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CARBONATE DEPOSITION/DISSOLUTION CYCLES AND CARBON DIOXIDE FLUX IN THE PLEISTOCENE

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ABSTRACT

The ice core record from Greenland and Antarctica indicates that Late Quaternary atmospheric CO₂ levels were elevated during glacio-eustatic sea-level highstands, and were at a minimum during sea-level lowstands. Some investigators have hypothesized that this CO₂ flux is driven by carbonate bank submergence cycles, which leads to the deposition of CaCO₃ and the release of CO₂ based on the formula:



It was further hypothesized that the CO₂ thus released would help drive global warming and terminate glaciations. This argument is patently false, as global warming and glacial melting are a prerequisite for bank flooding. The opposite consideration may have value, however, in that as soon as sea level lowers enough to expose carbonate banks, release of CO₂ by CaCO₃ deposition ceases and sequestering of CO₂ as HCO₃⁻ begins. This change in CO₂ may lower atmospheric levels and assist continued global cooling.

The global area of carbonate bank subject to glacio-eustatic submergence/emergence cycles is estimated to be 6 x 10⁵ km². During submergence, these banks release bicarbonate CO₂ at the rate of 200 g/m²/yr of carbon. Average submergence cycles last 10⁴ years, releasing 1.2 x 10¹⁸ grams of carbon as CO₂. During emergence, CO₂ is sequestered as bicarbonate by dissolution of CaCO₃, driving the equation above to the left. Studies of carbonate dissolution rates through rock volumes indicate that 75 m³/m²/yr of CaCO₃ is dissolved. Given Quaternary limestone densities of 2.0 g/cm³, this is equivalent to 18 g/m²/yr of carbon sequestered. Average bank emergent cycles last 10⁵ years, sequestering 1.1 x 10¹⁸ g of carbon.

The amount of carbon as CO₂ released during submergence cycles approximately equals that sequestered during emergence cycles, indicating no net loss or gain of CO₂ as regards carbonate banks during the Quaternary. During submergence, deposition is mostly as a layer on the bank surface, whereas during emergence, dissolution takes place both on the surface and throughout the volume of the exposed bank. This difference in the location of carbon flux allows banks to keep up with subsidence.

INTRODUCTION

The record of fluctuations in Late Quaternary atmospheric CO₂ (Figure 1), as derived from Antarctic ice cores (Barnola and others, 1987), has compelling similarity to curves from the Late Quaternary dealing with sea level, deep-sea oxygen isotope values, and sea surface temperatures (Genthon and others, 1987). The interaction of sea level with shallow carbonate bank deposition was examined in the "coral reef hypothesis" (Berger, 1982) as a means to elevate CO₂ levels in the atmosphere during interglacial episodes. Deposition of CaCO₃ results in evolution of CO₂ through interaction with bicarbonate ion, HCO₃⁻, as follows:



It was hypothesized that some of the CO₂ thus produced eventually passed to the atmosphere to be preserved in the ice-core record. Later investigations determined that the CO₂ changes recorded in the ice cores were helping drive climatic change in the Late Quaternary (Shackleton and others, 1983). Flooding of carbonate banks by glacio-eustatic sea level rise is necessary for the coral reef hypothesis to engage, therefore, the hypothesis cannot drive the climatic

CONDITION	ATMOSPHERIC CARBON LEVEL
Current	7.48×10^{17} g
Pre-Industrial	5.95×10^{17} g
Glacial Ice Maxima	4.26×10^{17} g
Ice Core Flux	1.69×10^{17} g
deposition/dissolution flux	11.50×10^{17} g

Table 1. Comparison of CO₂ levels in the atmosphere, expressed as grams of carbon. Data from Post and others (1990).

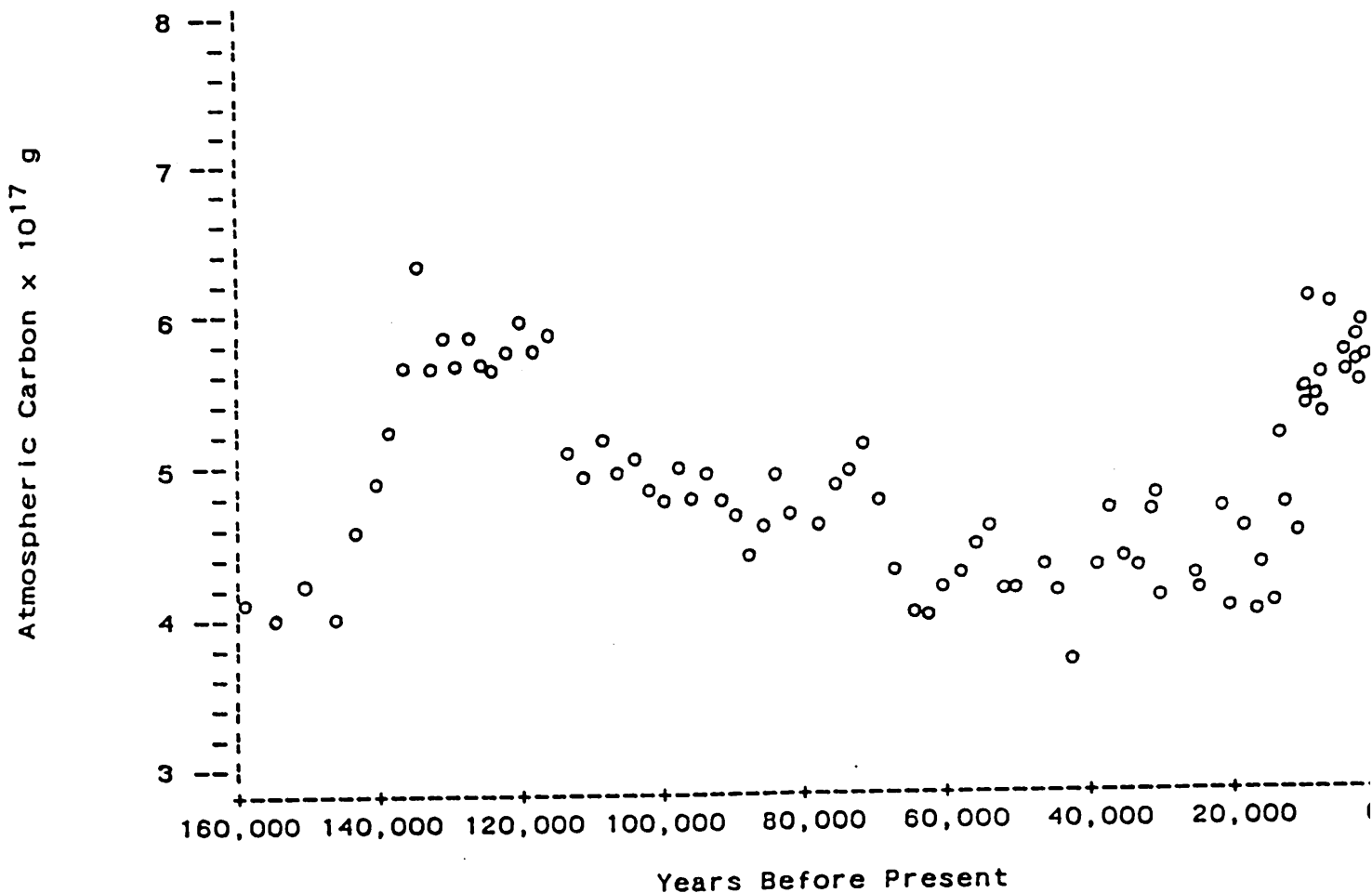


Figure 1. Concentrations of CO₂, as grams of carbon, in the atmosphere over the last 160,000 years, determined from trapped air bubbles in ice cores from Antarctica. Note the peaks at approximately 125,000 years ago and in the Holocene; the data is an analogue for Late Quaternary sea level change. Redrawn from Post and others (1990).

change responsible for ice retreat (Keir and Berger, 1985), as global warming would have to be well underway to produce banktop flooding.

The coral reef hypothesis tells only half of the story. The carbonate banks that produced CO_2 by CaCO_3 deposition during sea level high-stands become sinks for CO_2 during sea level low-stands when the banks are emergent and exposed to karst dissolutional processes. Dissolution converts aqueous CO_2 to bicarbonate ion, by reversing equation (1), and CO_2 is sequestered. The values of carbon transferred by these processes are not trivial (Table 1).

CARBON DIOXIDE FLUX

Deposition of CaCO_3 on Carbonate Banks

The morphology of most carbonate banks in the world is not ramp-like, but rather the banks are steep-sided platforms. A sea-level drop of 100+ m from modern levels would expose almost all carbonate banks. Because of the nature of carbonate bank bathymetry, the depositional sites lost by sea-level fall would not be replaced by new shallow bank at the lower sea-level position. A eustatic sea level fall typical of a Pleistocene glaciation results in a net loss of CaCO_3 deposition world-wide. The estimated bank area involved is $6 \times 10^5 \text{ km}^2$ (Smith, 1978), a value deemed conservative.

The net rate of CaCO_3 formation on submerged carbonate banks world-wide is at least $1 \times 10^3 \text{ g}$ of CaCO_3 per m^2 per year (Chave and others, 1972). CaCO_3 has a gram molecular weight of 100 (Ca = 40, C = 12, O = 16 x 3) and carbon represents 12% of that total, so deposition of $1 \times 10^3 \text{ g/m}^2/\text{yr}$ of CaCO_3 is equal to $120 \text{ g/m}^2/\text{yr}$ carbon. Equation 1 shows that for each gram of carbon sequestered in CaCO_3 during limestone deposition, an equal amount of carbon is evolved in CO_2 production. This value is similar to other studies (Keir and Berger, 1985), that presented a global value of $14 \times 10^{18} \text{ g}$ of CaCO_3 for Holocene carbonate production. Using 1×10^4 years for the time span of Holocene carbonate deposition yields $280 \text{ g/m}^2/\text{yr}$ of carbon evolved as CO_2 . These two different estimates, if averaged, provide a mean value of $200 \text{ g/m}^2/\text{yr}$ of carbon. This value will be used as a first approximation of sea-level highstand production of CO_2 carbon during CaCO_3 deposition on carbonate banks.

Dissolution of CaCO_3 on Carbonate Banks

When carbonate banks are emergent during sea level lowstands, dissolution occurs at the surface, in the vadose zone, and in the phreatic zone. This dissolution sequesters CO_2 carbon as bicarbonate ion (HCO_3^-). While data on surface denudation in karst areas is ample, studies of karst denudation including the surface and the underlying volume of carbonate rock are rare. The value for volumetric karst denudation, averaging eight available tropical and temperate studies, is $75 \text{ m}^3/\text{km}^2/\text{yr}$ (Ford and Williams, 1989, table 4.5). The value $75 \text{ m}^3/\text{km}^2/\text{yr}$ is equivalent to $75 \text{ cm}^3/\text{m}^2/\text{yr}$. Given an average density for Quaternary limestones of 2.0 g/cm^3 , this denudation value is equivalent to $18 \text{ g/m}^2/\text{yr}$ of carbon sequestered as bicarbonate ion ($75 \text{ cm}^3/\text{m}^2/\text{yr} \times 2.0 \text{ g/cm}^3 = 150 \text{ g/m}^2/\text{yr} \text{ CaCO}_3$, $\times 0.12 \text{ gC/gCaCO}_3 = 18 \text{ g/m}^2/\text{yr}$ of carbon). This value is probably an underestimate as it does not take into account mixing-zone dissolution in carbonate islands and banks (Smart and others, 1988; Sanford and Konikow, 1989), but will be used as a first approximation of sea-level lowstand sequestering of CO_2 carbon during CaCO_3 dissolution on carbonate banks.

CaCO_3 Deposition/Dissolution Cycles in the Quaternary

During the Quaternary, to a first approximation, sea-level highstands of sufficient magnitude to submerge carbonate banks have averaged 1×10^4 years in duration, while the intervening sea-level lowstands, when the banks were emergent, averaged an order of magnitude longer, or 1×10^5 years. Total carbon released from $6 \times 10^5 \text{ km}^2$ ($6 \times 10^{11} \text{ m}^2$) of global reef during a submergence in the Quaternary is therefore: $200 \text{ g/m}^2/\text{yr}$ carbon $\times 6 \times 10^{11} \text{ m}^2$ bank area $\times 1 \times 10^4$ years = 1.2×10^{18} grams of carbon, evolved as CO_2 . Total carbon uptake in CO_2 sequestered as bicarbonate ion by dissolution during a global bank emergence cycle is therefore: $18 \text{ g/m}^2/\text{yr}$ carbon $\times 6 \times 10^{11} \text{ m}^2$ bank area $\times 1 \times 10^5$ years = 1.1×10^{18} grams of carbon. The source/sink fluctuation of CO_2 , as driven by glacio-eustatic sea level change on carbonate banks, is approximately balanced.

DISCUSSION

The Quaternary glacio-eustatic sea-level fluctuations have not produced, through time, a net gain or loss of CO₂ carbon with regard to carbonate banks. The net deposition of new carbonate on the bank tops during sea-level highstands is matched by the sum of surface and subsurface dissolution occurring during the longer periods of bank emergence associated with sea-level lowstands.

Carbonate dissolution occurs routinely on the continents through karst processes, sequestering CO₂. During the Quaternary, glacial advances and retreats probably had an impact on this system. Paleozoic and Mesozoic carbonates exposed at high latitudes today were in many cases covered by thick ice and removed from the dissolution environment during ice maxima, decreasing the amount of CO₂ sequestered. Would this provide some compensation for the dramatically increased carbonate dissolution and concurrent CO₂ sequestering that occurs at the same time as carbonate platforms become exposed? Most likely not. The distribution of ancient carbonates on continents is not latitude dependent, while Quaternary carbonate distribution is strongly dependent on latitude; ice advance impacts only part of the carbonate dissolution regime on a continent, but the concurrent glacio-eustatic sea level change impacts the vast majority of the Quaternary carbonates. In addition, the shift in climate accompanying glaciation on continents often places carbonates in arid and semiarid environments into a wetter (pluvial) climatic regime, with a subsequent greater amount of carbonate dissolution. While quantitative figures are not available, qualitatively it may be that carbonate dissolution lost in high latitudes because of increased ice cover is regained at lower latitudes by a decrease in aridity.

During de-glaciation, all exposed carbonate platforms experience re-flooding to an approximation of their previous interglacial situation, and switch from a dominantly CaCO₃ dissolution (CO₂ sequestering) regime to a dominantly CaCO₃ depositional (CO₂ evolving) regime. On the continents, ice withdrawal leaves some carbonate outcrops mantled with thick till, but other carbonate areas are newly exposed by glacial quarrying of overlying rocks, as well as carbonate fragments exposed on till surfaces. These factors may well balance. Carbonates subjected again to dissolution at high latitudes may be balanced by reduced carbonate dissolution at lower latitudes as aridity returns.

It is difficult to develop models by which carbonates

in continental interiors can produce a major shift in CaCO₃ dissolution rates or volumes as ice sheets advance and retreat. Continental carbonate dissolution may not be cyclic during glaciation/deglaciation cycles, or if cyclic, is not of the same magnitude as the carbonate dissolution/deposition cycles found on Quaternary carbonate banks.

The mass balance of CaCO₃ deposition/dissolution cycles has implications for carbonate island development in the Quaternary. At first glance, it may seem that islands should not be able to keep up with isostatic subsidence, as there has been no net gain of carbonate on the platform since the beginning of the Quaternary. The mass balance model presented here deposits CaCO₃ only to the platform surface, but removes it from a 100+ m thickness during dissolution. Therefore the platform surface can grow upwards despite the mass balance. The model does imply that porosity is increasing with age in carbonate rocks, as shown for near surface rocks in Quaternary carbonate islands by Vacher (1988). Dissolution at depth is often associated with large fracture systems that parallel bank margins (Palmer, 1986), and may play a role in weakening bank margins, leading to margin collapse (Mullins and Hine, 1989). During the Quaternary, carbonate islands have progressively lost mass through their upper 100+ m while adding thin, low porosity limestone (relative to pre-existing limestones) to the bank top.

The CO₂ flux produced by CaCO₃ deposition/dissolution cycles on carbonate banks is at least 11×10^{17} g of carbon. This exceeds all past and current values, as shown in Table 1. The CO₂ flux shown in the Antarctic ice cores (figure 1) can certainly be explained solely by invoking carbonate bank deposition/dissolution cycles that accompany glacio-eustatic submergence/emergence cycles.

The CO₂ flux occurring through Quaternary carbonate bank submergence/emergence cycles is dependent on the position of sea level, and is therefore possibly only a response to climatic variations driven by other means, despite the large values of carbon flux involved. This is especially true for production of CO₂, which must await climatic warming to melt glacial ice and cause bank-top flooding leading to CaCO₃ deposition. During ice advance and sea-level fall, however, CO₂ sequestering can begin as soon as the bank top is exposed, which begins relatively early in a glaciation cycle. CaCO₃ dissolution can occur on a substantial scale with a sea level-fall as little as 10 m, and continue through the maximum sea-level depression and

most of the subsequent sea-level rise. In this manner, loss of CO₂ as bicarbonate to CaCO₃ dissolution may help promote global cooling, turning a minor sea-level fluctuation into a full-scale glaciation and sea-level depression.

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