
Changing Influences Between Life and Limestones in Earth History

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Extinction is forever.

(Anonymous)

Abstract

Coral reefs are among the most beautiful, diverse and fascinating ecosystems in the modern oceans. For anyone intrigued by reefs, their geologic history is a never-ending mystery series, complete with paradoxes to unravel and mass “murders” to solve given only partial texts and enigmatic clues. Limestones not only record much of the history of life on Earth, they are a major reason why life occurs on Earth! Moreover, they “go missing” at catastrophic events that, on several occasions, caused extinctions of more than half of all multicellular species. The production and preservation of reef limestones is intimately connected to the Earth’s biogeochemical cycles, especially of carbon, oxygen, nitrogen and phosphorus. Continental collisions, changes in sea-floor spreading rates, massive meteor impacts, and glacial-interglacial cycles with resulting changes in sea level, are all subplots in the history of reefs. The evolution of photosynthesis that triggered the first global “pollution” event, the escalation of predation as indicated by increasing prevalence of shells, and the ubiquitous and repeated development of mutualistic symbioses, provide analogies to modern environmental challenges. The Earth’s biogeochemical cycles, which have evolved over more than 4,000 million years, have been profoundly disrupted by human activities. Carbon dioxide in the atmosphere, for example, has increased more over the past 200 years than it did between glacial advances and retreats. Within this century, atmospheric CO₂ concentrations will rise to levels comparable to those 40–50 million years ago. The records preserved in limestones can provide scientists and policy makers with insights into likely consequences of human activities for the future not only of reefs, but of the diversity of ecosystems on Earth.

Keywords

Carbonate • Tectonics • Calcification • Biogeochemical • Carbon cycle

2.1 Reefs, Limestones, and Human History

Limestones and coral reefs have been used by human populations for most of human history. Not surprisingly, the features that made them useful are characteristics inherent to the environments in which reef creatures lived and the minerals from which they made their shells and skeletons. Reef ecosystems provided food to coastal populations, and where there were uplifted reefs near the shorelines, those

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humans utilized caves and springs for shelter and fresh water. Ancient limestones, moreover, are not restricted to coastlines. As limestones are everywhere prone to dissolution, cave formation, and freshwater springs, evidence of early human habitation can be found in limestone caves nearly everywhere they occur on land. Another characteristic of limestone, which early humans probably discovered when they lived in caves, is that it is softer than most other rocks and can be readily carved. In their caves they made holes for storage or hanging items; they also made implements, building material, decorative items and statues.

With the Industrial Revolution, limestones gained much additional economic value because many ancient underground reef provinces are major oil and gas reservoirs; those shallower are often important aquifers. Those same characteristics noted above, solubility and relative softness compared with many other kinds of rocks, are again key features. The porous to cavernous nature of many limestones make them exceptional hydrocarbon reservoirs. And their relative softness made drilling very feasible using early technology. As a result, the literature on ancient reefs and lesser carbonate buildups is vast. A few of the multitude of useful compilations include Milliman (1974), Wilson (1975), Bathurst (1976), Toomey (1981), Scholle et al. (1983), Fagerstrom (1987), Crevello et al. (1989), Riding (1991), James and Clarke (1997), Camoin and Davies (1998), Wood (1999), Stanley (2001), Kiessling et al. (2002), Pomar and Hallock (2008), and Swart et al. (2009). This chapter cannot provide the details available in these books. Instead it summarizes the significance of biogenic reefs and limestones within the context of environmental conditions through Earth history.

2.2 Biogenic Sediments and Reefs

Coral, oyster, and other biogenic reefs are produced by the combination of biological, chemical, physical and geological processes. Ideally, a biogenic reef is a significant, rigid skeletal framework that influences deposition of sediments in its vicinity and that is topographically higher than surrounding sediments. For example, a coral reef is a rigid skeletal structure in which stony corals are major framework constituents. Another term for a limestone structure or buildup produced by biological activity is **bioherm**. Less rigid accumulations of biologically produced sediments are often referred to as reef mounds (James 1997; Schlager 2003).

Calcareous shells and skeletons produced by a wide variety of protists, algae and animals become biogenic sediments upon the death of those organisms. The metabolic activities of some kinds of bacteria and microalgae also contribute to the biogeochemical precipitation of calcareous minerals, producing microbolites, stromatolites, and ooids in

the benthos, and lime muds (whittings) in seawater overlying shallow banks and shelves. While biogenic carbonate sediments can occur with siliciclastic sediments, carbonates are most prevalent in marine environments that are separated by distance or physical barrier from substantial influx of sediments from land.

Nearly 50 % of the modern ocean floor is covered by pelagic carbonate ooze, which includes minute calcareous plates produced by coccolithophorids (microalgae) and shells of planktic foraminifers (protists), both of which live primarily in the surface waters of the open ocean (Kennett 1982; Seibold and Berger 2010). Shells and skeletons of benthic organisms, as well as microbially produced particles, also are important sediment constituents, especially on continental shelves, in some coastal areas, and on oceanic banks and shoals. Although the area over which pelagic carbonates accumulate is many times greater than the total area of neritic accumulation, Morse and Mackenzie (1990) estimated that ~16 % of annual global carbonate production in modern oceans occurs on reefs, shelves and banks. Moreover, they estimated that more than 80 % of the pelagic production dissolves in the water column or on the sea floor, while only about 40 % of neritic production is lost to dissolution. Thus, neritic carbonates account for roughly a third of the annual carbonate sedimentation globally.

Whether biogenic constituents make up most of the bottom sediments or whether they are only minor contributors depends upon several factors. One factor is the rate at which sediments from land enter the marine environment via runoff from rivers and streams, thereby diluting the biogenic contribution. Another factor is the rate at which shells and skeletons are produced by biotic communities living in the marine environment. A third factor is the rate at which sediments, both terrigenous and biogenic, are removed from that environment by transport or dissolution. The biotic community not only produces sediments, it also affects rates of dissolution, physical breakdown and transport of sediments.

Lees (1975) recognized three classes of shallow-water carbonate sediments, based upon their major constituents. He called the simplest group “**foramol**” sediments after two of the most important constituents: benthic foraminifers and molluscs, especially fragments of snail and bivalve shells. Lees noted that foramol sediments are characteristic of temperate shelves, but sometimes dominate in tropical areas where reefs do not occur. Other common constituents of foramol sediments are fragments of coralline red algae, sea urchin spines and plates, bryozoans, barnacles, and worm tubes. James (1997) recommended using the term “heterozoan” to describe such assemblages because constituents other than foraminifers and mollusks commonly dominate. Lees’ (1975) second category is called “**chloralgal**” for its dominant constituent, the remains of

calcareous green algae such as *Halimeda*; foramol constituents are secondary components. Chloralgal sediments are prevalent in expansive shallows like Florida Bay and the Bahama Banks, and in **mesophotic** (=low light) settings including the lagoon behind the Ribbon Reefs of the northern Australian Great Barrier Reef. Lees' (1975) third sediment category is "**chlorozoan**", which is the typical sediment around coral reefs. Coral, along with coralline and calcareous algal remains, are the characteristic constituents, with the shells of larger benthic foraminifers, as well as molluscan and urchin shells or fragments, as secondary components. Larger benthic foraminifers, which depend on algal symbionts in a relationship very similar to that of corals and their zooxanthellae, may locally dominate sand-sized sediments. Bryozoan, barnacle, and worm shell debris are typically scarce in chlorozoan sediments because these organisms thrive in waters with richer food supplies than do corals. James (1997) combined the chlorozoan and chloralgal assemblages into the "**photozoan**" assemblage to reflect the dependence of both associations on photosynthesis.

Whether biogenic sediments accumulate in place or are transported elsewhere for deposition depends upon bottom topography, the strengths of waves and currents, and the ability of the benthic community to reduce sediment transport. Fagerstrom (1987) proposed "**guild**" terminology to characterize benthic organisms by their geological roles in reef communities (Table 2.1). He used the term "**buffers**" for organisms that project upwards from the sediment, slowing water motion and providing quieter places for sediments to settle. Organisms that live in or directly on the sediment, holding or encrusting it in place, can be considered "**binders**". Microalgae and bacteria grow and develop mats directly upon sediments, accumulating where wave and current motion is limited or intermittent. Bacterial filaments provide strength to these mats, which can resist as much as ten times more wave or current energy than is required to move similar unbound sediments (Grant and Gust 1987). **Stromatolites** are biogenic structures consisting of layered accumulations of microbolites, which include trapped or secreted sediment in algal or bacterial mats (Grotzinger and Knoll 1999; Reid et al. 2000). Ancient stromatolites produced the first bioherms in the fossil record. The best known modern stromatolites occur in Shark's Bay and elsewhere in West Australia (Logan et al. 1974; Reid et al. 2003), as well as several localities on the Bahama Banks (Dill et al. 1986; Reid et al. 1995) and elsewhere.

A variety of elongate, upward-projecting plants and animals can baffle water motion and trap sediments. On modern shallow shelves, seagrass beds effectively stabilize sediment over vast areas (Agawin and Duarte 2002). Seagrass blades slow water flow, allowing suspended sediments to settle out. Sediments are then held in place by

extensive seagrass root and rhizome systems, as well as by the holdfasts of algae living within the seagrass bed. Sediment-dwelling macroalgae are also effective buffers and binders, as are sponges, soft corals, sea whips and sea fans. In fossil reefs, a variety of less familiar organisms performed similar roles (Fagerstrom 1987; Wood 1999; Keissling et al. 2002).

The ultimate buffers are the biogenic framework constructors, which in modern tropical shallow-water environments are primarily stony corals. These organisms grow upward or outward in branching, massive or platy morphologies, secreting substantial quantities of calcium carbonate, while trapping even greater quantities of sediment within and in the lee of the reef framework. Encrusting coralline algae bind the reef framework and enclose sediments in massive, wave-resistant structures recognized as coral reefs.

The three-dimensional topography of the reef provides abundant habitats for the diverse array of organisms that dwell within the reef structure. Some of these organisms are encrusters, including coralline algae, many kinds of sponges and some kinds of sessile foraminifers and mollusks. Many produce shells or skeletons that contribute to reef sediments. Thousands of species are wholly soft bodied and have little direct influence on the reef structure. All contribute to the diversity and energy flow within the community.

A variety of organisms also contribute to the breakdown of the reef structure by boring into it or scraping away at it as they graze. Such organisms are known collectively as "**bioeroders**" (Neumann 1966) or "**destroyers**" (Fagerstrom 1987). Bioeroding organisms are a diverse and important component of the reef community (Chap. 4). Organisms that bore or etch their way into the reef include bacteria, fungi, several varieties of sponges, worms, clams, and urchins. Organisms that scrape away limestone as they graze algae include urchins, chitons, snails and fish. Many reef fish feed by biting off bits of coral or coralline algae, subsequently defecating sand. In a healthy, actively accreting reef, bioeroders contribute to the diversity of microhabitats within the massive reef structure. However, if reef growth slows in response to natural or anthropogenic environmental stresses, the rates of destruction can exceed rates of accretion (Glynn 1988; Hallock 2001).

2.3 Basic Carbonate Chemistry

The major chemical constituent of calcareous sediments and limestones is calcium carbonate (CaCO_3). Organisms secrete CaCO_3 typically either as calcite or aragonite (Morse and Mackenzie 1990; Hallock 2011). The obvious difference between these minerals is their crystal structure;

Table 2.1 Important roles (guilds) taxa play in carbonate buildups

	Framework builders	Encrusters	Binders	Buffers	Sediment producers	Bioeroders	Dwellers
Stony corals	XXXXXXXXXXXX	XXXXXXXXXXXX	XXXXXXXXXXXX	XXXXXXXXXXXX	XXXXXXXXXXXX		
Coralline red algae	XXXXXXXXXXXX	XXXXXXXXXXXX	XXXXXX	XXXXXXXXXXXX	XXXXXXXXXXXX		
Calcareous green algae			XXXXXX	XXXXXXXXXXXX	XXXXXXXXXXXX		
Seagrass			XXXXXXXXXXXX	XXXXXXXXXXXX			
Cyanobacteria	XXXXX**	XXXXXXXXXXXX	XXXXXX	XXXXXX	XXXXXXXXXXXX**	XXXXX	XXXXX
Non-calcareous algae			XXXXXX	XXXXXX			XXXXXXXXXXXX
Octocorals			XXXXXX	XXXXXXXXXXXX	XXXXXX		
Sponges	XXXXX**	XXXXX**	XXXXX**	XXXXXX	XXXXXX	XXXXXXXXXXXX	XXXXX
Foraminifers		XXXXXX			XXXXXXXXXXXX		
Echinoids					XXXX	XXXXXXXXXXXX	
Crinoids				XXXXX**	XXXXX**		
Bivalves	XXXXX**	XXXXXX	XXXXX**	XXXXX**	XXXXX**	XXXXX	XXXXX
Gastropods		XXXXXX	XXXXXX	XXXXXX	XXXXXX	XXXXXX	XXXXX
Other mollusks						XXXXXX	XXXXX
Bryozoans		XXXXX**	XX	XXXXX**	XXXXX**		
Brachiopods	*****	*****	*****	*****	X*****		
Barnacles					XX	XXXXX	XXXXXX
Annelids						XXXXX	XXXXXX
Fish					By bioerosion	XXXXXXXXXXXX	XXXXXXXXXXXX

XXXXX indicates relative importance in modern shallow-water reefs, XXXX** indicates that the group was more important in fossil buildups, and ***** indicates primarily important in fossil reefs

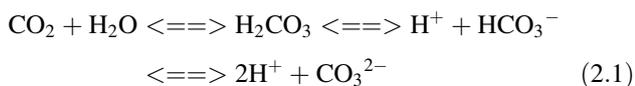
Table 2.2 Characteristics of the principle calcium carbonate minerals

Mineral name	Aragonite	Calcite	Mg-Calcite
Chemical composition	CaCO ₃	CaCO ₃	(Ca, Mg)(CO ₃) ₂
Crystal system	Orthorhombic	Rhombohedral	Randomly substituted MgCO ₃ in a disordered calcite lattice
Habit	Columnar or fibrous	Coarsely crystalline to massive	Coarsely crystalline
Fracture	Subconchoidal	Conchoidal	Disordered
Hardness	3.5–4	3	3 or less
Solubility	~1.5× more soluble than calcite	Least soluble, most stable form	At 25° C, <8.5 mol% MgCO ₃ is less soluble than aragonite
Other	Stronger than calcite per unit Ca ²⁺	More brittle than aragonite	At 25° C, >8.5 mol% MgCO ₃ is more soluble than aragonite
Biological advantages	For branching morphologies, muscle attachments	Requires less energy to precipitate and maintain under lower saturation states	Does not require genetic capability to exclude Mg; advantageous where strength is less important
Environmental advantages	Warm, supersaturated seawater with high Mg:Ca ratio	Most stable at lower carbonate saturation states—cooler waters, higher pressure, low Mg:Ca ratios	Thermodynamically controlled; chemistry varies with environmental conditions
Disadvantages under specific conditions	Metastable, soluble	Excluding Mg requires energy and genetic capability	Solubility, structural limitations

calcite forms rhombohedral crystals while aragonite forms orthorhombic crystals (Table 2.2). Crystal structure is biologically significant because aragonite is structurally stronger than calcite, which is important for organisms with upright or branching morphologies. Another difference is in the chemical stability of the minerals at temperatures and pressures found on land and in the oceans. Aragonite more readily precipitates in warm seawaters that are supersaturated with CaCO₃, but it is less stable in cooler seawaters and in freshwater.

In warm environments, calcite precipitation tends to be inhibited by Mg²⁺ dissolved in seawater. Thus, organisms must either expend energy to remove Mg²⁺ from the calcifying fluids or incorporate it into the calcite crystal structure, thereby producing Mg-calcite shells or skeletons (Hallock 2011). Mg-calcite is energetically advantageous in terms of calcification, but the resulting calcite is structurally weaker. The Mg²⁺/Ca²⁺ ratio in seawater, along with temperature, determines how much Mg²⁺ is incorporated in Mg-calcite shells. Over time, most aragonite and Mg-calcite either dissolve or recrystallize, so calcite predominates in ancient limestones.

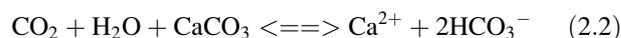
The solubility of CaCO₃ is easily misunderstood if one expects this substance to behave like other familiar solids. For example, table salt and sugar both dissolve faster in hot water than in cold. CaCO₃ is more soluble in cold water. The key to this intuitive discrepancy is in the reaction of carbon dioxide with water:



That is, carbon dioxide (CO₂) and water (H₂O) combine to form carbonic acid (H₂CO₃), which can then dissociate to hydrogen ions (H⁺) and bicarbonate (HCO₃⁻) or carbonate (CO₃²⁻) ions. The two-headed arrows indicate that the reaction can go either direction depending upon environmental conditions. The dissolved inorganic carbon concentration of a sample of seawater is the sum of the carbon in these four states. In surface seawaters, CO₂ is only a small fraction of the total carbon, often less than 1 %, while HCO₃⁻ typically dominates (Morse and Mackenzie 1990).

How much CO₂ can be dissolved in water and which state predominates depends primarily upon temperature, pressure, and concentrations of other dissolved materials (Morse and Mackenzie 1990). Cold water can hold far more CO₂ in solution than warm water; an example is a cold carbonated beverage, which loses CO₂ as it warms. Similarly, water under pressure can hold more CO₂ in solution. Addition of dissolved salts (i.e., increasing salinity) decreases the ability of water to dissolve CO₂. Surface waters of the ocean can hold less CO₂ in solution than deeper waters, and tropical waters hold less than temperate or polar waters.

Carbon dioxide and water react with CaCO₃ in the following way:



The more CO₂ that is dissolved in water, the more readily the water can dissolve CaCO₃. Conversely, any process that removes CO₂ from solution promotes the precipitation of CaCO₃. Since calcium ion (Ca²⁺) and bicarbonate ion (HCO₃⁻) are both abundant in seawater, modern tropical ocean-surface waters are most conducive to the precipitation

of CaCO_3 , while deeper and colder ocean waters are more apt to dissolve CaCO_3 .

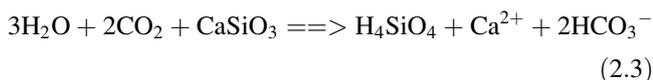
2.4 Limestones and Earth History

Limestones and dolostones are a major reason that life exists on Earth. Since limestones are CaCO_3 and dolostones are $\text{Ca,Mg}(\text{CO}_3)_2$, they store immense quantities of CO_2 in the Earth's crustal rocks. Without limestones, the concentration of CO_2 in the Earth's atmosphere would be about 100 times higher, similar to that of Venus, and the surface of the Earth would be nearly as hot as that of Venus (425°C) (Condie 1989).

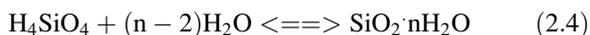
Carbon dioxide is referred to as a greenhouse gas because it absorbs heat energy. Most of the energy reaching a planet's surface from the Sun is visible light. The planet's surface absorbs that radiation, is warmed by it, and reradiates heat (infrared radiation) back into space. Carbon dioxide in the atmosphere acts as an insulating blanket by trapping part of the infrared radiation the planet would otherwise lose into space.

Venus and Earth are quite similar planets. A major factor in their histories, which culminated in life on Earth but not on Venus, is distance from the Sun. This determines the intensity of solar radiation falling on the planet's surface. Based on distance from the sun and without considering atmospheric effects, the average surface temperature of primordial Venus is estimated as 60°C and of primordial Earth as -30°C . Volcanic eruptions released water vapor, hydrogen sulfide, methane, ammonia, carbon dioxide, and other gases from these planets' interiors, producing atmospheres. Approximately 10 % of the gaseous volcanic emission was CO_2 . So both planets had insulating atmospheres and likely were somewhat warmer than estimates based only on distance.

Carbon dioxide is removed from the atmosphere during weathering of rocks (Berner 2006). Rainwater, in which carbon dioxide is dissolved, falls on rock (represented here by basalt – CaSiO_3), slowly weathering it away to dissolved silica (H_4SiO_4), calcium ions, and bicarbonate ions:



In lakes or oceans, dissolved silica precipitates out to form opal ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$):



while Ca^{2+} and HCO_3^- react to form CaCO_3 (Eq. 2.2 read right to left). Through geologic time, the opal crystallizes to

quartz and the CaCO_3 accumulations become limestone, dolostone or marble.

The solubility of CO_2 is strongly temperature dependent, as is the weathering reaction (Eq. 2.3), which further explains why Earth supports life while Venus does not. On primitive Venus, an average surface temperature in excess of 60°C inhibited dissolution of CO_2 . Weathering of crustal rocks was minimal and CO_2 rapidly accumulated in the atmosphere. Today the atmosphere of Venus is 95 % CO_2 and life is precluded by a runaway greenhouse effect (e.g., Rosenquist and Chassefiere 1995). In contrast, with a primordial atmosphere, daytime temperatures on much of the Earth's surface probably supported liquid water at temperatures of $0-25^\circ\text{C}$, which was optimal for CO_2 dissolution and weathering of basalt. As a result, CO_2 was removed from Earth's atmosphere and accumulated in crustal rocks. Today only about 0.04 % of the Earth's atmosphere is CO_2 and the average surface temperature of approximately 14°C (Axelrod 1992) readily supports life.

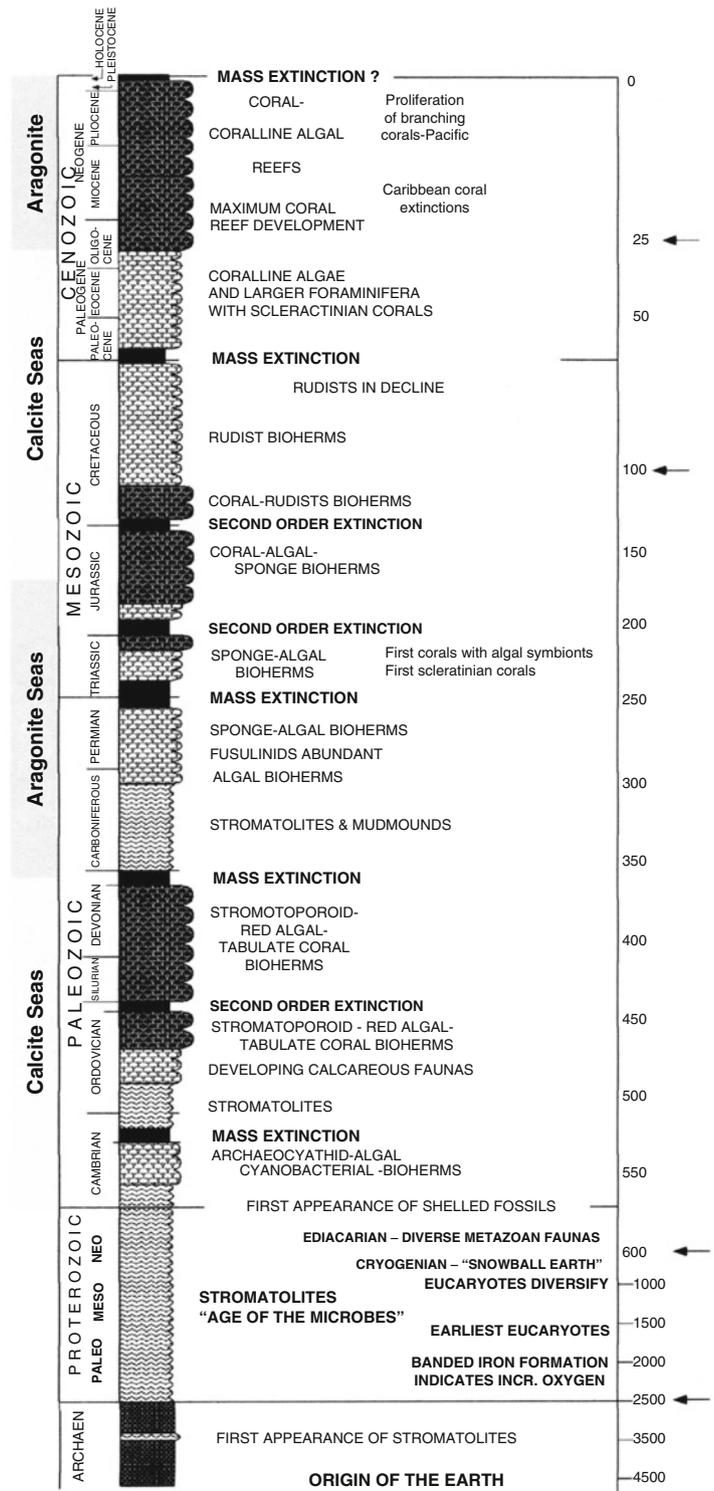
2.5 The Atmosphere and the Evolution of Life

During the first 1,000 Myr of Earth's history, most precipitation of CaCO_3 likely occurred spontaneously (abiotically) when concentrations of Ca^{2+} and HCO_3^- supersaturated warm waters. The evolution of life on Earth profoundly altered this relationship (Fig. 2.1). Microbes evolved the ability to utilize energy from chemical bonds or sunlight to produce organic matter (abbreviated below as CH_2O) from CO_2 (Canfield and Raiswell 1999; Riding 2000), using either hydrogen sulfide (H_2S) or water (H_2O) as the hydrogen donor:



If diffusion and mixing processes in seawater are limited relative to the rate of photosynthesis, removal of CO_2 from solution by photosynthesis can promote CaCO_3 precipitation (see Eq. 2.2). For example, on a warm, shallow, subtidal flat where cyanobacterial mats cover the bottom, CaCO_3 crystals may form in the water or within the mats (Pentecost 1991; Reid et al. 2003). The result can be the formation of stromatolites. By this mechanism, tremendous volumes of limestone were deposited in shallow shelf seas from about 2,800 to 600 million years ago (Ma) (Grotzinger 1989; Riding 2000). During this time, photosynthesis forever changed the Earth's atmosphere by removing CO_2 and producing free oxygen, resulting in oxygenated oceans and atmosphere essential for the evolution and survival of

Fig. 2.1 The geological time scale illustrating major reef-related events. The *arrows* along the right side of the figure note scale changes, with the scale greatly expanded over the past 100 million years, especially the past 25 million years



multicellular life forms (Lovelock 2000; Och and Shields-Zhou 2012).

During the ~4,600 Myr lifetime of the Sun, its luminosity has increased roughly 40 % as a part of the natural aging process of a star (Gilliland 1989). If the process of carbon dioxide removal from the Earth's atmosphere was purely

geochemical, the rate of removal would have declined as solar radiation intensified, and the Earth would have become warmer. But since the evolution of photosynthesis, life forms have influenced the concentrations of CO₂ and O₂ in the atmosphere. As solar radiation has intensified, rates of photosynthesis have likely increased (Lovelock 2000). The

long-term increase in rates of photosynthesis can partly account for the overall decline in CO₂ concentrations through geologic history of the Earth (Berner 2006).

However, the decline in CO₂ concentrations in the atmosphere has been neither uniform nor continuous. Global tectonic activity, which has not been constant through geologic time, is a major influence on input and withdrawal of CO₂ in the atmosphere (Eyles 1993). Over Earth history, volcanic rates have generally declined as the Earth's interior has progressively cooled (Drake 2000). Over the time scales of large-scale plate tectonic processes (10s–100s of Myr), volcanic rates have varied, slowing as large continental masses collided and speeding up as they rifted apart. For example, during the Cretaceous Period (the Age of the Dinosaurs), 150–65 Ma, the rates of oceanic rifting and subduction were substantially faster than modern rates. Atmospheric CO₂ concentrations, which were as much as five to ten times higher than present, produced greenhouse conditions in which high latitudes enjoyed temperate climates and polar regions were ice free (Mackenzie and Anderssen 2013). Thus, during intervals such as the Cretaceous, the long-term decline in atmospheric CO₂ concentrations temporarily reversed.

A critical driver of CO₂ decline has been the successive evolution of groups of photosynthetic protists and plants with new and more efficient pigments and enzyme systems. Proliferation of new organisms likely contributed to second-order declines in atmospheric CO₂ concentrations that triggered global cooling and culminated in major episodes of high-latitude glaciation. Prior to the Neoproterozoic, which began roughly 1,000 Ma (Fig. 2.1), bacteria were the major photosynthesizers. The evolution of the nucleated cell from the symbiosis of three or four different kinds of bacteria provided the evolutionary breakthrough that later made multicellular life possible (Margulis 1993). The evolution of green and red algae and of the primitive phytoplankton known as acritarchs ~1,200 Ma increased the efficiency of photosynthesis and therefore rates of CO₂ extraction. A major glacial event occurred in the Cryogenian Period of the Late Proterozoic, starting about 850 and ending approximately 635 Ma (Pierrehumbert et al. 2011). Global cooling associated with this extensive glacial episode slowed rates of extraction of atmospheric CO₂ by the biotic community.

The proliferation of multicellular life following the Cryogenian has been attributed to suitable atmospheric oxygen concentrations (Och and Shields-Zhou 2012). Shelled organisms first appeared ~570 Ma (Conway Morris 1993). Atmospheric oxygen concentrations also supported primitive land colonizers such as lichens and cyanobacteria (Yuan et al. 2005). The resulting organic acids and primitive soils increased rates of rock weathering, thereby increasing rates of CO₂ removal from the atmosphere. Diversification and proliferation of marine life were occurring by the Ordovician

Period, which culminated in another major glacial episode 458–428 Ma (Frakes and Francis 1988).

The evolution and diversification of land plants more than 350 Ma resulted in worldwide accumulation of vast quantities of coals in the Carboniferous Period (Fig. 2.1). Burial of these coals removed tremendous quantities of CO₂ from the atmosphere, contributing to Late Carboniferous glaciation. The evolution of advanced land plants with complex root systems also increased intensity of rock weathering and development of soils (Mackenzie and Anderssen 2013).

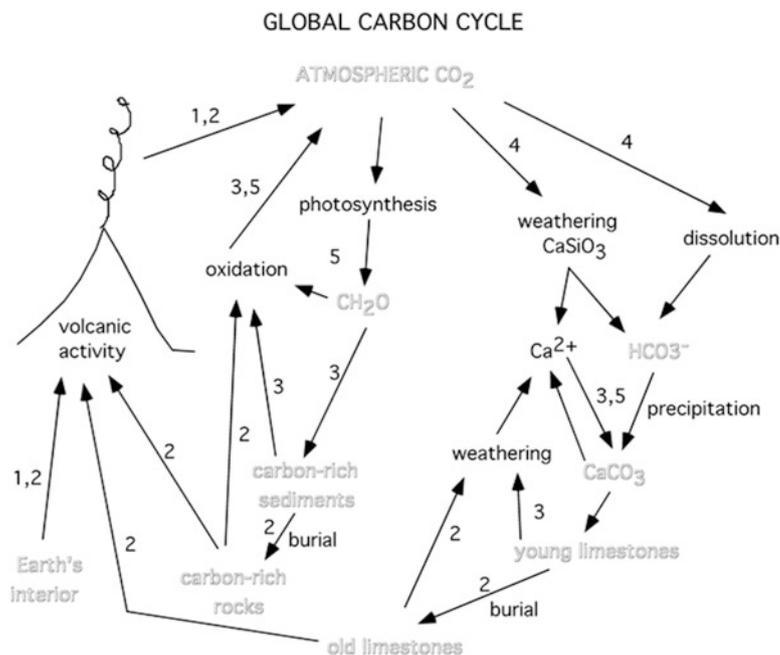
In the Mesozoic, many new taxa evolved with the potential to influence the distribution of CO₂ and HCO₃⁻ in the atmosphere, oceans, and sediments (Beerling and Berner 2005). During the middle Triassic to early Jurassic, several new groups of biogenic-sediment producers evolved and diversified, profoundly changing oceanic sedimentation and sequestration of organic matter. Planktic foraminifers and coccolithophorids, which represented new plankton lineages, began producing calcite shells and plates in the surface waters of the open ocean, so that their calcareous sediments today cover half the ocean floor (Kennett 1982). On shallow shelves, scleractinian corals and a variety of larger foraminifers developed symbioses with microalgae, greatly increasing their potential for carbonate production (Stanley 2003). High rates of CO₂ emission associated with rapid rates of seafloor spreading (i.e., volcanism) during the Cretaceous more than compensated for carbonate production by these new groups of organisms. And along with the new calcareous organisms, the proliferation of flowering plants on land and of extremely fast-growing diatoms in aquatic environments during the late Cretaceous and early Paleogene likely played a role in the global cooling that has occurred over the past 50 million years, culminating in the glacial advances and retreats of the Pleistocene over the past 2–3 Myr (Pagani et al. 2009).

Atmospheric CO₂ concentrations also vary on much shorter time scales. Concentrations were about 180–200 ppm during glacial advances and about 280 ppm during interglacials (Delmas 1992). These differences, their causes, and their significance is at the heart of modern studies of global climate change. Seasonal vegetation has such a strong influence on modern atmospheric CO₂ concentrations that differences between spring and autumn are routinely recorded at the Mauna Loa Observatory in Hawaii (Yajnik and Swathi 2012).

2.6 CO₂ and Time Scales

One of the key paradoxes of carbonates is that how rock weathering and limestone accumulation influence atmospheric CO₂ concentrations depends upon the time scale being considered (Kinsey and Hopley 1991). On the scale

Fig. 2.2 Simplified representation of the global carbon cycle over time. 1 Rates have slowed through Earth history. 2 Rates controlled by plate tectonics. 3 Rates change with sea-level fluctuations. 4 All of these processes influence rates. 5 Biological-scale processes



of Earth history, limestones are clearly important reservoirs of CO₂. This process can be summarized by the simplified expression:



Yet on time scales relevant to humans, Vescei and Berger (2004) and others have argued that production of limestones is a net producer of CO₂, based on the relationship shown in Eq. 2.2 (right to left), i.e., for each CaCO₃ precipitated from seawater, one HCO₃⁻ is converted to CO₂.

The key to understanding this paradox is recognizing that carbon exists in a variety of forms (Fig. 2.2). The ultimate source of carbon is from within the Earth. Volcanic activity delivers carbon to the atmosphere, where it primarily occurs as CO₂, or to the ocean, where it primarily occurs as HCO₃⁻. Organic carbon, produced mostly by photosynthesis (Eq. 2.6), occurs in short-term forms in living organisms, wood, soils, peat, water and sediments. Long-term storage of organic carbon occurs in hydrocarbon deposits and carbon-rich rocks such as coal and oil shales. Carbon in CaCO₃ sediments is recycled back into dissolved form when aragonitic lime muds from carbonate platforms such as the Bahama Banks are carried by currents into the deep ocean. Aragonite in limestone is also recycled during glacial advances when sea level can fall 100 m or more so that reef limestones are exposed to the air where they are recrystallized or eroded. CaCO₃ can be stored as limestones and dolostones within the Earth for millions to thousands of millions of years, until plate tectonic activity uplifts the rocks and exposes them to erosion, or until they are melted or metamorphosed by volcanic activity.

Figure 2.2 is a simplified representation of the CO₂ cycle, which is characterized by processes operating on four major time scales:

1. On the scale of Earth history and the evolution of life (10⁹ years–billions of years), CO₂ concentrations have been declining in the atmosphere to compensate for increasing solar output. Carbon has been stored in the Earth's crust as limestone and carbon-rich materials such as coal, oil shale, oil and gas.
2. On tectonic time scales (10⁶–10⁸ years–millions to hundreds of millions of years), atmospheric CO₂ has varied in response to changes in rates of volcanic activity, which are determined by rates of formation and subduction of the Earth's crust. Limestones and other carbon-rich rocks can be melted or metamorphosed by volcanic activity, recycling stored CO₂ back to the atmosphere-ocean pool.
3. On glacial/interglacial time scales (10⁴–10⁵ years–tens to hundreds of thousands of years), CO₂ in carbon-rich sediments is recycled when shallow-marine sediments are alternately deposited and eroded in response to sea-level rise and fall. During interglacial times when reefs are most actively accreting, the global oceanic HCO₃⁻ pool is more rapidly converted to CO₂ and CaCO₃, so atmospheric CO₂ concentrations rise somewhat. During glacial events, when sea level is low and reef limestones are actively eroded by CO₂ dissolved in freshwater, atmospheric CO₂ decreases and oceanic HCO₃⁻ increases.
4. Organisms typically act on biological time scales, which range from nanoseconds for enzymatic processes up to hundreds of years (<10³ years) for long-lived plants or fungi.

Humans, however, have perturbed long-term carbon cycles by extracting fossil fuels, which accumulated over hundreds of millions of years. Burning of fossil hydrocarbons has released huge quantities of CO₂ into the atmosphere. This process has shifted carbon from long-term storage in the Earth's crustal rocks to CO₂ in the atmosphere and oceans. At the same time, humans have tilled organic-rich soils, drained wetlands, and burned forests, thereby releasing carbon from shorter-term storage in soils and vegetation to CO₂ in the atmosphere. Deforestation, oxidation of organic matter in soils and wetlands, and widespread use of herbicides has also reduced rates of CO₂ removal from the atmosphere to short-term storage. Meanwhile, the decline in populations of reef-building corals has reduced calcification rates by these organisms. By disrupting both long and short-term carbon storage, human activities over the past 100 years have increased CO₂ concentrations in the atmosphere more than reef growth influenced CO₂ in the past 15,000 years. Within the twenty-first century atmospheric CO₂ concentrations are predicted to rise to concentrations comparable to those that occurred during the Eocene, 40–50 Ma, when the polar regions were nearly ice free (Feely et al. 2009).

2.7 Evolution and Carbonate Mineralogy

A geochemical paradox of declining concentrations of atmospheric CO₂ through time is that CaCO₃ has become increasingly easier for organisms to precipitate. Proterozoic oceans, responding to a more CO₂-rich atmosphere, were able to hold in solution comparably high concentrations of Ca²⁺ and HCO₃⁻, even in shallow water. Shallow-water CaCO₃ precipitation was probably a “daylight” activity, where photosynthesis within dense mats of cyanobacteria rapidly removed CO₂, creating local supersaturation of seawater with respect to CaCO₃. At night and possibly seasonally, seawater equilibrated with the atmosphere and became less supersaturated when photosynthetic rates slowed or stopped.

Approximately 570 Ma, a critical point was reached in the atmospheric-oceanic chemical system; shells evolved in several different groups of organisms. This event indicates that a geochemical threshold was reached; quite possibly atmospheric CO₂ concentrations dropped sufficiently so that low-latitude, shallow-water systems were consistently saturated with CaCO₃. Energetically, the protective and supportive advantages of a mineralized shell or skeleton finally exceeded the costs of shell precipitation and maintenance. Biomineralized organisms have since flourished in marine environments, secreting predominantly CaCO₃ or calcium phosphate shells or skeletons.

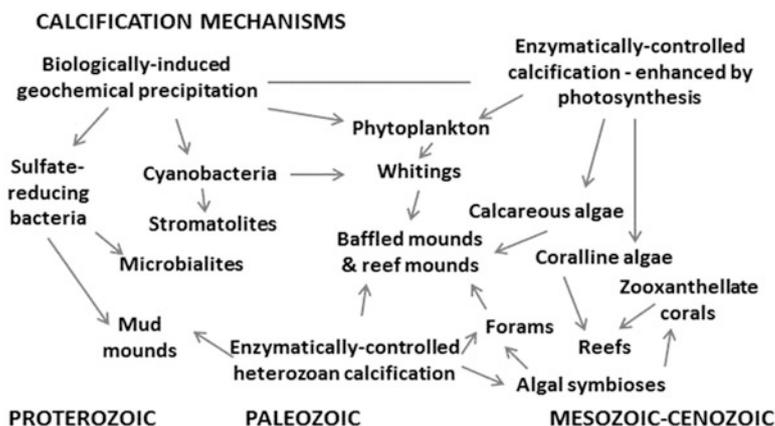
The succession of carbonate minerals through the geological record, both biogenic and inorganic, also indicates

geochemical influence (Sandberg 1983; Stanley and Hardie 1998; Hallock 2011). Although some of the earliest animals secreted calcium phosphate shells, calcite rapidly became the dominant shell material. Aragonite also appeared in shells in the early Paleozoic, though aragonitic algae did not produce significant bioherms until the Carboniferous. Aragonitic scleractinian corals did not evolve and construct reefs until the Triassic, only about 230 Ma (Stanley 2003). This trend reversed as aragonite production declined and calcite production increased during the Cretaceous Period, when atmospheric CO₂ concentrations rose as rates of volcanic activity increased at mid-ocean ridges and subduction zones. At the same time, rates of removal of CO₂ from the atmosphere by terrestrial weathering were relatively low because tectonic highlands were limited in extent (Eyles 1993). Aragonite-producing corals did not fully regain a dominant position until about 40 Ma, with the beginning of global cooling that led to the Neogene world of waxing and waning continental glaciers (Pomar and Hallock 2008).

Another critical factor controlling carbonate mineralogy is the Mg/Ca ratio in seawater, which is largely influenced by ion exchange at ocean-ridge systems (Hardie 1996). The alteration of new basalt at the seafloor removes Mg²⁺ from seawater and releases Ca²⁺; the rate of this exchange is dependent upon the rate of ocean crust formation. Thus, times of rapid seafloor spreading result not only in elevated concentrations of CO₂ in the atmosphere and HCO₃⁻ in seawater, but also higher Ca²⁺ concentrations in seawater. Such conditions are energetically more favorable for organisms that secrete calcite than those that produce aragonite. Conversely, when seafloor spreading rates slow, rates of Mg²⁺ removal from, and Ca²⁺ release into, seawater decline. The result is higher Mg/Ca ratios in seawater, which favors aragonite or Mg-calcite precipitation. Thus, tectonically-forced changes in seawater chemistry have influenced evolution and reef-building capacity of calcareous biotas, as well as the composition of carbonate cements (Stanley and Hardie 1998).

A second implication of the reduction of CO₂ in the atmosphere, and therefore the partial pressure of CO₂ in surface waters of the ocean, is the possibility that shortage of CO₂ can limit photosynthesis (Pomar and Hallock 2008). In shallow, warm, brightly illuminated waters, HCO₃⁻ is abundant and dissolved CO₂ is scarce. By using energy from photosynthesis to actively uptake Ca²⁺ ions from seawater, cells can use the calcification process to convert bicarbonate ions (HCO₃⁻) to CO₂ needed for photosynthesis (Cohen and McConnaughey 2003). Calcareous algae, which may have been the first multicellular organisms to utilize calcification this way, first appeared in the Cambrian. The Mesozoic diversifications of modern calcifying algae, including coccolithophorids in the plankton and melobesian green and coralline red algae in the benthos, along with the

Fig. 2.3 Calcification mechanisms and when they first were important in construction of biogenic reefs



proliferation of algal symbiosis in foraminifers, corals, and some bivalves, provide further evidence of biotic response to declining CO_2 concentrations in the atmosphere (Pomar and Hallock 2008).

Webb (2001) subdivided biomineralization into biologically-induced precipitation that is the by-product of metabolic activity, and biologically-controlled skeletogenesis that is enzymatically controlled. The first mechanism, which includes geochemical precipitation of CaCO_3 in response to CO_2 uptake by photosynthesis, was particularly effective in the Proterozoic under relatively high atmospheric pressures of CO_2 . The second mechanism, enzymatically controlled biomineralization, appeared in the Cambrian, probably when CO_2 concentrations declined sufficiently that the expenditure of energy for shell construction and maintenance became less than loss to predation without skeletal protection, at least in warm, shallow water (Fig. 2.3).

Precipitation of CaCO_3 induced by sulfate-reducing microbes is a type of biologically-induced calcification whose role in carbonate buildups has become increasingly recognized in recent years. Schlager (2000) referred to such carbonate textures in mud mounds at platform margin and upper slope depths as **automicrite**, in which microbial activity and decaying organic matter were key components (Monty 1995; Schlager 2000), and with marine cements as important secondary components. Pomar and Hallock (2008) suggested that automicritic boundstones represent a particular type of carbonate facies that predominated at times in Earth history when metazoan consumers were absent (e.g., Pre-Phanerozoic) or reduced in abundance (e.g., following mass extinction events). With few consumers, excess primary production in overlying waters allows organic matter to accumulate on the seafloor where it can be metabolized by microbial activity. For every two organic carbon atoms consumed during sulfate reduction, one of those carbons can be incorporated as CaCO_3 (Baumgartner et al. 2006), providing tremendous potential

for calcium carbonate precipitation where sufficient organic carbon substrate meets sufficient rates of exchange of seawater. Shelf edge and upper slope locations provide potential for organic accumulation, oxygen-minimum conditions, and water movement associated with internal waves (Pomar et al. 2012) or contour currents that provide necessary seawater exchange.

Enzymatically-controlled biomineralization mechanisms include (a) biomineralization by heterotrophic protists and metazoans, in which the energy source is ingested food; (b) biomineralization by mixotrophic protists and metazoans, in which photosynthetically derived energy significantly enhances calcification rates; and (c) biomineralization by photosynthetic protists (red and green algae, also coccolithophorids), in which photosynthesis provides energy for calcification and, at the same time, calcification can provide CO_2 for photosynthesis (Cohen and McConnaughey 2003; Pomar and Hallock 2008). The potential for calcification to provide CO_2 for photosynthesis became particularly advantageous when reduced atmospheric CO_2 concentrations began to limit aquatic photosynthesis in warm, shallow seas.

The strategies whereby photosynthesis provides energy for enzymatically-controlled biomineralization arose independently in several lineages of Foraminifera, Porifera, Cnidaria, and Mollusca, as well as in at least three divisions of algae. This mechanism has profound and almost paradoxical implications for atmospheric CO_2 concentrations. The very process that makes CO_2 instantaneously available for photosynthesis can be responsible for the long-term removal and burial of CO_2 as CaCO_3 .

Global cooling, on the other hand, reduces the rate of CO_2 burial by calcification. If organisms draw too much CO_2 out of the atmosphere, onset of glaciation lowers sea levels and reduces the habitats of warm-water calcifying organisms, as well as that of terrestrial plants. Lowered sea level also prevents burial of some limestones, instead exposing them to erosion and returning the HCO_3^- to the hydrosphere.

Paradoxically, as atmospheric CO₂ concentrations decline, aragonite, which is more rapidly recycled by freshwater weathering during glacial advances, becomes easier to precipitate in warm waters.

2.8 What Is Required to Accumulate CaCO₃

Although calcium carbonate sediments have been produced and limestones have been accumulating for more than 3,500 Myr of Earth history (e.g., Grotzinger 1989), major accumulations of limestone represent deposition during relatively small proportions of geologic time (Schlager 1981). Times and places for substantial sedimentary carbonate accumulation require an array of appropriate environmental conditions, as well as appropriate suites of carbonate-producing biotas. The classes of carbonate sediments (Lees 1975; James 1997), combined with the guilds of Fagerstrom (1987), can be merged into the concept of “carbonate factories” (Schlager 2000), including the tropical shallow-water factory, dominated by photoautotrophic, biotically-controlled skeletal production and abiotic precipitates; the cool-water factory, dominated by heterotrophic skeletal production; and the mud-mound factory, dominated by biotically-induced production (predominantly microbial) and abiotic precipitates that formed at or near the sea floor. Two additional factories involve production of carbonates within the water column: the neritic carbonate factory (whitings), which are biotically-induced by photosynthetic microbes and microalgae in highly supersaturated waters (Robbins and Blackwelder 1992), and the pelagic carbonate factory of biotically-controlled skeletal production, either directly associated with photosynthesis (coccolithophorids) or by planktic foraminifers, many of which host algal symbionts.

A major limiting environmental factor is that shallow, euphotic shelf areas suitable for prolific production and accumulation of reefal carbonates represent less than 2 % of either the Earth’s surface or the ocean volume. Furthermore, preservation of CaCO₃ is as important as production for accumulation and persistence in the rock record. Several factors influence both production and preservation potential within the limited available environments. One very important condition is the persistence or repeated submergence of substantial areas of shallow shelf at mid to low latitudes over sufficient time intervals so that limestones can accumulate, i.e., the presence of accommodation space (Pomar 2001). A second condition is relatively low input of terrigenous sediments and inorganic nutrients, especially nitrogen and phosphorus (Hallock 2001, 2011). A third condition is the presence of biota that can precipitate or enhance the precipitation of CaCO₃.

The persistence or repeated submergence of substantial areas of shallow shelf at mid to low latitudes is controlled by plate tectonics and climate, which together control sea level. Rates of sea-floor spreading influence the average depth of the ocean. When sea-floor spreading rates are high, the average depth of the ocean basins is shallower, pushing water higher onto the continental shelves (Kennett 1982). The relative proportions of continents that are colliding or overlying rifting centers also influences global and local sea level. For example, all of the major continents came together in the late Paleozoic to form the supercontinent of Pangea (Fig. 2.4). This can be compared to India colliding with Asia to form the Himalayas, but on a much larger scale. As the continents merged, spreading rates slowed, sea level relative to the continents receded, and there were few shallow-shelf areas; most that occurred were inundated by terrigenous sediments eroded from the highlands. Through the latest Paleozoic and into the early Mesozoic, Pangea remained as one supercontinent. Heat from the Earth’s interior accumulated beneath Pangea, thermally uplifting and rifting it apart. The supercontinent at this stage was somewhat analogous to Africa today, which has very narrow continental shelves and where eroding highlands plunge into deep rift valleys. As the continents rifted apart and moved away from one another during the Cretaceous (Fig. 2.5), they slowly subsided. Australia today is probably the closest analogue for continents in the Cretaceous, with generally low relief, passive margins on three sides, and a broad, shallow sea to the north between the continent and tectonically active Indonesia and New Guinea. In the Cretaceous, higher elevations were primarily in island arcs analogous to the Marianas Islands or Japan.

Sea-floor spreading rates and climate interact through a variety of feedback mechanisms to further influence sea level (Worsley et al. 1986). As the continents ground together to form Pangea, sea-floor spreading and overall volcanic rates slowed, further lowering sea level. Reduced volcanism resulted in reduced emissions of volcanic gases, including CO₂. As a result, the Earth’s climate was cooler. Conversely, as continents moved apart, sea-floor spreading rates increased, volcanic rates increased, and CO₂ emissions increased, triggering global warming in the Jurassic and Cretaceous. Relative sea level influences global climate because it alters the reflectivity (albedo) of the Earth; land is more reflective than water, while ice is more reflective than land. The higher the sea level, the more solar energy the Earth can capture and so the warmer the climate. Globally warm climates, known as greenhouse conditions, promote even higher sea level, because polar ice is minimal to non-existent. Finally, without polar ice, deep waters in the oceans are much warmer, so thermal expansion of the water further raises sea level.

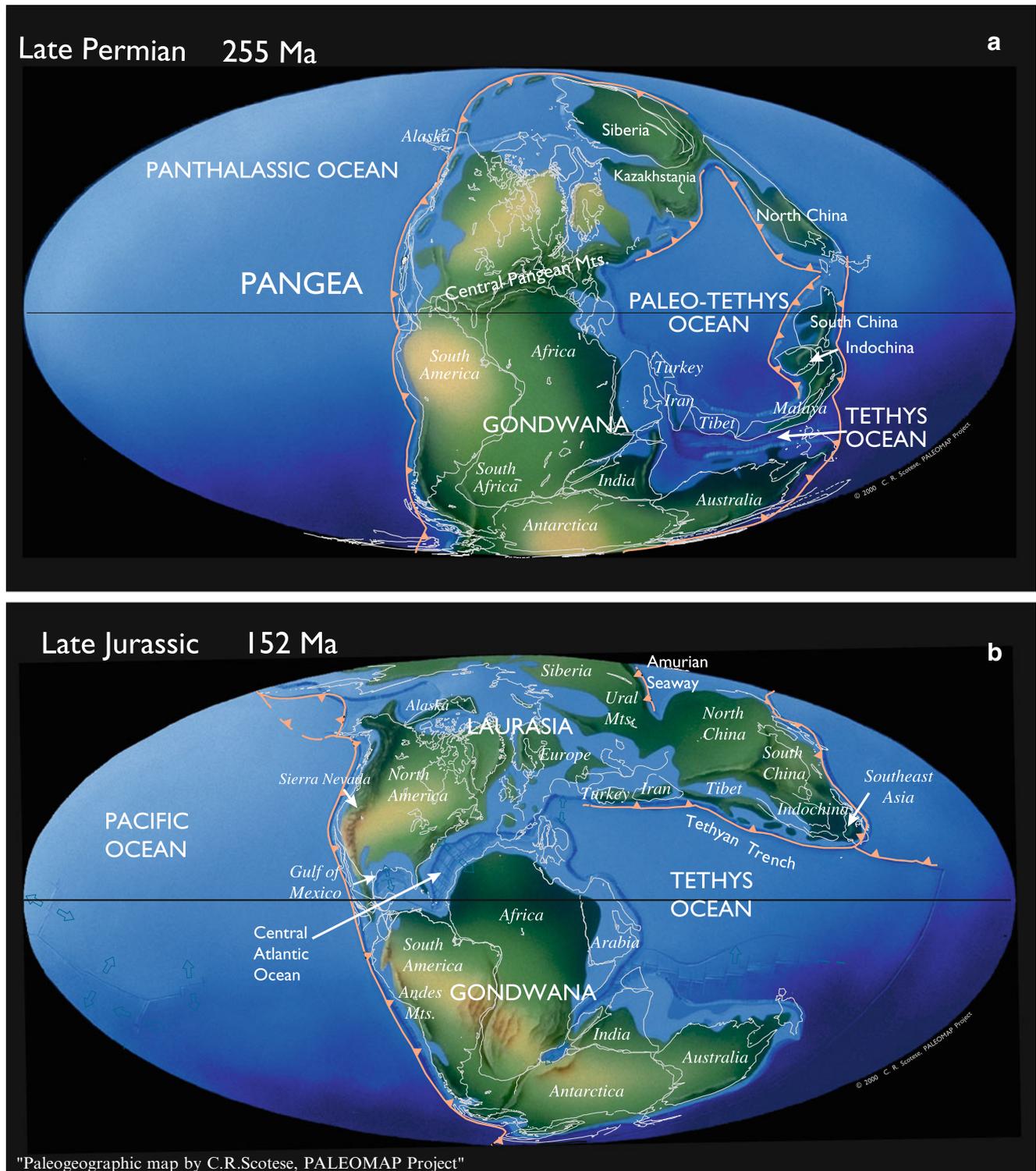


Fig. 2.4 Plate reconstructions for (a) the Permian Period, illustrating the supercontinent Pangea that formed during the late Paleozoic and (b) the Late Jurassic Period (Middle Mesozoic), illustrating the opening of the North Atlantic (From Scotese 2002)

The differential heating of the equator relative to the poles drives atmospheric and oceanic circulation. Plate tectonics control the positions and elevations of land masses relative to the oceans and so further influences atmospheric

and ocean circulation by providing passageways and barriers (Eyles 1993). For example, separation of Antarctica and Australia in the late Eocene and the opening of the Drake Passage between Antarctica and South America in the

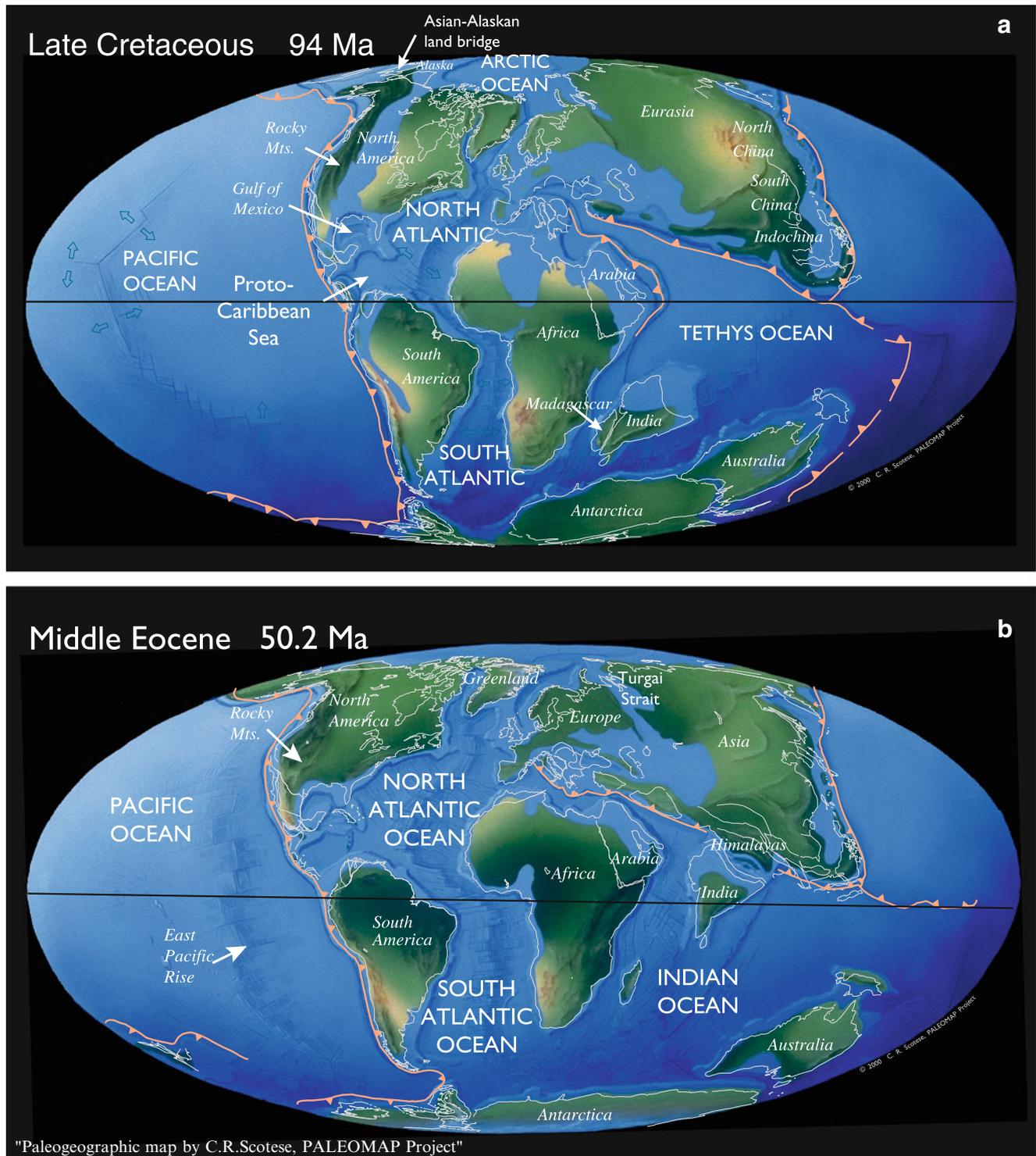


Fig. 2.5 Plate reconstructions for (a) the Late Cretaceous, after the breakup of Pangea, when circumtropical circulation was well developed and (b) the middle Eocene, illustrating somewhat restricted

circumtropical circulation and hints of future south circumpolar circulation (From Scotese 2002)

Oligocene (Figs. 2.5 and 2.6), enabled the development of the circumpolar current in the Southern Ocean (Flower 1999). This caused the climatic isolation of Antarctica and polar cooling. Closure of the Panamanian Seaway over the past few Myr restricted and ultimately terminated flow of the

Caribbean Current into the Pacific, diverting the current northward to accelerate the Gulf Stream (Lutz 2010). Delivery of warmer water to high northern latitudes increased snowfall, contributing to glaciation (Raymo 1994).

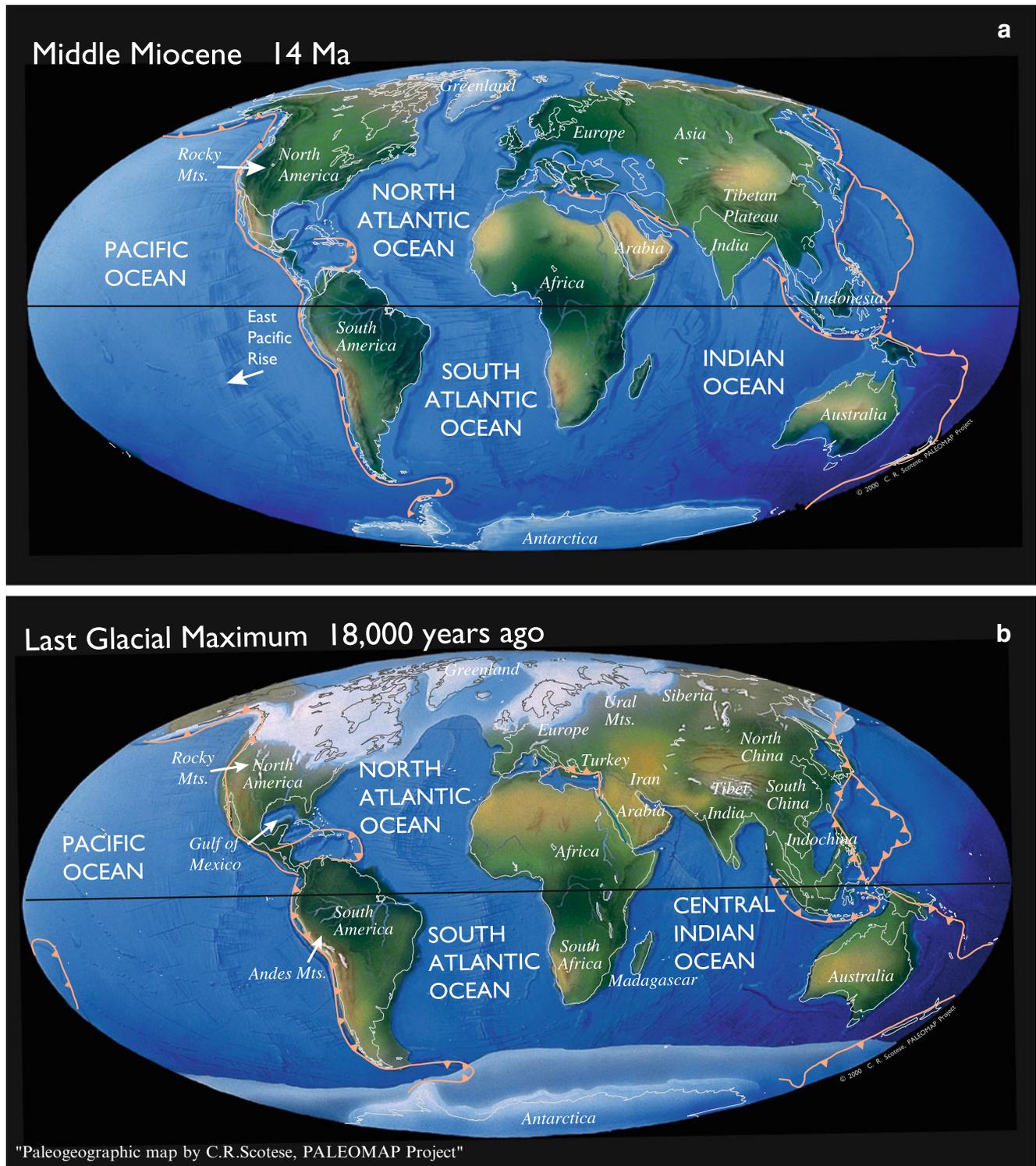


Fig. 2.6 Plate reconstructions for (a) the middle Miocene, when the Central American Seaway was still open but circumtropical circulation diminished as India and the Middle East collided with Asia, while south

circumpolar circulation was complete and (b) the Pleistocene – the last glacial maximum, when sea level was about 130 m lower than at present (From Scotese 2002)

Global climate is strongly influenced by CO_2 concentrations in the atmosphere (Pearson and Palmer 2000), and therein lies yet another paradox of limestones

and coral reefs. Times of global warming (Fig. 2.1) were times of widespread limestone deposition, but not of coral-reef development (Stanley and Hardie 1998; Hallock 2011).

For example, paleo-isotopic evidence indicates that tropical sea-surface temperatures during the Cretaceous and early Paleogene were at least 28–32 °C (Pearson et al. 2001), while seawater in the polar regions and deep seas was 10–15 °C warmer than today (Flower 1999). Yet coral reefs did not widely flourish until the Oligocene Epoch, with the onset of global cooling under declining atmospheric CO₂ concentrations.

2.9 History of Biogenic Reefs Through Time

The Geologic Time Scale (Fig. 2.1) has five major divisions called Eons, each of which is characterized by the appearance of major groups of organisms that proliferated and profoundly influenced the subsequent Eon. The earliest history of the Earth is referred to as the Hadean Eon, which lasted ~600 Myr during which time the newly formed planet was cooling. The Archean Eon, ~1,500 Myr long, was the time when prokaryotic microbial life appeared, proliferated and diversified, leaving the earliest evidence for stromatolites, for photosynthesis, and ultimately, for the first free oxygen (Dobretsov et al. 2008).

The Proterozoic Eon was truly the “Age of the Microbes”, but it was also a time of profound environmental change. Many microbes were driven to extinction or “underground”. Some adapted by developing symbioses with other microbes (producing nucleated, eukaryotic cells) that allowed them to survive the Earth’s first “pollution” event – the Great Oxygenation Event (Holland 2006) of shallow aquatic systems, which occurred between ~2,400 and 2,000 Ma (Paleoproterozoic). The first evidence for eukaryotic organisms has been found in some of the youngest rocks that are considered Paleoproterozoic. Oxygen is toxic to all cells to some degree, which is why eukaryotic cells have anti-oxidant defense mechanisms. Once cyanobacteria developed photosynthesis, using sunlight to fix water and carbon dioxide into organic matter, their proliferation was assured. At the same time, anaerobic bacteria became restricted to anaerobic environments, were forced to adapt, or perished.

Evidence for very early oxygenation of shallow aquatic environments is found in banded iron deposits, which occur on the ancient cores of all the continents and have been utilized as iron ores by human populations for thousands of years (Cloud 1973). Iron (Fe) comes in two forms, reduced Fe²⁺ and oxidized Fe³⁺. Igneous rocks are rich in Fe²⁺, which is quite soluble in water. However, if there is free oxygen in the atmosphere or dissolved in water, the Fe²⁺ oxidizes to Fe³⁺, which is very insoluble. The most likely way that immense quantities of iron could accumulate with alternating layers of chert was when the atmosphere still lacked oxygen. As water weathered rocks on land, Fe²⁺

readily dissolved, along with H₄SiO₄. The Fe²⁺ laden rivers and streams flowed into lakes, lagoons or shallow-shelf areas, where cyanobacteria were actively photosynthesizing and oxygenating the waters. The iron oxidized, producing iron oxides that accumulated as sediments.

Calcium is also very abundant in volcanic rocks, and is readily dissolved out of those rocks by CO₂-rich rainwater, resulting in fresh waters laden with Ca²⁺ and HCO₃⁻ flowing into shallow waters where active photosynthesis induced precipitation of CaCO₃, resulting in stromatolites or whiting-type muds. Mesoproterozoic age stromatolitic limestones also occurred nearly worldwide, sometimes alternating with shales that alternate green and red because they were deposited under either anoxic (green shales) or oxygenated (red shales) conditions.

Eukaryotic protists that emerged in the Mesoproterozoic included the red and green algae. Other eukaryotic innovations, including evidence for sexual reproduction and multicellularity, first appeared in the Mesoproterozoic, fully developing in the final Era of the Proterozoic. The Neoproterozoic Oxygenation Event (Och and Shields-Zhou 2012), during which multicellular organisms began to proliferate, partly coincided with extensive glaciation during what is known as the Cryogenian Period. The final period of the Neoproterozoic, the Ediacaran, is known for its diversity of novel fossils of soft-bodied organisms that represent most known animal phyla, as well as several enigmatic ones (Knoll et al. 2006). Stromatolites and other microbolites remained the dominant reef structures through this final Era before the emergence of shelled metazoans that heralded the Phanerozoic Eon (Grotzinger and Knoll 1999).

Whether Proterozoic or Phanerozoic, microbes have been producing microbolites and stromatolites for more than 3,400 Myr; shell-forming animals for just 570 Myr (Fig. 2.1). Factors that have controlled the formation of biogenic reefs through time include climate, ocean chemistry and circulation, availability of habitat, and existence of reef-forming biotas. The history of reef development and reef-building biotas has not been continuous. Instead, it has been characterized by long periods of persistence of simple mud-mound or reef-mound communities, followed by episodes of development of complex baffler and framework-building communities, then termination of the complex communities by major extinction events. The compendium edited by Kiessling et al. (2002) provides a comprehensive view of distributions, biotas, and dynamics of Phanerozoic reefs; the summary below provides only a brief glimpse of reef history.

Kiessling (2001) defined four basic reef types: (a) true reefs constructed largely by a framework of skeletal remains of reef-building organisms; (b) reef mounds, where the remains of skeletal reef-building organisms and mud matrix are about equally important; (c) mud mounds, which have

only minor skeletal components; and (d) biostromes, which have abundant skeletal components but minimal depositional relief. These categories, as well as other ways that reefs have been classified, are more convenient than mutually exclusive. Even within individual reef structures, there may be a colonizing stage by a binder community, a diversification stage by a baffling and binding community, and a climax stage of framework builders, binders, dwellers, and destroyers (Fagerstrom 1987).

From 3,400 to 540 Ma, prior to the appearance of shelled animals, whether stromatolitic buildups developed was controlled primarily by suitability of physical and chemical environments. Stromatolitic limestones and dolostones accumulated where seawater was warm enough and shallow enough for photosynthesis by cyanobacteria to promote CaCO_3 precipitation over sufficient area and time to be preserved, or where organic matter accumulated on the sea floor under conditions that sustained carbonate precipitation in conjunction with sulfate reduction or other microbial processes. With the evolution of the Foraminifera, as well as multicellular life such as worms and trilobites, that bulldozed through the algal mats, eating and disrupting them, stromatolite preservation potential declined (Conway Morris 1993; Bernhard et al. 2013). Kiessling (2001) noted that microbial activity has become less prominent in reefs over time, though stromatolites remain “uncommonly common” even in Holocene sediments (Reid et al. 1995, 2003).

2.9.1 Paleozoic Era: Time of Ancient Animal Life

The first biomineralized animal communities to act as significant bafflers appeared in the lower Cambrian Period, from about 550 Ma (Wood 1999). The archaeocyathids or “ancient cups” are thought to have been calcified sponges; their erect skeletons trapped calcareous muds, which may have been chemically precipitated in response to photosynthesis in cyanobacterial mats or in the plankton. Calcified cyanobacterial/algal mats and encrusters formed major components of the archaeocyathid reef mounds. Trilobites and sponges were among the inhabitants. “Reef tracts” produced by these communities were extensive in Siberia, southern Australia, and Antarctica, which lay in low latitudes at that time (Copper 1994). By the Middle Cambrian these primitive sponges were mostly extinct, so microbial processes again largely produced the reef mounds that have been preserved (Rowland and Shapiro 2002).

The second major diversification of calcified algae and animals capable of producing, trapping and binding large volumes of calcareous sediments began in the Ordovician Period (~500 Ma). Sponges and the earliest corals played major baffler roles, cyanobacteria persisted as binders, while

trilobites and primitive snails grazed the algae or fed upon microbe- and algae-rich muds (Webby 2002). By the Middle Ordovician, a greater diversity of calcified animals had evolved. These organisms were more prolific sediment producers, more effective sediment bafflers, and included taxa with the potential to construct framework. Important contributors included bryozoans; stromatoporoids (calcareous sponges); and *Solenopora*, which have long been considered calcareous red algae, though Riding (2004) argued that they were chaetetic sponges. The early reef mounds provided a multitude of niches for trilobites, brachiopods, snails, cephalopods (including ancestors of the chambered *Nautilus*), other animals that fossilized, and probably many soft-bodied organisms that left little or no fossil record.

By the Late Ordovician, tabulate and rugose (horn) corals had become important components of the reef community (Webby 2002). A typical succession (e.g., James 1983; Copper 2002) consisted of a baffler-colonizer community of stalked crinoids and bryozoans that trapped muds and began to accumulate a structure. Soon this habitat was invaded by sponges, solitary horn corals, small tabulate corals, and massive stromatoporoids, which together constructed larger skeletal structures and trapped calcareous muds and sands. Algae, smaller corals, bryozoa, brachiopods, clams, snails, trilobites and other arthropods found shelter or food within the reef. Encrusting stromatoporoids bound the skeletal elements together, and typically overgrew and eventually dominated the whole structure. In this climax phase, which may have been very wave resistant like a modern coralline algal ridge, the diversity of species was low.

Interesting comparisons can be made between the Middle Paleozoic (Ordovician to Devonian) bioherms and modern coral reefs. The shells and skeletons were predominantly constructed of calcite, whereas modern corals and calcareous algae secrete aragonite skeletons (Stanley and Hardie 1998). Individual structures in the Paleozoic were often similar in size to small patch reefs, connected by expanses of calcareous sands or muds, so regional accumulations of limestone were comparable in scale to modern reef tracts (Webby 2002). However, there was no strong evidence for algal symbiosis in the calcifying animals and calcareous algae were of limited importance. Thus, primary calcification mechanisms responsible for precipitation of most of the early to middle Paleozoic limestones were likely biologically-enhanced geochemical precipitation, with microbes continuing to play major roles, and biomineralization by animals. Extensive Devonian reef complexes along the northern margin of the Canning Basin, Western Australia, as well as others found in Alberta, Canada, Belgium and Germany, are comparable in size to, or even larger than, modern western Atlantic reef systems like the Florida Keys reef tract (Stanley 1992; Webb 2002).

In the Late Devonian (~360 Ma) a major extinction event eliminated most of the reef-building coral-stromatoporoid communities. Subsequently, carbonate production was predominantly microbial, including automicrites in deeper-water mounds and stromatolites and calcimicrobolites in shallower water. Corals and stromatoporoids continued their presence in some Canadian reef mounds. Early Carboniferous buildups scattered around the world were mud mounds containing mostly automicrites and cements, sometimes associated with crinoids and bryozoans. Rugose corals, chaetids, and brachiopods were among the metazoan taxa that diversified the mud mounds as carbonate-producing metazoan communities recovered (Webb 2002).

Late Carboniferous biotas contain many unusual and taxonomically problematic groups that mostly represent binder and baffler communities. Wahlman (2002) recognized several types of buildups along a spectrum, depending upon whether major components were algal, sponge or bryozoan, and whether environmental controls were temperature, water depth, light penetration, etc. A prominent feature was the prevalence of aragonite-producing phylloid algae and problematic aragonite-producers identified as *Paleoaplysina*, that may have been codiacean algae or possibly hydrozoans. The evolution and diversification of large, structurally complex fusulinid foraminifers represent the strongest evidence for algal symbiosis in important calcareous-sediment producing taxa in the Paleozoic. These two groups, the phylloid algae and the fusulinids, may represent the first major proliferation of organisms calcifying to enhance photosynthesis. On a global scale, the continents were colliding to form Pangea. Glaciation was occurring; reduced atmospheric CO₂ concentrations (Sandberg 1983) and higher Mg/Ca ratios in seawater reflected reduced seafloor spreading rates (Stanley and Hardie 1998). Both factors were conducive to aragonite precipitation and to calcification to enhance photosynthesis (McConnaughey and Whelan 1997; Pomar and Hallock 2008). Moreover, interglacial sea-level rise provided accommodation space for carbonate buildups, while subaerial dissolution and cementation during sea-level regression promoted lithification of carbonate sediments, increasing their preservation potential.

The Permian, which was the last period of the Paleozoic, was characterized by tectonic and volcanic activity as the assembly of Pangea came to its climax (Fig. 2.4). Numerous shallow seas and basins developed and were destroyed during this period (Weidlich 2002). A combination of the variety of regional environmental conditions during deposition, and the economic resources that resulted, have contributed to the diversity of biotas and interpretations of Permian reefs and limestones.

Among the most studied buildups are those of the Permian Basin in west Texas and southeastern New Mexico, USA

(Weidlich 2002). The long-lasting but discontinuous accumulation of the Capitan reef complex has revealed that macrofauna were not essential to the buildup. According to Weidlich (2002), the most important constituents of the Capitan Reef limestones include micro-framework produced by diverse assemblages of low-growing algae and microbes. These rocks are also notable for extensive geochemically precipitated cements, to the extent that more than three-quarters of the limestone can be micro-framework of low-growing producers and carbonate cements that precipitated in seawater, especially under hypersaline conditions. A diverse community of bafflers and binders included sponges, bryozoans, crinoids, and brachiopods that trapped and bound muds and coarser sediments produced by the community (Wood 1999). An immensely diverse sediment-producing dweller group, such as foraminifers (including fusulinids), snails, clams, small corals, brachiopods, cephalopods, and arthropods, thrived in these buildups.

Further demonstrating the diversity of Permian carbonate factories, the succession of buildups in the Permian Basin are quite different from three other carbonate factories that Weidlich (2002) described from the Middle and Late Permian elsewhere. The Tethyan carbonate factories, preserved in limestones deposited on the shelves, basins and terrains to the east of Pangea, were characterized by a diversity of reef types and macro-reef builders with high percentages of carbonate mud. Other oceanic (island-arc) terrains lacked macro-reef builders, instead were characterized by calcimicrobes and carbonate muds. The fourth carbonate factory, with abundant bryozoans, brachiopods and crinoids, was a cool-water facies.

2.9.2 The End-Permian Mass Extinction

The Permian-Triassic boundary (PTB) was characterized by the most extreme mass extinctions of the Phanerozoic. Barash (2012) reviewed the extinctions, geochemical signals, and discussed the series of events that likely contributed to the severity and timing. Estimates of extinction of 96 % of marine invertebrates and 70 % of terrestrial vertebrates are common in the literature. The first major extinction event occurred in the mid to late Permian (260 Mya), primarily affecting marine benthic organisms. Subsequently, the events of the PTB at 251–252 Mya also impacted the plankton, with near complete collapse of marine ecosystems.

The assembly of Pangea, which ended in the mid/late Permian, resulted in a land mass that stretched pole to pole. The Panthalassa Superocean covered roughly two-thirds of the Earth's surface. The Tethyan Sea was bordered on the west by Pangea and was partly separated from Panthalassa by smaller land masses to the east.

The PTB events apparently involved successive environmental changes that became increasingly inhospitable to protists and metazoans (Barash 2012). Extensive, explosive volcanism spewed ash, aerosols, and gases such as CO₂ and H₂S, chlorine and fluorine into the atmosphere in multiple locations. The eruptions that produced the Siberian Traps represent one of the largest volcanic outpourings in Earth history, certainly in the Phanerozoic. Moreover, the magma passed through and burned vast coal beds, releasing much more CO₂. And the eruptions occurred in exactly the time interval, 250–252 Mya, as the PTB mass extinctions. Global warming likely was interrupted by episodes of “volcanic winters”, when ash and aerosols reduced light reaching the Earth’s surface, thereby reducing photosynthesis and primary productivity. Conversely, when atmospheric conditions allowed sufficient sunlight to reach the sea surface, volcanic ash likely fertilized high rates of primary productivity by cyanobacteria. Warming of deeper ocean waters, combined with excess sinking of organic matter, promoted superanoxia, which ultimately spread to shelf environments. Further global warming likely resulted from the release of methane from gas hydrates in marine sediments. Sulfur and halogen-rich volcanic aerosols eroded the stratospheric ozone, further impacting organisms, while allowing high-energy, short wavelength (ultraviolet) solar radiation to reach the Earth’s surface and further contribute to global warming. Certainly all of these factors would have devastated marine and terrestrial protists and metazoans. Moreover, Barash (2012) further discusses multiple meteor impacts that have been documented within the same time interval, proposing that they further contributed to the collapse of eukaryotic organisms and communities.

2.9.3 Mesozoic Era: Time of Intermediate Animal Life

The PTB was followed by a prolonged episode (at least 6–8 Myr) in which bioherms produced by metazoan communities are absent in the rock record (Flügel 2002). The few, small, Early Triassic buildups that have been recorded were produced by microbial processes, especially associated with low oxygen conditions. When substantial carbonate buildups reappeared in the Middle Triassic, microbial contributions continued to be primary or at least secondary components.

Because rates of sea-floor spreading continued to be low, Mg/Ca ratios in seawater were conducive to “Aragonite Seas” (Fig. 2.1) from the late Paleozoic through the Triassic Period (Stanley and Hardie 1998). In the Middle Triassic, sponge-algal communities gradually resumed production of reef mounds and included among their subsidiary fauna the first scleractinian corals, which produced aragonite skeletons

(Stanley 2003). According to Flügel (2002), coralline sponges were the major baffle and frame-building organisms in many Triassic reefs; among the very diverse sponge biota were Mg-calcite and aragonite producing taxa. By the late Triassic, the scleractinian corals had diversified and new forms restricted to shallow, brightly illuminated waters very likely hosted zooxanthellae (Stanley 2003). Corals and coralline sponges produced framework, while other sponges, as well as bryozoans, bivalves and serpulid worms, were more minor constructors. Calcareous green algae (producing aragonite) and coralline red algae (Mg-calcite) contributed significantly to Middle and Late Triassic reefs (Flügel 2002). Associated fossilized taxa were a diverse group of ammonites, brachiopods, bivalves, snails, echinoderms, foraminifers, and worms.

The story of Triassic reef development at first glance looks like a progression from microbial to sponge-algal to coral-sponge (metazoan-dominated) reefs. In reality, the global-environmental instability that peaked with the PTB continued, with relatively short pulses of reef blooms, setbacks, and episodes of diversification (Flügel 2002). Yet the importance of photosynthesis in reef construction was evident, both in the significant contributions of calcified algae and the emergence of zooxanthellate corals.

The end-Triassic mass extinction abruptly terminated reef-building assemblages. Estimates of the percentages of surviving taxa differ among published reports. For example, Wells (1957) estimated that ten scleractinian genera survived into the Jurassic, while Flügel (2002) suggested as few as 3 of 77 Triassic coral genera survived into the Jurassic, with only slightly higher survival in key reef-associated sponge genera. More recently, Lathuiliere and Marchal (2009) reported at least 20 surviving genera. Moreover, the causes of the extinction event are not well constrained, though ocean acidification associated with emplacement of the Central Atlantic Magmatic Province is a primary suspect (Martindale et al. 2012). As discussed earlier for the PTB, massive volcanic events can produce a cascade of detrimental environmental conditions. The lack of preservation potential associated with ocean acidification also can amplify the apparent abruptness of an extinction event.

Following extinctions at the end of the Triassic, Jurassic reef-building communities slowly reestablished, requiring about 8 Myr to produce significant buildups. The breakup of Pangea and associated acceleration of sea-floor spreading rates resulted in generally rising sea level, increasing atmospheric CO₂, and declining Mg/Ca ratios in seawater. Several evolutionary events, as well as environmental trends, emerged in the Jurassic that fully developed in the Cretaceous Period, with profound influence on global carbonate production and accumulation, and upon global carbon cycles. The appearance of calcareous nanoplankton including coccolithophorids in the Early Jurassic, and of the

planktic foraminifers in the Middle Jurassic, provided the potential for carbonate production throughout the surface oceans and accumulation of pelagic carbonates in deep-sea settings (depending upon ocean chemistry). On the shallow shelves, large bivalve species proliferated as carbonate producers, and trapping carbonate muds produced by the neritic whiting factory. By the Cretaceous, bivalves dominated shelves and platforms, especially in tropical seas (Höfling and Scott 2002; Johnson et al. 2002).

Leinfelder et al. (2002) grouped Jurassic reefs into three basic types: coral, siliceous sponge, and pure microbolite, with coral-microbolite intergrades among the most prominent. These authors also noted that buildups produced largely by bivalves also were relatively common. The breakup of Pangea provided extensive “trailing-margin” continental shelves where mixed terrigenous and carbonate sedimentation was prevalent. Nutrients carried into the shelf environments by terrestrial runoff likely promoted plankton densities and accompanying whittings that favored filter-feeding sponge and bivalve assemblages over zooxanthellate corals (Leinfelder et al. 2002). Pomar and Hallock (2008) also noted that microbolite buildups were associated with excess organic matter, low oxygen, and sulfate reduction in outer shelf/slope settings.

The 80 Myr Cretaceous Period is characterized by widespread carbonate depositional systems, including reefs, platforms and pelagic carbonates. The term “Cretace” refers to chalk (pelagic-carbonate) terrains that are widespread in northern Europe (Harbaugh 1974). Two global “crises” resulted in extinctions and association changes that influenced both benthic and planktic biotas, one crisis in the mid-Early Cretaceous and the other in the early-Late Cretaceous (Höfling and Scott 2002).

The most important metazoans in Cretaceous buildups were the rudistid bivalves. There is little evidence that rudists had algal symbionts; the prevalence of carbonate muds in most rudist buildups indicates that water transparency may have been poor. Skelton et al. (1992) interpreted rudists as having been super bafflers, trapping huge quantities of mud and actually growing upward supported in mud. Characteristically, rudist thickets and buildups have relatively few species and few associated organisms. Banktop habitats occupied by rudist taxa may have been somewhat analogous to those of modern seagrass beds; rudist thickets trapped sediments carried in by the currents as well as sediments produced in situ by the breakdown and bioerosion of the rudists themselves. Because exceptional high-latitude warming occurred in the Cretaceous, the low latitude banktop habitats were consistently very warm and often hypersaline. The more biologically complex bivalves may have been better able to survive these extremes than zooxanthellate corals (Johnson et al. 2002), whose symbiotic

relationship is particularly sensitive to temperatures above 30 °C (Wooldridge 2013).

Geochemical conditions also favored rudists over corals (Stanley and Hardie 1998; Pomar and Hallock 2008). The rudists secreted outer shells of calcite, with an inner layer and muscle insertion sites of aragonite (Skelton 1976). Proportions of aragonite to calcite varied in different lineages of rudists; some secreted shells were as much as 60 % aragonite, though many were less than 30 % (Kauffman and Johnson 1988; Skelton and Gili 2012). Whatever the proportions, the predominance of rudists over wholly aragonitic corals represented a decline in aragonite production associated with photosynthesis. Rapid sea-floor spreading enhanced removal of Mg^{2+} from seawater at mid-ocean ridges, thereby promoting calcite precipitation (Stanley and Hardie 1998). Volcanic emissions associated with rapid spreading rates also elevated CO_2 in the Cretaceous atmosphere, making aragonite more soluble and therefore less energetically advantageous to produce (Hallock 2011). As noted by Pomar and Hallock (2008), tropical environmental conditions during the Cretaceous favored biologically controlled metazoan calcification combined with neritic production of biologically-induced whiting-type calcitic muds. Photosynthetically-enhanced calcification by scleractinian corals with zooxanthellae was largely restricted to higher latitude and mesophotic (low-light, deeper) shelf margins.

2.9.4 Cretaceous Boundary Extinctions

A major biotic crisis ended the Cretaceous Period. While this mass extinction event is best known for the demise of the dinosaurs, rudist bivalves also became extinct (Johnson et al. 2002), as did most shallow-water, tropical carbonate-producing protists and animals (MacLeod and Keller 1996). Few calcareous tropical species survived the terminal Cretaceous extinction event.

During the Cretaceous many scleractinian corals occupied deeper shelf and upper slope environments, perhaps to escape warm, saline waters or direct competition with rudists (Johnson et al. 2002). As a result, at least nine genera (Rosen 1998) and possibly 26 genera (Fig. 13.9) survived the extinction. The terminal Cretaceous event was similar to those of the early Cambrian, late Ordovician, late Devonian, and late Permian in that reefs generally vanished a million years or more before the final extinction events (Copper 1994). Thus, episodes of environmental perturbation or climatic deterioration that caused collapse of reef ecosystems preceded the terminal extinction events, which geologists have used to define significant boundaries in geologic time.

Two major competing explanations for mass extinctions, including the Cretaceous-Paleogene (K-P) boundary extinctions, are bolide (meteor or comet) impacts and extensive volcanic episodes (Alvarez 2003). Because bolide impacts are instantaneous events, while extensive volcanism can take place over 100,000 to a million years or more, scientists with evidence for more gradual events at the Cretaceous/Paleogene boundary have tended to favor volcanism as the cause (Officer and Drake 1985). There is now conclusive evidence, including the Chixculub crater on the Yucatan Peninsula in Mexico, for a massive bolide impact at the K-P boundary (Alvarez 2003). However, there is also ample evidence for copious and rapid eruptive volcanic activity over a wide area in India prior to the K-P boundary (Bhattacharji et al. 1996). Most importantly, the mechanisms are not mutually exclusive as a cause of mass extinctions. On the contrary, if a bolide impact occurred during a period of environmental deterioration resulting from volcanism, already stressed ecosystems would more likely have been pushed to collapse.

Either bolide impact or massive, long-term eruption of flood basalts would have catastrophically impacted shallow-water, photosynthetic, carbonate-producing reef organisms. Either process would have profoundly influenced ocean chemistry in ways detrimental to CaCO_3 production. The energy of a meteor passing through the atmosphere would have oxidized nitrogen in the atmosphere, resulting in global acid rain that would have acidified shallow oceanic waters, dissolving CaCO_3 . Volcanism emits large quantities of hydrogen sulfide (H_2S), which would have oxidized to sulfur dioxide (SO_2) and hydrated to sulfuric acid (H_2SO_4), resulting in global acid rain. Furthermore, the earthquake caused by a 10 km diameter bolide hitting the Earth could have eliminated all nutrient-depleted shallow-water environments worldwide, just by stirring the oceans (Hallock 1987). Deeper oceanic waters, where there is insufficient light for photosynthesis, are substantially richer in inorganic dissolved nitrogenous and phosphatic compounds that are needed by plants to photosynthesize, than most photic surface waters. These nutrient-rich waters represent approximately 98 % of the total ocean volume (Hallock et al. 1991). Such a tremendous shock would have generated tsunamis and internal waves, rapidly mixing deeper waters into shallow waters and stimulating red-tide-like blooms of a few, fast-growing species of phytoplankton (disaster species – Fischer and Arthur 1977; Copper 1994).

Whatever occurred, among the lessons to be learned from end-Cretaceous and other major extinction events are that the most prolific carbonate-producing protists and metazoans are particularly sensitive to environmental perturbations because they thrive within relatively narrow environmental limits. Waters in which they proliferate must be warm but not too warm, clear and well illuminated but

with not too much biologically damaging ultraviolet radiation, nutrient-depleted, and highly supersaturated with respect to Ca^{2+} and HCO_3^- . Most reef-building organisms live at low latitudes on shelves and banks in the shallowest 100 m (330 ft), and thrive at depths less than 20 m (66 ft), in an ocean that averages 3,800 m (12,500 ft) in depth (Kennett 1982). Waters suitable for shallow-water reef development make up less than 1 % of the ocean volume under optimum conditions; suitable benthic habitat is far less. Thus, regional or global events that eliminate habitat for reef-building and reef-dwelling plants and animals can eliminate huge numbers of species and are recorded in the rock record as mass extinction events (Hallock 1987). Because reef species are often highly specialized to their environment, many specializations are lost in these events, while less specialized, more opportunistic species typically survive.

2.9.5 Cenozoic: Time of Recent Animal Life

Paleocene and Eocene shallow-water limestones tend to be dominated by the fossil remains of bryozoans, coralline algae, sponges, and foraminifers (Hallock et al. 1991; Copper 1994). High atmospheric CO_2 concentrations and greenhouse climate, which reached an apex during the Cretaceous, continued for another 20 Myr into the Cenozoic (Berner 2004). Diversification of coral assemblages occurred much earlier than extensive reef construction (Frost 1977). Pochon et al. (2006) postulated that *Symbiodinium* zooxanthellae in corals originated in Early Eocene, with subsequent episodes of divergence during times of global cooling. Nearly all the major circumtropical frame-building genera of scleractinian corals had evolved by the latest Eocene (Veron 2000). Thus, the Eocene, like the Cretaceous, was a time of diverse coral assemblages and widespread occurrences of carbonate-producing biotas with limited coral-reef construction. Frost (1977) suggested that the capacity to construct massive wave-resistant reef structures developed long before such structures were widely produced, suggesting geochemical control, as further discussed by Pomar and Hallock (2008).

Consistent with high atmospheric CO_2 concentrations and low Mg/Ca ratios in seawater (Stanley and Hardie 1998), prolific calcification by calcitic larger foraminifers and coralline red algae (e.g., Plaziat and Perrin 1992) recovered faster than comparable aragonite production by corals and calcareous green algae. The best known larger foraminiferal limestones are the Eocene Nummulitic Limestones of Egypt, from which the Pyramids were built. Shallow-water limestones of Eocene age that are rich in fossils of larger foraminifers are widespread in mid to low latitudes (Beavington-Penney and Racey 2004). Larger foraminiferal fossils can be found in Oregon, southern England and other localities as high as 51° N latitude

(Adams et al. 1991; Perrin 2002). Their complex shells, by analogy with modern larger foraminifers, appear to have been highly adapted to house algal symbionts. Shallow-water limestones dominated by coralline-red algal nodules were also common (Bryan 1991). Paleocene-Eocene limestones dominated by coralline algae or larger foraminifers are common hydrocarbon reservoirs where deeper in the subsurface and major aquifers where they are nearer the surface.

High-latitude cooling began in the middle Eocene, with widespread Antarctic glaciation at the Eocene-Oligocene boundary, which DeConto and Pollard (2003) attributed to declining atmospheric CO₂ concentrations. Reefal buildups were similar to those of the earlier Eocene both in relative scarcity and composition (Perrin 2002). As the Atlantic Basin expanded, the Caribbean province became more isolated from the Tethyan/Indo-Pacific realm. Based on morphologies, coral families were traditionally assumed to have arisen in the Indo-Pacific. However, Fukami et al. (2004), based on molecular genetics, showed that several Atlantic coral taxa are genetically distinct and represent endemic taxa. Those authors suggested that the divergence occurred near the Eocene-Oligocene boundary.

Coral communities flourished circumtropically beginning in the late Oligocene. By the early Miocene, reefs and reef-associated biotas worldwide had expanded their latitudinal distributions by more than 10° north and south (Adams et al. 1991), reaching their acme in the mid Miocene (Perrin 2002). The expansion in reef-building capacity corresponded to increasing Mg/Ca ratios in seawater (Stanley and Hardie 1998) and falling atmospheric CO₂ concentrations (Pearson and Palmer 2000), both of which promoted aragonite precipitation in warm, tropical waters.

Paradoxically, many coral and larger foraminiferal species were lost from Caribbean faunas at the end of the Oligocene, and many more became extinct during the Miocene (Edinger and Risk 1994). There were also extinctions of Indo-Pacific corals, but far fewer (Veron 2000). Closure of the Tethys Seaway further isolated the Atlantic/Caribbean reef biotas (Pomar and Hallock 2008). Progressive blockage of the Central American Seaway (Fig. 2.6) probably accounted for environmental changes that resulted in many Caribbean extinctions (Edinger and Risk 1994). Throughout the Paleogene, flow through the Central American seaway was bi-directional (Nisancioglu et al. 2003). Because the Atlantic has higher evaporation rates compared with rainfall rates than the Pacific, sea level in the Pacific is slightly higher than in the Atlantic. As a consequence, when the Central America seaway was open, water had to flow from the eastern Pacific into the Caribbean (Haug et al. 2001). However, the easterly trade winds forced surface waters to flow westward from the Caribbean to the eastern Pacific. As long as the Central American passageway was wide and

deep, two-way flow was accommodated by westward surface flow and eastward subsurface flow, probably at depths in excess of 50–100 m (Maier-Reimer et al. 1990). However, as the Isthmus emerged, flow was constricted and surface flow likely reversed during calm weather. As a consequence, nutrient-laden eastern tropical Pacific waters were more frequently and consistently introduced into Caribbean surface waters.

Edinger and Risk (1994) observed that shelf-edge and slope-dwelling coral genera were nearly eliminated in the Atlantic in the early Miocene. The corals that survived were mostly banktop species capable of tolerating higher nutrients and higher sedimentation rates, as well as higher bioerosion rates (e.g., Hallock 1988). Larger foraminifers revealed the same trends. Slope-dwelling taxa were nearly eliminated, while shallower-dwelling taxa of bank tops and restricted environments thrived (Hallock and Peebles 1993). Other banktop biota, including octocorals and calcareous algae, became more important components of the Caribbean benthos than on comparable Pacific reefs.

Since the middle Miocene, there has been progressive high-latitude cooling, compression of tropical habitats, and increasing temperature gradients between high and low latitudes (Lear et al. 2003). Pochon et al. (2006) noted that the majority of extant *Symbiodinium* lineages have diversified since Middle Miocene. Some global cooling likely benefited the coral-*Symbiodinium* symbiosis, which is sensitive to high light under elevated temperatures (Wooldrige 2013). Pomar and Hallock (2008) further postulated that Neogene cooling supported the co-evolution of zooxanthellate corals and coralline algae into shallow, high-energy waters, where their carbonate production potential is highest.

2.10 Pleistocene and Holocene Reefs

Northern hemisphere climatic deterioration accelerated ~2.6 Ma with the onset of the Pleistocene Epoch (Fig. 2.1). The climatic fluctuations strongly influenced tropical reef-associated biotas in a variety of ways. Some taxa became extinct. Others, like the fast-growing *Acropora* and *Montipora*, diversified and now account for ~25 % of modern Indo-Pacific coral species (Veron 2000). Successive isolation and mixing of populations, which typically accompanies fluctuations in sea level, have long been recognized as mechanisms promoting evolutionary diversifications (Hallam 1985). Veron (2000) further proposed the process of reticulate evolution whereby populations were separated by changes in sea level and surface currents, and when reconnected, allopatric speciation had occurred, but some closely related taxa then hybridized, increasing the genetic diversity of resultant

reconnected taxa. Pleistocene glacial advances and retreats induced such successive isolation and mixing events, which likely contributed to the very high extant species diversities of *Acropora* and *Montipora*.

A fascinating paradox of limestones and climate is that active reef building and coral evolution occurred during the Pleistocene, despite high-latitude climatic deterioration that resulted in as many as 21 glacial advances and retreats (Delmas 1992). Sea-level fluctuations of as much as 140 m (450 ft), caused by repeated accumulation and melting of Northern Hemisphere and Antarctic continental glaciers, accompanied cyclic reduction and expansion in the areas of warm, tropical seas. The solution to this paradox may be that tropical climatic, geochemical, and topographic conditions during interglacials were nearly optimal for reef-building. Atmospheric CO₂ concentrations were relatively low (though not as low as during glacial advances) and subtropical/tropical sea surface temperatures were nearly ideal. Both factors promoted aragonite calcification by corals and calcareous green algae, which in turn enhanced their rates of photosynthesis and biological productivity.

Times of rising sea level are also favorable for reef building, providing space for accumulation of substantial thicknesses of reef limestone, which have high probability of preservation in the rock record. Except for active tectonic areas, most shallow shelves on trailing continental margins subside at rates of a few centimeters per 1,000 years (Schlager 1981). In contrast, the most actively accreting portion of a reef system can grow upward at rates of at least 4 m/1,000 years, and under exceptional conditions as much as 20 m/1,000 years (Hubbard, this volume). But reefs most rapidly accrete when growing in water depths of less than 20 m, where there is plenty of sunlight for photosynthesis. The only circumstances in which reefs can accrete upward at high rates for more than about 5,000 years, and produce more than 20–30 m thicknesses of limestone, are if the shelf rapidly subsides or sea-level rises. Thus, during times of interglacial sea-level rise, the margins of continental shelves, limestone banks, and volcanic islands provided ideal locations for thick sequences of reef-associated limestones to accumulate (Pomar 2001).

2.11 Conclusions

The history of reefs is like a fascinating and ongoing novel, full of paradoxes and unexpected feedback mechanisms. One of the most difficult concepts to understand is that limestones are both storehouses and sources of CO₂, depending upon the times scale being considered. Through geologic time, limestones have stored CO₂ and are therefore responsible for a livable planet. Yet on the shorter time scales of glacial cycles, interglacial reef building may move as much as

100 ppm of HCO₃⁻ from the bicarbonate pool in the oceans to CO₂ in the atmosphere. Erosion of young, predominantly aragonitic-coral limestones and sediments occurs when sea level falls, sequestering CO₂ from the atmosphere to HCO₃⁻ in the oceans. On human time scales, reefs are relatively minor players in the CO₂ story. Fossil fuels, like ancient limestones, represent long-term storage of CO₂ in the Earth's crust. Human activities, especially the burning of fossil fuels, have added more CO₂ to the atmosphere in 100 years than reef building did in 15,000 years.

The major lesson to be learned from the history of reefs is that they are constructed by complex and specialized biological communities. Because these systems are highly adapted to a limited range of environmental conditions, they are extremely sensitive to local, regional and global environmental perturbations. Environmental crises, culminating in global mass-extinction events, have repeatedly caused the demise of whole communities of reef-building organisms and the myriad of organisms that depended upon reef structures for habitat. Subsequent recovery of reef-building communities required millions of years.

Some individuals argue that humans are simply part of nature; that exploding human populations are naturally generating the present episode of mass extinction from which the Earth will recover in 10 or 20 million years. But from a human perspective there is a difference between a mass extinction event caused by a meteor impact and the ongoing one being caused by human activities. Human intelligence has reduced biological limitations on both the growth rate of human populations and the environmental damage that any individual human can cause. Is it too much to hope that human intelligence can be utilized to bring an end to the current human-generated mass-extinction event before the most specialized and diverse biological communities, like coral reefs and rain forests, are lost to future human generations? A few human cultures, notably Micronesian inhabitants of atolls and coral pinnacles, are known to have developed sustainable societies in resource-limited habitats. Can “modern” humans develop a sustainable global society based on recognition of globally-limited resources? Or do humans simply represent another of the “disaster” species that proliferate globally at mass-extinction events; in this case, the Anthropocene Mass Extinction?

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