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Non-steady state carbonate recycling and implications for the evolution of atmospheric P_{CO_2}

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Abstract

Most treatments of the Phanerozoic evolution of the carbon dioxide content of the atmosphere (P_{CO_2}) assume a steady state closed system. Release of CO_2 by mantle degassing and by biogenic precipitation of carbonates and their metamorphism in subduction zones balances the consumption by continental aluminosilicate weathering. Small perturbations in this balance bring about changes in P_{CO_2} , but given the small size of the atmospheric CO_2 reservoir relative to the rate of fixation by weathering, mechanisms that maintain this apparently precarious balance dominate current thinking. At present, the Atlantic and Indian oceans are major depocenters of CaCO_3 , but subduction of ocean floor and the deposits on it is minimal in these basins. The locus of metamorphic regeneration of CO_2 is restricted to the trenches off Central America. This is due to global asymmetries in the age of crust being subducted, in the distribution of oceanic carbonate productivity, and in the carbonate compensation depth, coupled with the poor preservation of old carbonate sediments. There is no causal relationship between the metamorphic release and weathering uptake of CO_2 and subsequent deposition of carbonate on timescales shorter than a complete cycle of opening and closure of a basin. We hypothesize that the low present-day P_{CO_2} is maintained by a time lag between: (1) mantle outgassing and metamorphic regeneration related to orogenic events in the geologic past, and (2) consumption driven by recent mountain building in the Tethyan zone and in the Western Americas. If this is true, then at the present 'kinetic minimum' both the terrestrial biosphere and the weathering rates are CO_2 limited. Atmospheric P_{CO_2} levels are controlled by weathering reactions only at this limit. In epochs of tectonic stability, outgassed CO_2 can accumulate in the atmosphere to very high concentrations with no obvious limit. Thus, as in the past, the current ice age will persist for tens of millions of years, possibly until the closure of the Atlantic recycles the first deep carbonate depocenter since the destruction of the Tethys. A greater understanding of all these processes is required for the geochemical evolution of the Earth surface environment to be simulated.

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1. Introduction

1.1. CO_2 and climate

The contemporary interest in global climate

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change, both in the future and in the geologic past, has focused strongly on the importance of the role of atmospheric CO₂ concentration (P_{CO₂}) in modulating the greenhouse effect that is dominated by water vapor. Carbon dioxide is the only additional major non-anthropogenic, photochemically stable, polyatomic, tropospheric gas after H₂O, and there is a broad consensus that changes in P_{CO₂} are a major driver of climate change. (This coupling of P_{CO₂} and temperature has recently been questioned [1–5].)

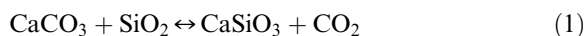
There is no doubt, given the fossil and isotopic records, that there has been a steady deterioration in Earth surface temperatures over the last 60 m.y., from essentially global tropical conditions with ocean bottom water temperatures of ~12°C to the present ice age conditions [6]. In the contemporary Earth surface environment, CO₂ is close to being a limiting nutrient for terrestrial vegetation, especially C3 plants (trees, shrubs, etc.). Strongly enhanced growth is observed in greenhouse experiments with artificially increased P_{CO₂} [7], and greatly reduced growth results at P_{CO₂} ≤ 150 ppmV (c.f. preindustrial interglacial value is ~280 ppmV). C4 plants, mainly grasses, are much more resilient to both low P_{CO₂} (limit ~20 ppmV) and low P_{H₂O}. Between 8 and 5 Ma, a drastic change in the relative preponderance of C3 and C4 plants occurred in response to decreasing P_{CO₂} [8]. Consistent with this limitation, there are strong seasonal oscillations in atmospheric P_{CO₂}, especially in the Northern Hemisphere where, at high latitudes, the total amplitude is about 5% of the average background value [9]. For reasons not entirely understood, the Ice Age glacial maxima are accompanied by a 30% decrease in P_{CO₂} [10,11]. Thus, present-day atmospheric P_{CO₂} levels are not only weakly buffered against the effects of short-term biospheric and climatic change, but appear to be close to the minimum value geologically.

1.2. Carbon cycle on geologic timescales

In the long-term carbon cycle on multimillion-year timescales, the ocean, atmosphere, and biosphere are considered as one reservoir. The primary sources of atmospheric CO₂ are thought to

be the direct input from mantle outgassing, probably with a subduction-related component, and metamorphic breakdown of carbonates in active orogenies in oceanic and continental arcs (e.g. the Southwest Pacific and the Western Americas). The dominant CO₂ consuming weathering reaction is the incongruent degradation of the high temperature aluminosilicate minerals in igneous and metamorphic rocks to residual clays, dissolved cations, and silica.

A balance between weathering uptake and metamorphic release of CO₂, mediated by the precipitation of CaCO₃, appears intuitively reasonable. Spreading of the seafloor into subduction zones delivers the sedimentary calcite to loci of metamorphic CO₂ regeneration through the so-called Urey reaction [12] and releases the CO₂ consumed in weathering reactions.



The above reaction is really only a schematic representation, where SiO₂ represents degraded fluvial and aeolian cation-poor clays, products of continental weathering, or biogenic opaline tests of diatoms and radiolarians in the sedimentary section. Reaction rates become significant in water-saturated thermal regimes (≥150°C), the upper bound of the oil maturation window [13,14]. In support of this idea one could look at the large gas fields in failed rift and back-arc settings, e.g. the North Sea and Indonesia, which are dominated by CO₂, making production of light hydrocarbons difficult [14]. Some of this CO₂ is derived from decarboxylation and other reactions that eliminate oxidic functional groups in the maturing hydrocarbons. Stable isotope ratio of carbon is useful in distinguishing the source of this CO₂. Organic material is depleted in ¹³C (δ¹³C less than ~−20‰), marine carbonates have δ¹³C of ~0‰, and mantle-derived CO₂ ranges between −5 and −8‰. The carbon isotopic composition of CO₂ discharge in seismic zones is heavy suggesting that the major source is decomposition of carbonate bearing rocks, i.e. Urey-type reactions, rather than of organic carbon [15].

While the chemical environment of the surface of the Earth is controlled by these diverse reac-

tions associated with the interactions of the continental and oceanic crust and the oceans themselves with the mantle, quantification is difficult. In particular, the time-constants of the mantle interactions, millions to tens of millions of years, are very much longer than those of the crust and atmosphere, a few tens of thousands of years. The search is for feedbacks or other mechanisms that will act to stabilize the atmospheric composition in the habitable range that appears to have obtained without significant interruption for at least the past 700 m.y. and probably much longer.

2. The regeneration of CO₂ consumed in weathering

A peculiarity of the contemporary system is that even if it is at overall steady state, the individual reservoirs are not. Continental platform carbonates deposited during high sea-level stands (the Australian Great Barrier Reef is the only present-day analog) are being weathered and re-deposited in the deep sea [16–18]. So also is the calcium and associated bicarbonate derived from aluminosilicate weathering. As on the continents, large amounts of CO₂ are being stored as limestone in the deep sea on geological timescales [18]. To satisfy the steady state assumption, a proportion of this, an amount equal to that derived from aluminosilicate weathering, undergoes subduction recycling (Eq. 1). The question is how this proportioning is controlled in reality. Consider a ‘Flatland’ scenario where carbonates are being deposited uniformly over the ocean in response to inputs of calcium and bicarbonate that have been constant over the age of surviving seafloor. Here, the carbonates are uniformly being subducted, both the aluminosilicate and limestone weathering derived portions. That is to say, at a given time, there is more CO₂ released by subduction metamorphism than consumed by weathering of aluminosilicates, resulting in a huge atmospheric excess. A formal budget is complicated by the fact that neither the sedimentation of biogenic calcite nor its subduction and metamorphism are uniform in space and time.

2.1. Oceanographic controls on carbonate deposition

The upper ocean is saturated with calcite and in low and middle latitudes aragonite [19]. Given the prevalence of shallow water organic or inorganic limestones in the sedimentary record back to the Archean, this must be the geologic norm [20]. However, both organic and inorganic phases are unusual in that they have retrograde solubility – the solubility increases rapidly with hydrostatic pressure and with decreasing temperature, i.e. oceanic depth [21]. In the relatively isothermal regime of the deep sea there is some depth, corresponding to the transition to pressure-induced undersaturation, below which carbonates cannot accumulate. This phenomenon is responsible for the carbonate compensation depth (CCD) (Fig. 1a). Necessarily, this is a statistical concept in the observational sense, based on the analyses of core tops whose sample distribution is quite heterogeneous, especially in the Southern Ocean [18,22]. Empirically, a kinetic lag is observed in the dissolution of carbonates such that the CCD rarely coincides with the equilibrium calcite saturation horizon (CSH) as calculated from laboratory thermodynamic data and water column measurements of the CO₂ system [19]. The CCD is usually deeper than and sub-parallel to the CSH [22].

2.1.1. Sea level

The average CCD varies in time in a way that is broadly synchronous between the ocean basins [23] (Fig. 2). This depth is primarily determined by the location of the major limestone formation areas [18]. If deposition of platform carbonates is dominant, as at times of high sea-level stands, then the ocean as a whole will become less saturated, and the CSH and CCD will be shallow. When sea level is relatively low, as at present, the major depocenter is the deep sea, e.g. in the contemporary Atlantic and Indian oceans (Fig. 1a), and the horizons will be at great depth. It follows that there is a rough parallelism between the average depth of the CCD and sea level [16,17] (Fig. 2). The inference is that shallow water biogenic deposition of CaCO₃ is more effi-

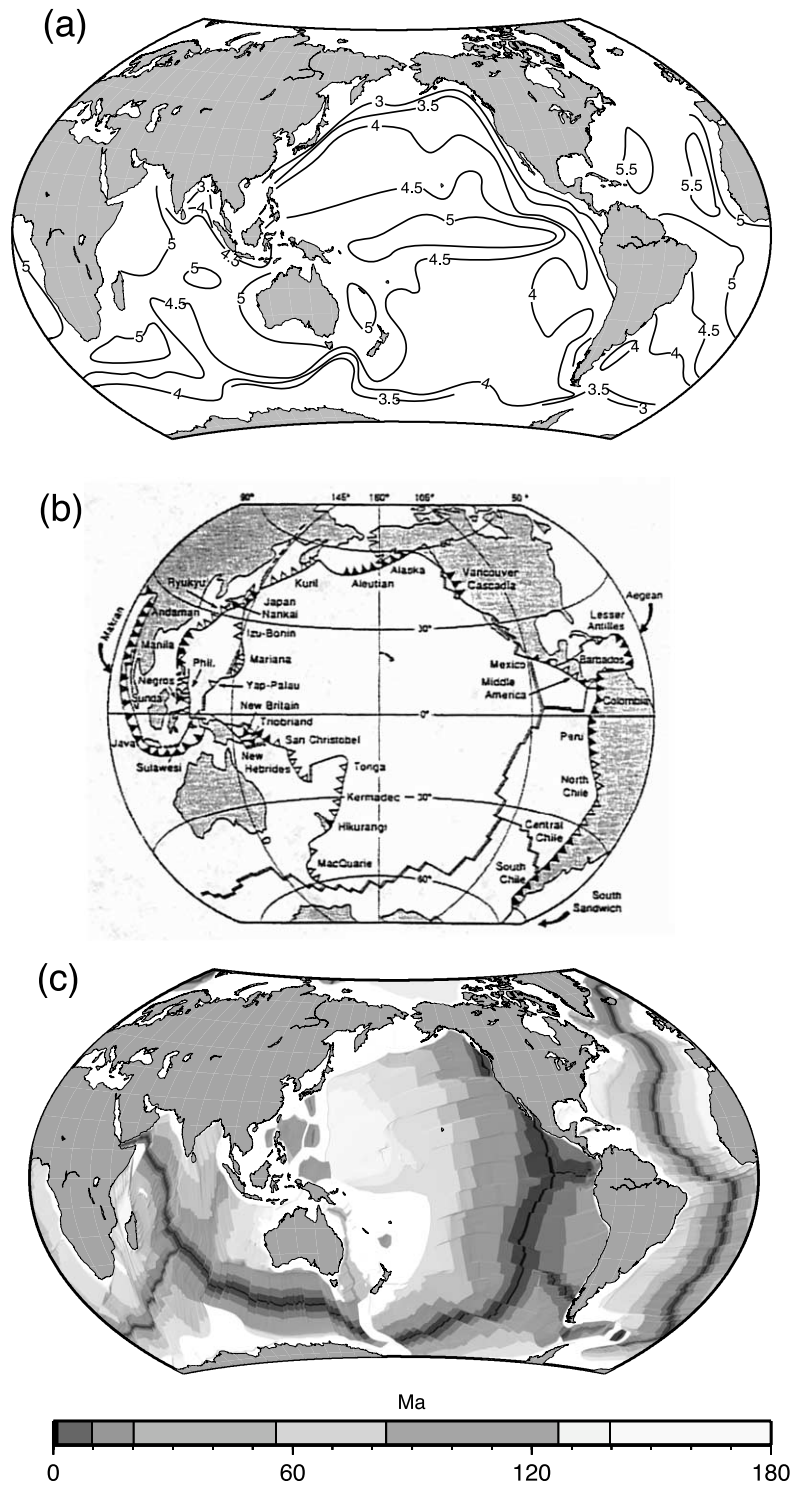


Fig. 1. (a) The global topography of the observed CCD in km [18]. (b) Subduction zones (barbed lines) of the world ocean. The solid and open bars indicate trenches with and without accretionary prisms, respectively, and double lines are oceanic ridges. Reproduced from [25] by permission of American Geophysical Union. (c) The age of the seafloor as determined from magnetic lineations [26].

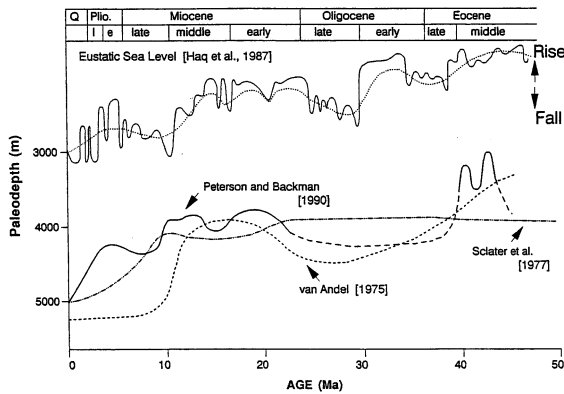


Fig. 2. Reconstruction of the variations in the global average depth of the CCD over the last 50 m.y. determined from paleo-depth back tracking of DSDP and ODP sediment cores (Peterson and Backman [70]). Comparison is made to CCD reconstructions of Sclater et al. [71] and van Andel [23] and to relative changes in eustatic sea level derived from seismic stratigraphy [72]. The dotted line superimposed on the sea level curve is visually determined long term variation. Reproduced from [16] by permission of American Geophysical Union.

cient, limited only by light and accommodation space, whereas the rates of oceanic precipitation depend on the availability of the essential nutrients, P and N. Thus, at times of low sea level there is increased storage of calcium and bicarbonate in dissolved form in the oceanic water columns.

2.1.2. Ocean circulation

Topography is induced on the CCD by the path of ocean circulation. The North Atlantic and Antarctic surface waters that sink during convective processes to ventilate the deep ocean are supersaturated with respect to calcite by a factor of ~ 2 . At present the approximate pressure-induced saturation depth for these cold high latitude waters is 5–6 km for the North Atlantic and 4–5 km for the Antarctic. This range reflects the difference in the initial degree of atmospheric CO_2 equilibration with the mixed layer (North Atlantic) and upwelling derived source waters (Antarctic). As the deep water masses propagate laterally away from their areas of vertical convective injection, they accumulate metabolic CO_2 from the settling decomposing remains of plank-

tonic organisms. This makes the water mass more acidic and drives it towards undersaturation, augmenting the simple thermodynamic P–T effect. This evolution is partially compensated by the dissolution of sedimentary carbonate of biogenic origin. In the contemporary ocean the net effect is a shoaling of the horizon from ~ 5.5 km in the North Atlantic adjacent to one of the major convective sources, to ~ 3 km in the old deep and bottom waters of the distal North Pacific far from the convective centers of the Arctic and Southern Ocean [18,22] (Fig. 1a).

2.1.3. Burial preservation

Secondary topography is induced on the CCD by burial-related preservation under areas of high productivity, i.e. by the kinetic lag in dissolution. At the low temperatures ($\sim 1^\circ\text{C}$) and relatively small degrees of undersaturation ($\sim 50\%$) characteristic of the deep ocean, dissolution lags accumulation by several thousand years [22]. This time lag is sufficient to allow accumulation into sedimentary depths, where reaction rates are controlled by pore water diffusion rather than directly by the ambient undersaturation of the free water column. This is best seen in the eastern tropical Pacific (Fig. 1a) where high productivity and associated high carbonate sedimentation rates induced by upwelling of nutrient rich waters along the equatorial divergence zone depresses the horizon by ~ 1 km. The effect is accentuated by the presence of fast seafloor spreading and high standing oceanic ridges (Fig. 1b), which project well above the local CCD.

2.2. Subduction metamorphism of carbonate

Just as the oceanic distribution of calcareous sediments is heterogeneous, so, too, is the occurrence of subduction zone recycling. The overwhelming proportion of subduction is located in the Pacific and its adjacent western seas [24,25], far removed from the major carbonate depocenters in the Atlantic and Indian Oceans (Fig. 1a,b). Elsewhere, there is only minor plate consumption, at the Antilles and Scotia arcs in the Atlantic, the Makran and the Andaman–Sunda–Java trenches in the northeast Indian Ocean [25] (Fig. 1b). The

crust entering these subduction zones is generally older than 50 Ma, and >100 Ma off southern Java [26] (Fig. 1c). Thus, the contemporary weathering export of continental platform carbonates, deposited at times of high sea-level stands, is predominantly to long-term storage in the abyssal Atlantic and southern Indian oceans where the CCD is deep and the subduction recycling negligible.

2.2.1. Before the evolution of calcareous plankton (~140 Ma)

A number of factors make it difficult to quantify the rate of subduction remobilization of carbonates in the Pacific. The highly asymmetric distribution of crustal ages [26] (Fig. 1c) results in much of the subducting crust in the Northwest Pacific being older than the time of evolution of the calcareous plankton (~140 Ma). Prior to this time carbonate deposition was presumably either biogenic on continental shelves and oceanic islands, or inorganic in the deep sea. The latter probably occurred as ‘whittings’, precipitation induced by the uptake of CO₂ by non-calcareous organisms and atmospheric exchange due to seasonal warming, as observed today on the Bahama Banks [27]. A reliable record of ancient deep sea deposition is contained in the sedimentary section

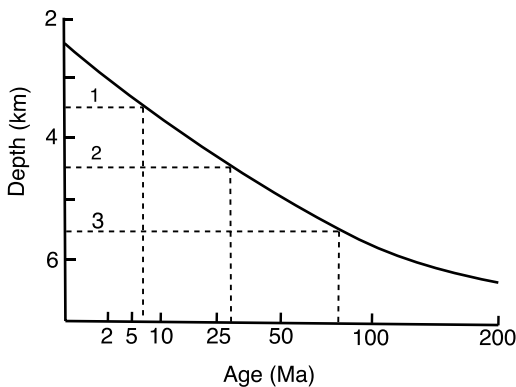


Fig. 3. The relationship between the mean basement depth (corrected for sediment loading) and crustal age in the North Atlantic and Pacific oceans. The square root of age relationship to depth holds out to ~70 Ma. Dashed lines 1, 2 and 3 indicate the maximum age of the crust where carbonate accumulates when the CCDs are 3.5, 4.5, and 5.5 km, respectively. Modified after [24] by permission of American Geophysical Union.

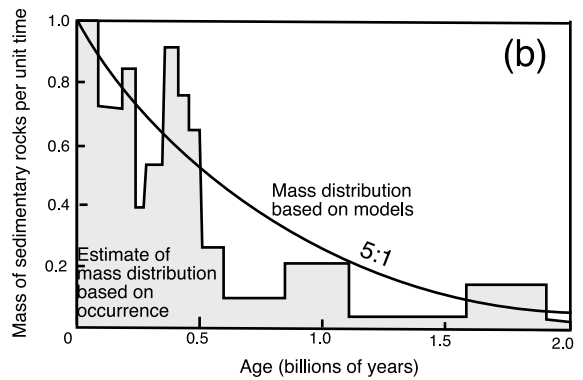
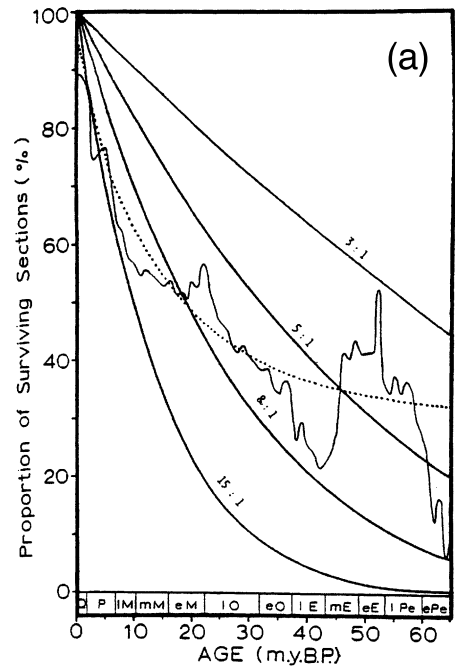


Fig. 4. (a) Percent of sampled DSDP sections surviving as a function of age. The curves are for the linear model of sediment recycling of Garrels and Mackenzie [35]. This assumes that: (1) deposition, destruction and preservation operate at constant rates, and (2) the probability of destruction of sediment of any age in any time period is constant and proportional to the mass of sediment of that age. Values for the ratio of total deposition to present-day preservation of 3, 5, 8 and 15 to 1 are plotted as solid curves. The dotted curve is an empirical estimate of the overall trend of the data. Reproduced from [34] by permission from Elsevier. (b) Mass of all sediments surviving on the continents as a function of age. The model line is for the linear case, as in (a), with a ratio of total deposition to present-day preservation of 5:1. The histogram is a summary of the observed occurrence of sediments. Modified after [35] by permission from author.

in and on the lavas of ophiolites of Jurassic and earlier times. In all reported cases the basal metalliferous sediments or umbers, the regional deposits from hydrothermal black smoker effluents, are siliceous [28–30]. By contrast, the much more numerous equivalent sections cored by the oceanic drilling projects are calcareous [31], save for the few holes in the Northwest Pacific that have reached the oldest Jurassic oceanic basement rocks [32]. While late stage silicification is well known in contemporary hydrothermal sulfide deposits, e.g. on Juan de Fuca Ridge [33], ubiquitous silicified metalliferous sediments strongly suggest a carbonate-free, opal-dominated depositional environment on the pre-Jurassic volcanic structures of deep sea and island arc origin now preserved in ophiolites.

2.2.2. Intermediate age

In the Southwest Pacific, crust of intermediate age (80–125 Ma) is being consumed (Fig. 1c). Since this section of the crust formed at relatively unproductive tropical and subtropical latitudes at a time of shallow CCD [23], carbonate accumulation was low. A high standing CCD greatly restricts the area available for primary deposition

almost regardless of spreading rate, because the thermally controlled age–depth relationship of the seafloor goes as the square root of the age [24] (Fig. 3). With an average CCD of 3.5 km at 50–100 Ma only crust out to ~10 Ma would accumulate carbonate. At the present CCD average of 4.5 km, crust out to ~30 Ma is available. In the contemporary North Atlantic, carbonate can accumulate out to about 70 Ma crust. In addition to the shallow CCD, the ridge axis was remote from all but aeolian sources of detrital sediments, diminishing the clay cap preservation of carbonate. The long sediment cores recovered by the drilling programs, DSDP and ODP, consistently show a strongly decreasing degree of preservation with age [34], much more so than the equivalent continental forms [35] (Fig. 4). Hiatus formation is a regional event and is associated with increasing bottom current activity [16]. Hence, passage of the seafloor through the CCD resulted in redissolution of carbonates accumulated when the crust was younger and higher standing [34]. The same is true for the younger crust (20–50 Ma) being consumed to the east, under South America. In general this dissolution process acts to recycle carbonate back to the axial

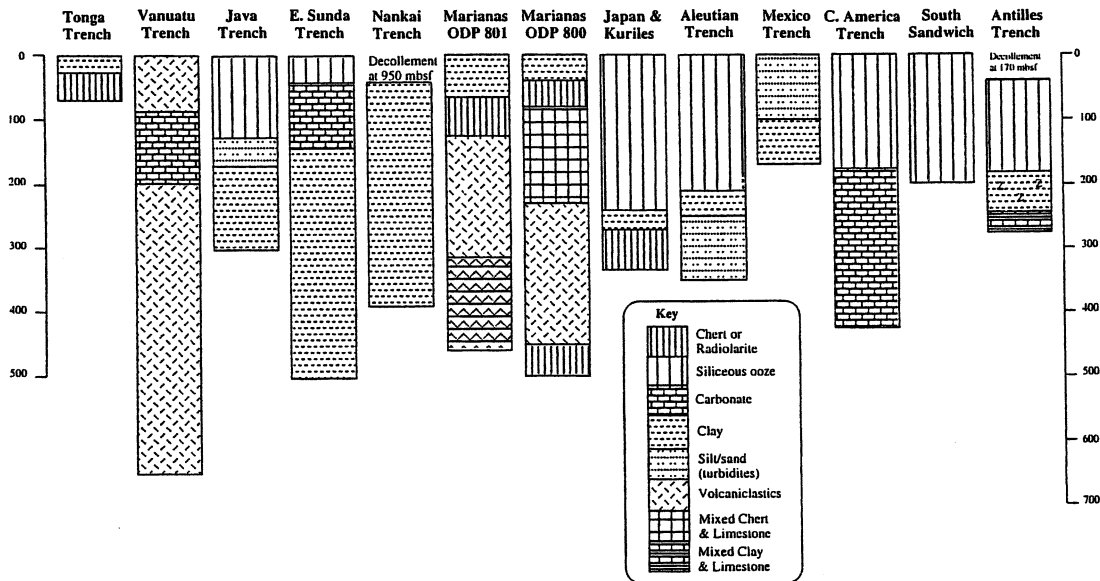


Fig. 5. The average sedimentary columns being subducted at 13 trenches. These synthetic columns are estimated from drill cores and seismic reflection profiles. Note the rarity of carbonate-rich sections. Reproduced from [36] by permission from Elsevier.

high or to the Atlantic and Indian oceans (or to shallow water deposits), i.e. away from the subduction zones.

It would appear that the combination of the depth evolution of the CCD, the distribution of oceanic productivity, and the rate of formation (depth) and age of subducting crust makes the west coast of Central and South America between 10°S and 20°N the locus of metamorphic recycling of CO₂ in the contemporary global subduction system (Fig. 1). Here carbonates from the equatorial high productivity zone are being delivered to the subduction zone on timescales < 15 m.y. and with minimal penetration of the CCD. Release from the other much older systems of crustal consumption, especially in the western Pacific, provides a background determined by events prior to the 100 m.y. time frame and clearly cannot represent any short-term link.

2.2.3. Sedimentary sections entering subduction zones

These inferences, based purely on considerations of the configurations of the subducting plate boundaries and of the mechanisms controlling the topography of the CCD, find confirmation in recent compilations of the actual sedimentary sections entering the various subduction zones [36,37] (Figs. 5 and 6). The compilations are derived from the existing suite of ocean drilling cores and were developed in an attempt to assess the geochemical contribution of subducting sediments to arc volcanics. The sediments on old crust descending under the predominantly oceanic arcs (Tonga, Aleutian, Mariana, Philippine, Japan, Antilles, and Scotia) are essentially devoid of limestone as a distinguishable lithologic unit (Fig. 5). The same is true of the trench off Mexico where the accreting boundary was well north of the equatorial carbonate section being subducted. Only in the Central America Trench is a substantial (~250 m) carbonate section being subducted. These reconstructed sediment columns are representative of their various subduction zones to the extent that their compositional variations are clearly reflected in the associated arc volcanics [38]. The most exhaustive analysis of the complete suite of relevant cores (29 sites; Fig. 6) has shown

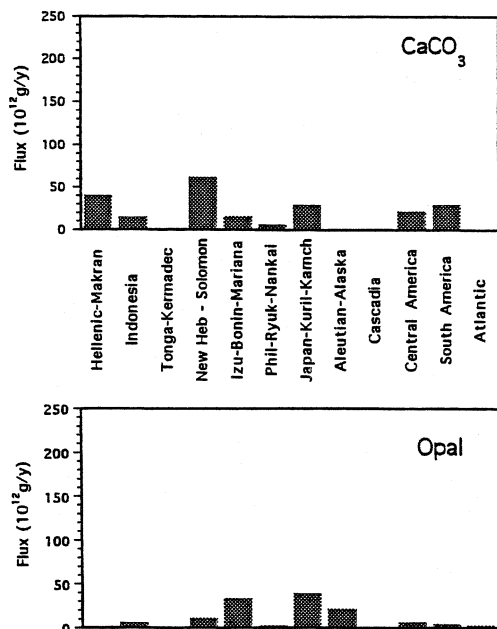


Fig. 6. The masses of carbonate sediments being delivered to the subduction zones based on compiled analyses of drill cores from 29 locations outboard of the major trenches. For carbonate $100 \cdot 10^{12}$ g/yr is equivalent to 10^{18} mol C/m.y. and for opal $\sim 2 \cdot 10^{18}$ mol Si/m.y. Note that the molar delivery rates of these two major biogenic components are quite similar. Reproduced from [37] by permission from Elsevier.

that, while the oceans are a strong net sink for carbonate sediments, very little is being subducted currently [37]. The Tertiary and Recent accumulation of marine sediments, both biogenic and detrital, is far from steady state since these detailed observations show that only a small fraction is being delivered to the contemporary subduction zones for recycling. Assuming complete regeneration of subducted carbonate to CO₂, this flux would be $2 \cdot 10^{18}$ mol C/m.y. [37].

3. Other sources of metamorphic CO₂

3.1. Vein calcite

Altered oceanic basement rocks recovered by drilling show common occurrences of vein calcite precipitated inorganically during weathering reactions with seawater at low and intermediate tem-

peratures [39–41]. Occluded seawater and the basalts contributed approximately equal amounts to calcium (and Sr as determined by the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios). This precipitation appears to progress to old ages where the crust is thickly mantled with sediment [40,42]. Processes in such semi-closed reaction systems are not significantly influenced by environmental changes in the overlying water column and thus are not sensitive to changes in the continental weathering cycle. However, they do result in a relatively constant background flux of CO_2 , if the vein calcite is subsequently broken down during subduction zone metamorphism. Staudigel et al. [39], using admittedly sparse data (three holes, DSDP 417A, 417D, 418A in Cretaceous crust on the Bermuda Rise, maximum depth sub-basement 536 m, $\sim 70\%$ recovery), estimate the global uptake flux in forming the veins at $\sim 2.5 \cdot 10^{18}$ mol C/m.y. More recently that result was confirmed by Alt and Teagle [41] at $(1.5 \sim 2.4) \cdot 10^{18}$ mol C/m.y. This could be the upper limit for the total return flux of CO_2 during the subduction of seafloor in times prior to the radiation of the calcareous plankton and is sensitive to rates of subduction but not to those of continental weathering.

3.2. Orogenic metamorphism

To some unknown degree, CO_2 consumption in orogenic belts, the loci of weathering, is accompanied by metamorphic release within the orogen itself. The global compilation of CO_2 -rich springs [15] is suggestive in this regard, since they are known to be concentrated in tectonically active areas. An excellent discussion of the geothermal fields of China and their relationship to regional tectonics by Kearey and Wei [43] confirms this impression. Kerrick and Caldeira [44] have attempted to estimate this metamorphic release in the Alpine–Himalayan orogen from the observed and inferred abundances of metamorphosed calcareous pelites. Their calculated CO_2 flux is substantial ($\sim 10^{18}$ mol C/m.y.) and certainly too high, since they ignored the strongly diachronous evolution of the collision zone. It should be noted, however, that this flux is comparable to that for the subduction zone under contemporary Central

America. Thus, this may be comparable to the CO_2 release that accompanied the prior closure, by subduction, of the Tethys Ocean that led to the orogen itself. The closure of the Tethys appears to be the only instance in the geologic record of the wholesale recycling of a major deep sea carbonate depocenter. Nesbitt et al. [45] have calculated that infiltration-driven metamorphic decarbonation reactions during the Cenozoic extension of the American Cordillera could have released $\sim 5 \cdot 10^{18}$ mol C/m.y. to the atmosphere between 60 and 40 Ma.

Conversely, Selverstone and Gutzler [46] have presented strong evidence that carbon is stored in a stable form at deep and mid-crustal levels in the Tethyan orogenic belt as metamorphic dolomite and marble from limestones and as graphite from organic carbon. They suggest that $\sim 10^{19}$ mol C has been transferred to this reservoir over the 125 m.y. history of the combined orogenies, an aggregate flux of $\sim 0.1 \cdot 10^{18}$ mol C/m.y. Since rapid back-thrusting and unroofing of metamorphosed, ‘subducted’ continental crust is a major feature of the orogen, especially in the Himalaya, the rate of recycling of this material by weathering may be high. Given the enormous, tectonically generated exposures of aluminosilicate rocks in these mountain belts, there can be no doubt that while active, they are a strong net sink for CO_2 . However, as activity wanes and the orogen collapses, the metamorphic flux could eventually dominate over the weathering sink.

If carbonate sediments survive at mid to lower crustal levels in orogenic belts [46,47], the time-scale of orogenic metamorphism is considerably longer than that of the orogen itself. This means that the general diffuse release of CO_2 from eroded mountain belts should provide a constant background flux that integrates the effects of orogenic episodes over perhaps hundreds of millions of years. Such a flux is almost required in the absence of a substantial one related to oceanic subduction [39].

4. CO_2 at kinetic minimum

In the simplest case of a relatively constant,

slowly varying background flux from continental metamorphism and axial hydrothermal releases, the atmospheric P_{CO_2} is determined mainly by the consumption rate in weathering which depends on tectonic activity to maintain a flux of material to be eroded and weathered. Given the present low atmospheric P_{CO_2} and its instability with respect to short-term biological and climatological changes, it is likely that its level is the result of a time lag between the general metamorphic release from rocks of widely different ages and tectonic histories, and contemporary weathering uptake. That is to say, on the present Earth, the P_{CO_2} levels are at the minimum possible value, which we will call the ‘kinetic minimum’. This is obviously the case for ^4He , the major isotope of helium. It is produced by the alpha-decay of U and Th and thus has a source function similar to that of CO_2 -mantle outgassing at spreading centers and release during crustal metamorphism [48]. These fluxes probably change only slowly in time. The sink is infinite, escape to space by the ‘thermal evaporation’ of Jeans [49] and by the much more complicated non-thermal processes involving collisional excitation by high-energy charged particles [50]. However, the atmospheric concentration, ~ 5 ppmV, is relatively high and is maintained kinetically by the energy barrier to the achievement of the thermal escape velocity in the

upper atmosphere [50]. In the case of atmospheric CO_2 , the sink is continental weathering of aluminosilicate rocks, infinite until the rocks are exhausted. With an infinite sink and relatively constant source, there is still ~ 280 ppmV of CO_2 in the atmosphere, which, by analogy with ^4He , is kinetically maintained.

To the extent that glacial epochs are sustained by very low levels of P_{CO_2} , the present climatic regime will persist until a major tectonic perturbation occurs. Migration of the continents away from the poles may be an ameliorating influence through albedo changes and other effects [51]. The only obvious ways to increase significantly the P_{CO_2} over the next few tens of millions of years are: (1) the cessation of activity in the orogenic belts and their collapse, or (2) the reclosure of the Atlantic and the large-scale subduction recycling of the CO_2 presently stored in ancient abyssal limestones. Parenthetically, even this new source of CO_2 could be countered by increased orogeny associated with the continued northward drift of Australia. The durations of previous glacial epochs in the Phanerozoic have been several tens of millions of years [52,53], comparable to those of major orogenic episodes. Plate motion determines the positions of continents, albedo and the possible extent of periglacial and tropical weathering environments; plate interactions deter-

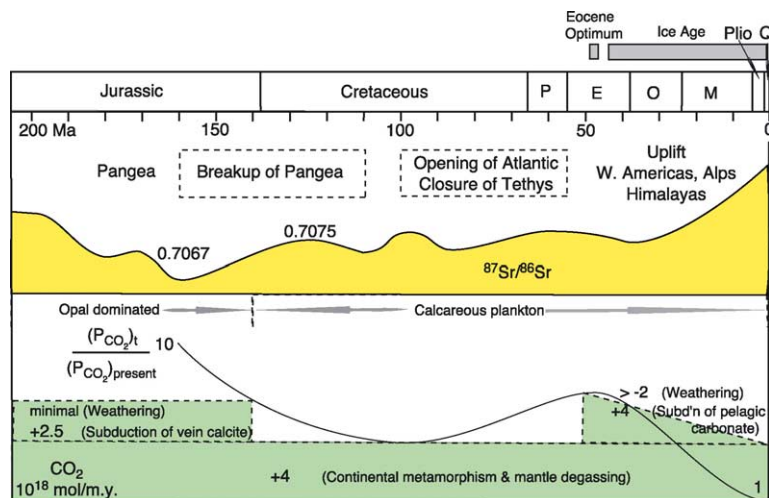


Fig. 7. Schematic illustration of the conceptual evolution of atmospheric CO_2 discussed in the text. Not drawn to scale.

mine both orogeny and CO₂ draw-down and also metamorphism, subduction and CO₂ release. It is difficult to separate these effects with present information.

5. Conceptual evolution of the past P_{CO₂}: a scenario

If the supply and consumption of CO₂ are related only at the limit of the kinetic minimum in P_{CO₂}, then an evolutionary history of the atmospheric CO₂ levels in the Cenozoic/Mesozoic (Fig. 7) can be outlined qualitatively from considerations much different from models assuming steady state [54]. The pronounced minimum in the marine ⁸⁷Sr/⁸⁶Sr ratio at 160 Ma (~0.7067) can be accounted for by the combined input of hydrothermal activity and limestone weathering alone, and the radiogenic continental supply was minimal. This suggests that the weathering environment was senescent: on 'Flatland' (Pangea) weathering rates were more rapid than the transport processes removing weathered material from the area (transport limited [55] regime). Eventually a thick mantle of highly weathered material accumulated over fresh bedrock, until it was essentially devoid of aluminosilicate weathering. With the sink term thus minimized, degassed CO₂ could accumulate conservatively over tens of millions of years to atmospheric P_{CO₂} levels at least an order of magnitude greater than present, levels similar to those in modern soils.

Subsequent continental breakup led to the exposure and erosion of thermally uplifted rifted margins and to reorganized and perhaps accelerated seafloor spreading and subduction. The rift margin elevations were not great if the present topography around the Red Sea, the Gulf of California and the East African Rift valleys is representative. The elevation was certainly not sufficient to induce glaciation, as advocated by Eyles [53], except locally, e.g. the Ruwenzori on the western Rift. The net effect was probably a slow drawdown in P_{CO₂}, since the sediments (and crust) being subducted were very poor in carbonates. A larger proportion of Pangea probably drained in-

ternally. About one-third of the present continental area has closed drainage [56] where the weathering products from the effluent basins are being stored as playa deposits, red beds and other continental sediments, e.g. the Basin and Range Province and Salton Trough in the American West [57]. There is a relatively steep but short-lived rise in the marine strontium isotope ratio at the time of breakup of Pangea (160–110 Ma). The isotopic rise may have been caused by the rapid release of the soluble playa salts to the oceans following the opening of the drainages by rifting and faulting, on a much smaller scale the probable fate of the Salton Trough over the next few hundred thousand years.

The establishment of full-scale ocean basin formation in the Atlantic was accompanied by the relative migration of the major Pacific spreading centers towards the Western Americas and the initiation of continental orogenies there [58]. However, the resulting acceleration of weathering and CO₂ consumption was compensated for to some degree by the parallel closure of Tethys, then a young, low latitude carbonate depocenter probably similar to the eastern Pacific today. Assuming, very crudely, an onset of closure at 100 Ma along the entire 10 000 km length of the Alpine–Himalaya chain at a convergence rate of 8 cm/yr for the 50 m.y. prior to final collision [59], then subduction of a 200-m carbonate section would result in a flux of metamorphic CO₂ of 4·10¹⁸ mol/m.y. Taking the extreme assumption that the subduction margin was an Andean-type continental arc, then by analogy with the contemporary Western Americas the net weathering consumption of CO₂ would have been ~125·10⁶ mol/km arc length/yr [60], equivalent to 1.25·10¹⁸ mol/m.y. for the entire arc. It appears more likely that the margin was of the Indonesian type with volcanoes situated on basement that was close to sea level [61]. Thus, these estimates are quite uncertain and, for the CO₂ consumption, certainly high. However, it is apparent that the closure of the Tethys Ocean that led to the continental collisions generated a substantial additional flux of CO₂ over the normal background from continental metamorphism and mantle outgassing (presently estimated at ~4·10¹⁸ mol/m.y. [62,63]), one

that has not recurred to any significant degree. Thus, the closure probably sustained the climatic optimum in the early Eocene [52,64]. This episode of globally extreme warmth ended with the elevation of the Western Americas and the collisional development of the Alpine and Himalayan chains.

With Tethys closed, the only significant subduction of carbonates occurred in the resulting orogen and in the eastern equatorial Pacific. Continued plate reorganizations progressively shrank that subduction regime until the present configuration stabilized off Central America about 6 Ma [65,66]. As in the American West, the development of relief in the collision zone by erosion and local isostatic adjustment was autocatalytic and rapid. The consumption of CO₂ exceeded any compensating supply. Uptake by the Himalaya–Tibet region alone is $\sim 10^{18}$ mol C/m.y. [67] and from the entire Tethyan regime probably twice this. The resulting climatic deterioration was itself autocatalytic, through frost-shattering. Once significant areas of periglacial and glacial conditions are established, weathering is further accelerated through ice action, the most efficient mechanism for surface area creation and slope destabilization [68,69]. The polar location of continents may be more important in this phase than their subsequent albedos, since the area of potential frost action is greatly increased. The P_{CO₂} continued to fall until locked at the kinetic minimum observed in the recent past.

6. Conclusion

Contemporary observations of deep sea carbonate sedimentation and subduction cast doubt on the steady state assumption of the long-term carbon cycle. Carbonate sedimentation and accumulation is ubiquitous in the Atlantic and Indian oceans at all but the greatest depths because of the presence of young bottom waters of close convective origin. In the Pacific, on the other hand, due to metabolic CO₂ aging along the hydrographic flow trajectories, it is restricted to the high-standing ridges of the southeastern East Pacific Rise and the highly productive equatorial

zones. The difficulty of preserving marine carbonates means that only very young crust will provide a significant metamorphic source of CO₂ upon subduction. Such subduction is ‘accidental’ in that there is no fundamental requirement for it to occur at any particular time or place relative to the variations in the locations of the CaCO₃ depocenters, nor are subduction-prone deposits formed preferentially in response to changes in weathering rates. Since there appear to have been little carbonate sedimentation in the deep sea prior to the radiation of the calcareous plankton ~ 140 m.y., subduction related metamorphism cannot be crucial to the overall CO₂ budget. Certainly, in the contemporary environment, the rates of weathering consumption and subduction recycling of CO₂ are coupled very weakly, if at all. Both processes occur, but they are mechanically unrelated.

The contemporary situation, we propose, is P_{CO₂} level at a kinetic minimum. The atmospheric levels are very low relative to the values necessary to account for past thermal optima and also unstable with respect to seasonal and orbital perturbations. In this case, most aspects of the terrestrial carbon cycle, both biological and inorganic, are limited by the atmospheric P_{CO₂}.

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