanic values derived assuming characteristic "flux fit" M, k, and kM values as in figures 2 and 5. Note that although reasonable approximations of the global and oceanic data are obtained assuming no transfer, the model curve and mass-age values for post-Jurassic continental carbonates exhibit inverse slopes. Symbols as in figure 1.

consequences of carbonate partitioning among the two principal carbonate reservoirs.

As with other aspects of such systems, two endmember scenarios for rate of transfer are within reason and span a range of possibilities: (1) coccolithophorids and planktonic foraminifera arose and diversified rapidly in the Jurassic and Cretaceous, respectively, and effected an abrupt transfer of calcite to the deep oceanic reservoir; and (2) pelagic calcifiers arose in the Mesozoic and diversified slowly, causing gradual transfer of calcite to deep oceans. Quantification of the first scenario yields reservoir trends dissimilar from those defined by mass-age data, in that an abrupt removal of about $6.2 \times 10^{20}$ g Ca/My (present oceanic flux) would result in a precipitous global-cratic mass decrease and the exponential decay of cratic, oceanic, and global reservoirs back to the point in time ($T_i$) of transfer initiation (fig. 8). Because of poor agreement between such model trends and mass-age data, it is unlikely that late Mesozoic coccolithophorid and planktonic foraminiferal productivity, as recorded by extant carbonate ooze, was at all comparable to present levels (fig. 8).

Conversely, quantification of the second scenario, wherein deep-marine calcifiers arose and then effected a more-or-less gradual transfer of carbonate to deep oceans, yields model trends in good agreement
Fig. 8. Model trends for the various carbonate reservoirs as in figure 7, but here calculated assuming abrupt transfer between cratonic and pelagic reservoirs at 145 my. Note agreement between oceanic data and the model curve, but inverse post-Jurassic continental model-data trends, and that the abrupt decrease in the size of the model global reservoir is not reflected in global mass-age data.

with mass-age data (fig. 9). Best-fit curves indicate that plankton carbonate was first delivered to the major deep ocean basins about 145 my ago \((T_1)\) and that total oceanic accumulation rate has been increasing gradually since that time, at a rate of about \(0.04 \times 10^{20}\) g Ca/ my (fig. 9).

While this model is little different from qualitative patterns of carbonate deposition suggested by others (for example, Hay, 1985; Milliman, 1974; Southam and Hay, 1977), the implications of such a scenario have been little appreciated. If pelagic protozoan carbonate productivity has indeed been gradually increasing at the expense of shallow shelf and reefal metazoan productivity, and if this pattern continues into the near geological future, carbonate flux to cratons will approach zero in about 100 my (fig. 10). Complete cessation of shallow water carbonate deposition will occur at that time, and, much in the manner of banded iron-formations, cratonic carbonate sequences will only then be available for scrutiny where present in the older rock record.

In 1950, Kuenen first recognized the potential ramifications of such a pattern of rock cycling and the "geoeconomy" of sedimentary carbonate calcium as he stated: "During the Cretaceous, pelagic (calcifiers) began to extract large quantities of lime from the oceans and to deposit their tests in the deep sea. Gradually, the hoard (of cratonic limestone) put by on the continents . . . is thus taken out of circulation and frozen on the floors of the oceans. Computation . . . shows that in
Fig. 9. Model trends as in figure 8 calculated assuming linear transfer of carbonate (0.045 x 10^20 g Ca/my) between cratonic and pelagic reservoirs over the past 145 my. Note general agreement between mass-age data and model curves for all three reservoirs.

Fig. 10. Past (A), present (B), and future (C and D) mass-age trends, each over a 400 my time interval, for the various carbonate reservoirs; model trends calculated as in figure 9. Arrows indicate the initiation of cratonic-to-oceanic transfer at a (present time of) 145 my ago. From A (400 my interval beginning 100 my ago), note a progressive increase in carbonate calcium flux into the oceanic reservoir and a progressive decrease in flux to the continental reservoir. In C and D, also note complete cessation of cratonic carbonate deposition in about 100 my as planktonic calcifiers transfer the entire global carbonate flux to deep ocean basins.
another 100 to 150 million years the whole of the accumulated capital of lime (on cratons) will have been squandered by pelagic organisms. A shortage (of carbonate) will then set in and necessitate some kind of adaptation of future life on the Earth.”

However, it is important to note that one alternative scenario also yields good agreement between model trends and mass-age data. In addition to the evolution and diversification of planktonic calcifiers, other processes such as eustatic sealevel change may also have influenced patterns of limestone and dolostone accumulation in deep and shallow settings.

Conventional wisdom has long held that cratonic carbonate accumulation is enhanced when sites of limestone deposition occur: (1) in low latitudes, (2) in shallow water, and (3) far-removed from areas of significant terrigenous clastic influx (for example, Wilson, 1975; Bathurst, 1975). Virtually all estimates of global sealevel variation suggest an increase in continental freeboard since the late Mesozoic (for example, Hallam, 1984: Vail, Mitchum, and Thompson, 1977). In addition, data from Harrison and others (1983) demonstrate that for lower coastal areas and continental shelves, every 10 m change in sealevel roughly corresponds to a 1.0 percent change in area covered by epicratonic seas. Hence, eustatic sealevel change may have had a profound effect on areas and rates of cratonic carbonate accumulation. If sealevels have indeed been falling since the late Mesozoic and if the accumulation rate of shallow water carbonates is favored in areas of clear, shallow marine water, then the gradual transfer of carbonate from shallow to deep settings may reflect availability of shallow tropical settings rather than any biologic influence related to net productivity of coccolithophorids and planktonic foraminifera.

Such a pattern is also amenable to quantification, in that estimates of global sealevels may be treated as simple partitioning parameters wherein an invariant carbonate calcium flux is divided between deep and shallow sites of accumulation on the basis of positions of global sealevel. When freeboard values from either Hallam (1984) or Vail and others (1977) are used as proxy values to partition an invariant finite long-term global flux, model trends exhibit excellent agreement with mass-age data for oceanic, continental, and global reservoirs (fig. 11).

This agreement should not, however, be perceived as an unequivocal demonstration of some genetic link between eustasy and patterns of sedimentary carbonate cycling, as a large redundancy exists among the input data. Specifically, the areal distribution of marine lithofacies, in particular the extent of shallow marine carbonates, is one of the principal criteria by which first-order sealevels have been determined (for example, Hallam, 1984). In essence, agreement between carbonate mass-age data and model trends derived by applying some sealevel partitioning parameter to a fixed carbonate flux merely reflects a linear relationship between areas and volumes of shallow water marine carbonate. In spite of this redundancy, such models do demonstrate the
Fig. 11. Model trends for the various carbonate reservoirs calculated using first-order values of global sea level for Hallam (1984) as partitioning parameters whereby a finite global carbonate calcium flux was divided between continental and oceanic reservoirs. These accumulation masses were then cycled employing characteristic long-term "flux-fit" decay constants as in figures 2 and 5. Note good agreement between the mass-age data and model curves for all three reservoirs. Symbols as in figure 1.

plausibility of eustatic control on mass-age trends of cratonic carbonates. Decreasing areas of shallow tropical seas, decreasing rates of accumulation in cratonic settings, and increasing rates of accumulation of deep marine carbonate ooze, may well reflect increasing continental freeboard since the late Mesozoic.

CONCLUSIONS

Available data on mass-age relationships among extant limestone and dolostone units indicate that all sedimentary carbonates comprise about $3500 \times 10^{20}$ g of carbonate Ca, cycling at a rate of about $8.6 \times 10^{20}$ g/my. Of the two principal reservoirs that make up this system, deep-sea ooze includes about $285 \times 10^{20}$ g of carbonate calcium, cycling at a rate of about $5.4 \times 10^{20}$ g/my. The pelagic reservoir has increased in mass at the expense of continental carbonates since the Mesozoic.

As noted above, two alternative models for such transfer are plausible. Inversely proportional deep-shallow marine carbonate fluxes may record biologically mediated "calcite pull" mechanisms wherein planktonic calcifiers act as the primary and causative agents of carbonate removal from continental settings. The validity of such an explanation ultimately is based on the central role of various biological processes in initiating the precipitation and preservation of marine carbonate ooze. Alternatively, physicochemically mediated "calcite push" mechanisms may be responsible for the gradual transfer of carbonate to deep marine
settings, and these should reflect the importance of decreasing sealevel in determining sites of carbonate deposition. Such an explanation ultimately is based on the central role of various physicochemical processes in determining rates of precipitation and preservation of biogenic marine carbonate in shallow cratonic settings.

At present, it is not possible to choose between the two models. If biological processes are a primary cause of transfer, at era-interval time scales a wide variety of biota-based explanations could be offered. It is possible, for example, that calcium and/or carbonate ion concentrations more severely limit rates of calcification by marine metazoans than by marine protists. In essence, the planktonic fauna may be outcompeting the benthonic biota for finite calcium carbonate resources. An analogous argument has been offered with respect to silica by Harper and Knoll (1975), who suggested that the explosive diversification of diatoms is recorded as an inverse relationship between average test weight of long-range radiolarians and species diversity of post-Jurassic diatoms.

Although calcium and/or carbonate availability may give rise to an inverse relation between protozoan and metazoan carbonate productivity, it is also possible that other limiting nutrients such as phosphorous are more important determinants of shallow versus deep marine carbonate biomass accumulation. It could even be postulated that various groups of zooplankton, feeding on planktonic calcifiers, have evolved the ability to compress more tightly carbonate fecal material, and that the greater density of these pellets has provided a more effective mechanism of carbonate transport to sites of accumulation above the CCD.

If, on the other hand, physicochemical processes related to global eustasy are the primary cause of the recent Phanerozoic shallow-to-deep carbonate transfer, a similar number of explanations could be suggested but only as unconstrained speculation. Except generalizations that relate cratonic carbonate deposition to shallow tropical areas of carbonate supersaturation, there is no compilation of data on cratonic carbonate occurrences and marine water chemistries that might serve as a basis for the evaluation of different physicochemical scenarios. If cratonic carbonates indeed made up most of the pre-Mesozoic global carbonate reservoir, then it is likely that either the latitudinal extent of shelf-reefal systems or vertical accumulation rates in such settings has been decreasing since that time.

In addition, many individuals have now argued that periods of marine flooding also coincide with elevated atmospheric CO₂ (Fischer, 1983; Sandberg, 1985) and lower carbonate saturation in shallow seas (Wilkinson and Given, 1986). While a case could be made that enhanced shoal water carbonate accumulation, coincident with lower shallow marine carbonate saturation state, may reflect lower carbonate saturation gradients during periods of marine transgression, a lack of data on relationships between physicochemical parameters and carbonate accumulation rates in modern seas precludes meaningful speculation about
older Phanerozoic systems. Collectively, we know very little concerning the relative importance of biological versus physicochemical processes in the generation of carbonate sequences, even in modern shelf-reefal settings. Nor is it well understood what carbonate distributions and accumulation rates might be like in the absence of either now-dominant metazoan calcifiers or now-prevalent carbonate-supersaturated ambient marine fluids.

In either case, the importance of various biological and/or physicochemical processes are not recorded by mass-age data on sedimentary carbonate reservoirs because such data make no comment on mechanisms responsible for the partitioning of carbonate in global oceans. However, one basic difference between any biologically-mediated “calcite pull” and any physicochemically mediated “calcite push” model is that the former suggests the geologically imminent cessation of cratonic carbonate formation, whereas the latter is entirely compatible with deep-water carbonate formation throughout the Phanerozoic, particularly during pre-Mesozoic periods of continental emergence.

Although various individuals have now suggested that deep marine carbonate accumulation only began in Mesozoic time, such an interpretation is neither required nor suggested by mass-age data on the various global carbonate reservoirs. On the basis of limestone-dolostone sequence masses alone, there is no reason to doubt that deep marine carbonate ooze deposition was a dominant sedimentary process in Paleozoic oceans, particularly during periods of continental emergence, such as the Permo-Triassic.

Regardless of the ultimate cause (or causes) of post-Mesozoic growth of the deep oceanic reservoir and demise of the continental reservoir, the direction, timing, and magnitude of this transfer provide a framework in which to evaluate genetic relationships between tectonic setting and characteristic reservoir cycling rates. Decay constants for oceanic and continental carbonates are about 0.0025 and 0.020/my, respectively, and these reflect the dominant processes of carbonate destruction in each tectonic setting. The longer half life of continental carbonates \( T_{50} = 380 \) my compared to that of oceanic oozes \( T_{50} = 50 \) my reflects more sluggish continental destruction rates, primarily via subaerial weathering. Similar rates are characteristic of all cratonic sedimentary sequences (Veizer and Jansen, 1985). Most oceanic ooze, on the other hand, is ultimately obliterated at subduction zones, and general agreement between pelagic ooze half-life and that of basaltic oceanic crust \( T_{50} = 55 \) my; Gregor, 1985; Sclater, Jupart, and Galson, 1980) reflects the importance of this process in the cycling of oceanic carbonates.

Finally, mass-age data bear directly on various interpretations of the completeness of the deep sea stratigraphic record. Specifically, Davies and Worsley (1981) suggested that decreasing oceanic sediment accumulation rate with age is a consequence of post-depositional destruction of sediment on the seafloor. While dissolution during and
soon after deposition may be an important process in the short-term cycling of deep and shallow marine carbonate components (for example, Anders, Krueger, Sadler, 1987; Walter and Burton, 1987), such is not the case over period-scale time intervals. Positive covariance of sea level and cratonic carbonate flux and sealevel and the CCD (for example, Sclater, Boyle, and Edmond, 1979) indicate that lower accumulation rate in older oceanic sections reflect an increasing accumulation rate toward the present. If so, long-term measures of marine cratonic and oceanic carbonate productivity may more closely reflect the availability of calcium and carbonate ions to calcifying protozoan and metazoan marine biota than any secular variation in temperature, nutrient supply, and/or patterns of faunal diversity.

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