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Carbonate systems along nutrient and temperature gradients: some sedimentological and geochemical constraints

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Abstract Research over the past several decades has clearly demonstrated that changes in the ocean environment have had major impacts on carbonate systems. Changes in climate, ocean circulation and seafloor spreading rates have influenced temperature and seawater chemistry, including carbonate saturation state and nutrient availability, and thereby have determined boundary conditions for the biota that form carbonate platforms. In turn, the biota determine accumulation rates and facies zonations, thus controlling platform geometry and facies dynamics. In the first section of this paper, we examine how nutrient availability influences carbonate facies associations. We first discuss the role of temperature and nutrient gradients in the modern ocean and their influence on biotic associations. Then we discuss how carbonate sedimentation can be characterized along nutrient gradients. In the second section, we review proxies currently used to reconstruct paleoproductivity in open ocean environments and discuss their applicability to neritic carbonate systems. We highlight the variety of existing proxies and their limitations, and suggest that multiple lines of evidence are needed for valid interpretations. Our short review discusses sedimentological, biogenic, and geochemical proxies that can be used to reconstruct past nutrient fluxes and to constrain paleo-oceanographic controls over the distribution of carbonate associations. However, it also reveals that more data and case studies are needed that integrate shallow and deep water carbonate sequences and elucidate the links between temperature vs. nutrient supplies changes and facies in ancient carbonate sequences.

Introduction

Studies of modern carbonates over the past three decades have analysed the distribution of skeletal-grain associations and their relationship to temperature and other oceanographic parameters (e.g., Chave 1967; Lees and Buller 1972; Carannante et al. 1988; Nelson 1988). Models of ancient carbonate system evolution, on the other hand, have mainly focused on relative sea level and regional tectonics as the controlling forces that determine platform geometries and facies associations (e.g., Kendall and Schlager 1981; Crevello et al. 1989; Handford and Loucks 1993). Nevertheless, it is becoming increasingly evident that changes in the global climate and ocean environment have also had major impacts on the evolution of carbonate systems, affecting the distribution and abundance of carbonate-forming biota. Climate and ocean circulation, which affect temperature (Lees and Buller 1972; Milliman 1974; James 1997), composition of seawater and carbonate saturation state (Hallock 1996; Stanley and Hardie 1998) and nutrient availability (e.g., Hallock and Schlager 1986; Carannante et al. 1988; Hallock 1988, 2001), determine the boundary conditions for the biota that form carbonate platforms. In turn, the biotic community determines accumulation rates and facies zonations, thus controlling platform geometry, character of the sediments and facies dynamic and zonation, as well as the overall rate of growth. Clearly, carbonate facies models should be seen in the context of temporal changes in oceanographic and climatic boundary conditions. However, the wide spectrum of environmental factors controlling the nature and evolution of carbonate systems as can be recognized in modern settings is hard to reconstruct in ancient settings, especially going back in time where a non-actualistic approach is required. Long-term trends in the variation of carbonates through time reflect evolutionary and cyclic changes in the environments in which carbonate formed. But how can these be interpreted in terms of climate and oceanography, and how much can we extrapolate present-day oceanographic relationships to the geological past? Establishing reliable

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criteria to differentiate between carbonates deposited in cool water from those produced in warmer water under elevated nutrient supply (both representing the Heterozoan Association; see James 1997) is a critical issue in the study of carbonate systems and their climatic significance.

In this paper, we discuss proxies that can be used to reconstruct the oceanographic controls over the distribution of carbonate associations. More specifically, we wish to address the effect of nutrient availability on carbonate systems, and discuss which sedimentological, biogenic and geochemical tools and proxies can be used to interpret such changes. We first discuss oceanographic factors controlling neritic carbonate accumulations and the role of nutrient gradients in the modern ocean in controlling patterns of neritic carbonate accumulation. Then we review geochemical proxies, which were developed to reconstruct paleoproductivity in pelagic settings, and discuss their applicability to neritic carbonate systems. Finally, we highlight the variety of existing proxies and their limitations, concluding that multiple lines of evidence are needed to reach convincing interpretations.

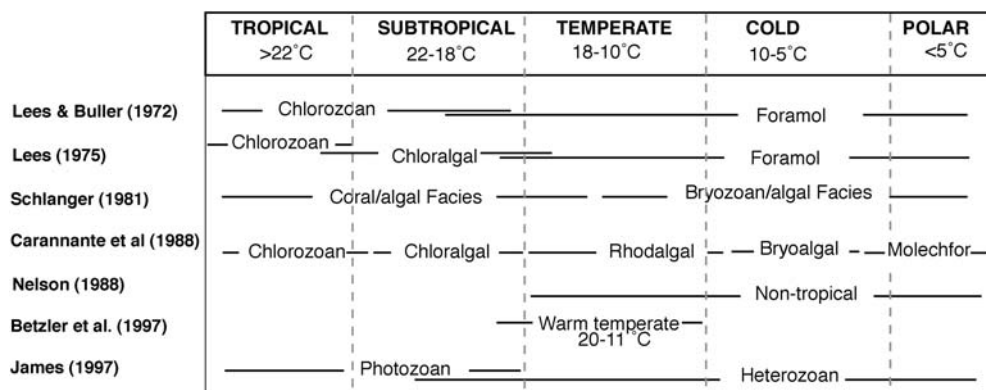
Oceanographic settings of carbonate accumulation

Temperature

The role of latitude and temperature changes over the biogenic associations forming carbonate facies has long been recognized and has led to a number of classifications and related terminology summarized in Fig. 1. Carbonate sediments have been seen in an oceanographic perspective since the fundamental work of Lees and Buller (1972) and Lees (1975) who recognized that modern carbonates are influenced by temperature and salinity in the ocean and classified the distinctive biogenic associations along temperature gradients (and salinity changes) as Chlorozoan (dominated by zooxanthellate coral and calcareous algae), Chloralgal (dominated by calcareous algae) and Foramol assemblages (Fig. 1). These terms have been expanded and further detailed by Carannante et al. (1988) in a study on the modern Brazilian Shelf.

Schlanger (1981) also observed a gradient in biotic association along the Emperor Chain in the Pacific. For an in-depth discussion of studies of facies characteristics, skeletal assemblages and global distribution of modern shallow marine facies, the reader is referred to Nelson (1988), who introduced the term 'non-tropical' to draw attention to the extensive carbonate deposits outside the tropical environments. Since then, although these different biotic associations do not necessarily relate to specific temperature ranges, a certain paleoclimatic connotation has been linked to the different assemblages. Carannante et al. (1988) clearly pointed out that fossil Foramol (or non-tropical) assemblages are not necessarily indicative of cool-water settings, and that in addition to temperature, a number of factors related to the oceanographic setting such as nutrient supply, turbidity and depth of deposition may trigger the deposition of Foramol-type skeletal assemblages even in the tropics. James (1997) introduced the terms Photozoan and Heterozoan to decouple skeletal assemblages and associations from a temperature connotation. These terms have the advantage of relating skeletal assemblages to their trophic requirement (light-based photosynthesis versus other sources) rather than water temperature alone. These two modes, the Photozoan and Heterozoan associations (James 1997), show a clear distribution in the modern ocean, both with respect to latitude and ocean circulation. Photozoan associations tend to dominate tropical and subtropical western ocean basins, whereas Heterozoan carbonate systems tend to occur on cooler eastern sides of the oceans and other more localized areas that are impacted by upwelled nutrient-rich waters or by nutrient-enriched terrestrial runoff, as well as at temperate to polar latitudes. Pomar (2001) expanded recognition of the light requirements of the carbonate associations and recognized a euphotic (high light) assemblage dependent upon abundant light in clear shallow waters (e.g., corals and calcareous algae), an oligophotic (low light) assemblage (red algae and larger foraminifera) in somewhat deeper waters (~30–150 m), and photo-independent biota.

Fig. 1 Overview of the most used classifications of neritic carbonates and approximate



Nutrients

Since the seminal work of Lees and Buller (1972), there has been an increased awareness of the relationship between carbonate sedimentation and nutrient supply (Hallock and Schlager 1986; Carannante et al. 1988; Birkeland 1987; Hallock 1988). The term “nutrients” refers primarily to inorganic fixed nitrogen and phosphate ions required by photosynthetic organisms to synthesize proteins for cell maintenance, growth and reproduction (see Hallock 2001). A separate term, “trophic resources”, can be used to include both organic matter (i.e., “food”) in all environments and inorganic nutrients in environments where light or chemical energy is available for synthesis of organic matter (Valentine 1971; Hallock 1987). Rates of nutrient supply are a primary controlling mechanism for benthic communities in shallow, tropical environments (Hallock and Schlager 1986; Birkeland 1987; Hallock 2001). Nutrients can be delivered either by terrestrial runoff or marine sources such as equatorial, coastal, or topographic upwelling. Characteristics of the oceanic waters within a region generally provide “background” conditions, i.e., the clearest waters and minimum nutrient supply. Locally, upwelling or terrestrial runoff can add nutrients and thereby influence the benthic biota. A discussion of nutrient influence on carbonate sedimentation cannot be entirely decoupled from associated oceanographic parameters such as turbidity, source of nutrient supply, currents, depth of the euphotic zone¹, thermocline², and nutricline³.

Actualistic studies have shown that changes in the trophic resources affect the character of the substrate and turbidity of the water column (e.g., Hallock 1987). Changes in the physiochemical characteristics of the environment have an important effect on the nature of the biotic assemblages and affect diversity, dominance, trophic structure, and stability (Valentine 1971; Stanton and Dodd 1976; Brasier 1995a, 1995b).

Temperature influences carbonate-producing biota in two major ways. In ectothermic organisms (those whose body temperatures are close to ambient), chemical reaction rates associated with metabolism are temperature

dependent and tend to double for every 10 °C rise in temperature (Hochachka and Somero 1984). Thus, an ectothermic animal requires approximately half as much food to live in waters that are 15–20 °C as it needs to live in waters that are 25–30 °C (Hallock et al. 1991). Furthermore, temperature controls CO₂ solubility and CaCO₃ saturation, and thereby influences the amount of energy required to calcify and maintain skeletal carbonate. Photosynthetic enhancement of aragonite precipitation by zooxanthellate corals and calcareous green algae is most advantageous in warm waters that are supersaturated with respect to CaCO₃ (Hallock 2001). On the other hand, cooler waters require greater energy expenditure to precipitate and maintain aragonite and therefore favor calcite-secreting coralline red algae, larger foraminifers, and animals that lack algal symbionts (Hallock 1996).

Nutrient gradients—an ecological perspective

Carbonate sedimentation and reef development can be characterized along nutrient gradients (e.g., Hallock 1987, 2001; Triffleman et al. 1992; Fig. 2). Chlorophyll concentrations in surface waters can be used as proxies for nutrients (Fig. 2) with the caveat that those estimates are temperature dependent. Diversity of habitats in surface waters also is partially controlled by nutrient availability, which explains why taxonomic diversity often appears to be inversely related to nutrient supplies (Longhurst 1967; Hallock 1987).

From an ecological perspective, three main transitions in community structure can be recognized in tropical waters along a nutrient gradient, from oligotrophic to mesotrophic, from mesotrophic to eutrophic and from eutrophic to hypertrophic (see Figs. 2, 3). Each of the four associations is characterized by a different primary limiting factor. Nutrient limitation restricts competition for substrate in oligotrophic environments. Competition for substrate is characteristic of mesotrophic environments. As abundant nutrients stimulate plankton blooms, eutrophic benthic environments are light limited. And, in hypertrophic environments, so much organic carbon is produced in surface waters that oxygen depletion limits the benthos (see Figs. 2, 3; Hallock 2001).

In clear, nutrient-deficient (oligotrophic, chlorophyll concentrations <0.1 mg/m⁻³, see Fig. 2), tropical/subtropical oceanic waters the most successful shallow benthic carbonate producers are zooxanthellate corals, which both feed and photosynthesize, recycling scarce nutrients (Hallock 2001). Because calcification rates seem to be mainly a function of photosynthesis and light, corals can accrete at rates up to 10 kg CaCO₃ m⁻² year⁻¹ (e.g., Kinsey 1985). In this oceanic environment, nutrient limitation is the main control over carbonate-producing biota (Hallock and Schlager 1986).

As nutrient supplies increase (surface water chlorophyll concentrations of about 0.1–0.5 mg/m⁻³; see Fig. 2), benthic macroalgae, including calcareous green algae,

¹ The euphotic zone corresponds to the uppermost water layer, where photosynthesis takes place, and may extend from a few meters to 200 m in clear waters.

² In the surface layer of water, temperature and salinity are uniform because the water is mixed, primarily by wind. Below this mixed layer, temperature decreases rapidly over a short distance. The interval where temperature changes is called thermocline.

³ The sharp change in density at the thermocline associated with temperature decrease creates a barrier, inhibiting mixing of water from the upper layer with that below the barrier, where nutrients are found. Nutrients that support phytoplankton in the mixed layer are mostly recycled from the decay of organic matter within that layer. As light decreases with depth, phytoplankton growth slows enough to allow dissolved nutrients to build up in the water. The depth where nutrient concentration increases is called the nutricline. If the mixed layer is deep, the nutricline and thermocline coincide. If the mixed layer is shallow, the nutricline and thermocline are separated.

Fig. 2 Nutrient gradients in low latitude waters, presented in milligrams of chlorophyll per cubic meter of seawater

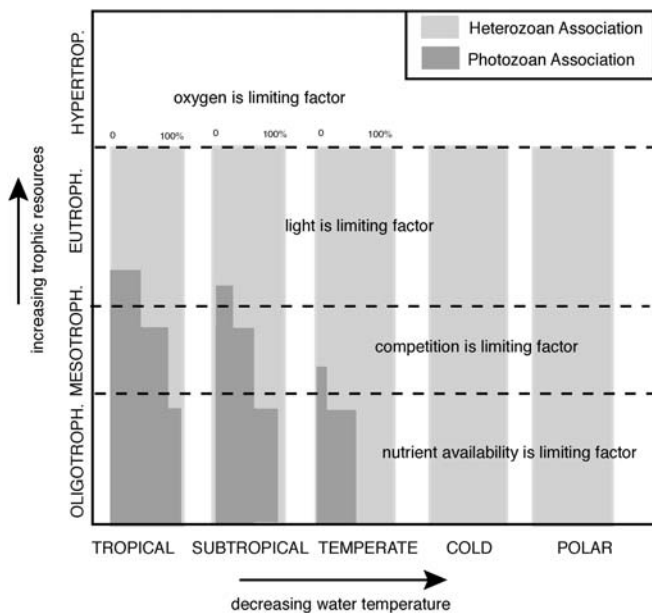
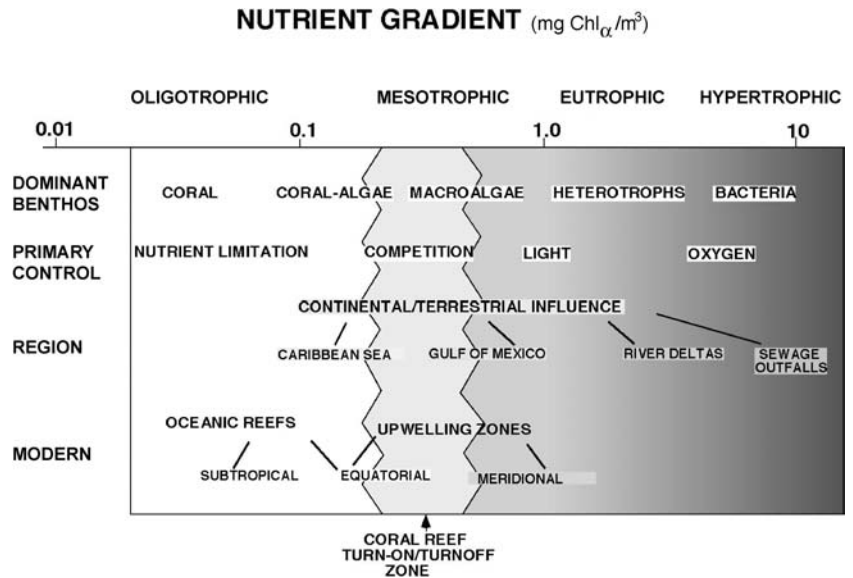


Fig. 3 Schematic representation of the distribution of Photozoan-Heterozoan carbonates with respect to common temperature zones and the nutrient gradient. The width of the bars indicate estimated abundance of each association from 0–100%

become more competitive for substrate and the calcareous algae become significant contributors of skeletal material. Echinoids and gastropods that graze upon the macroalgae also increase in abundance and contribution to sediments (Hallock 1988). Mesotrophic conditions refer to such an intermediate nutrient flux where light penetration is sufficient to support prolific calcareous algal production, and where dissolved and particulate nutrient supplies are sufficiently high to favor algae and sponge domination of the benthos, including abundant bioeroding faunas. Molluscan and echinoid contributions, particularly by grazing taxa, can also be significant. Bioerosion rates also

increase, converting coral framework to sediment. Growth rates of corals may remain high, but net framework production declines as coral cover declines, and especially as increasing bioerosion rates convert framework to sediments. With rising nutrients levels, symbiotic animals cannot compete with faster growing macroalgae and sponges (Birkeland 1987). Competition for substrate is a major controlling factor in this environment.

As nutrient flux increases, due to runoff or upwelling, elevated nutrient flux supports significant phytoplankton densities in the water column and reduces light reaching bottom-dwelling communities. At chlorophyll concentration of 1 mg m^{-3} or more (see Fig. 2), light penetration is restricted to a few meters at most. Light is the limiting factor in this environment. Primary production within the water column provides abundant food sources for filter- and detritus-feeding benthos, including bivalves, sponges, ascidians, and echinoderms. Bioerosion can become very significant, with rates up to $6.5 \text{ kg CaCO}_3 \text{ m}^{-2} \text{ year}^{-1}$ as reported by Kinsey (1985) in Hawaii.

The final transition is controlled by oxygen supply to the benthos. Hypertrophic environments occur where nutrient flux to surface waters is sufficiently high to support dense populations of phytoplankton (Fig. 2). The supply of organic matter frequently outpaces oxygen supply to benthic communities, resulting in episodic hypoxia or anoxia in the benthos. Under very high nutrient flux, oxygen supply to the benthos at the sediment-water interface may eliminate most macrofauna and favoring only taxa able to tolerate low oxygen concentrations (Fig. 2). This environment is strongly influenced by primary production in the overlying surface waters, as well as by physical and chemical factors that influence input and solubility of oxygen, such as mixing processed driven by waves and currents, water temperature and salinity (Hallock 2001).

In cooler waters, the combined effects of reduced carbonate saturation and reduced energy needs eliminate

the competitive advantages that zooxanthellate corals and calcareous green algae have in warmer waters. Where nutrient supplies are low in temperate to polar waters, coralline red algae and bryozoans are most competitive because of their lower maintenance requirements (Lukasik et al. 2000). A limited assemblage of rotaliid larger foraminifera, with their low Mg-calcite shells and algal symbionts, can extend into cool-subtropical/warm temperate euphotic waters, beyond the range of significant coral and calcareous algal contributions. Higher nutrient flux into cool surface waters, which stimulates plankton blooms (including diatoms), reduces light penetration and increases flux of siliceous diatom frustules and organic matter to the seafloor, favoring filter-feeding bivalves or detritus-feeding assemblages. Additional limiting factors, such as geochemistry of water masses, can be associated with these transitions in non-tropical waters (James 1997).

Trophic gradients in modern and ancient settings

In this section, we will discuss examples of carbonate associations formed in modern oceans under a particular nutrient state, and show examples of how these may change geographically and temporally in response to changes in nutrients.

In geologic terms, "oligotrophic" includes the range of conditions that, above the necessary temperature threshold, support true coral-reef framework (Fig. 2). The sensitivity of carbonate systems to increasing nutrient flux appears to provide the key to why drowned reefs may occur in close proximity to seemingly thriving reefs (Hallock 2001). Shelves and carbonate banks in the western Caribbean and Gulf of Mexico are excellent examples of how nutrient dynamics influence reef turn-on and turn-off (terminology of Buddemeier and Hopley 1988). The Alacran Reef on the Yucatan Peninsula has some of the highest accretion rates recorded of the Holocene (Macintyre et al. 1977), yet is surrounded by drowned reefs. Chlorophyll plumes, as visualized by Coastal Zone Color Scanner (satellite) imagery, indicate mesotrophic conditions in the western Caribbean, especially along the Yucatan Peninsula (e.g., Garrett 1985). Upwelling occurs where the northward-flowing Caribbean Current encounters topographic features (Hallock 2001). Prolific calcareous algal occurs on shelves of the Nicaraguan-Honduran continental shelf and Nicaraguan Rise (Roberts and Murray 1983; Hine et al. 1987). Natural mechanisms for short-term eutrophication of an oceanic reef community are megaplumes triggered by large submarine volcanic eruptions (Vogt 1989). Another commonly invoked hypothesis, that of rising sea level and flooding of the shelves by anoxic water (e.g., Arthur and Schlanger 1979; Copper 1994), could certainly increase nutrient flux and profoundly change shallow-water communities. However, it would probably not directly eliminate them by oxygen stress because surface-mixing processes on open shelf environments typically oxygenate waters as deeply as light can penetrate.

Furthermore, even very rapid sea-level rise occurs on time scales of at least decades (e.g., Blanchon and Shaw 1995), while community change in response to nutrients can occur on the order of years (e.g., Smith et al. 1981; Cockey et al. 1996). Nutrifaction was probably an important factor in the drowning of Cretaceous through Eocene guyots during passage through the "latitude crisis zone" coinciding with the paleoequatorial upwelling belt of high productivity (Larsen et al. 1995; Wilson et al. 1999). Final drowning of these banks was likely caused by the combination of decelerated carbonate accumulation, guyot subsidence, and eustatic sea level rise (Ogg et al. 1995; Wilson et al. 1999). Today, Canton Atoll, Fanning Atoll, and several others in the equatorial Pacific are exposed to some of the highest inorganic nutrient concentrations found in open ocean surface waters (Smith and Jokiel 1975a, 1975b), supporting the Larsen et al. (1995) hypothesis (see Hallock 2001). Taxonomic make-up of Cretaceous and early Paleogene carbonate-producing communities likely contributed, since the biotas were not framework builders, but rather maintained upward growth of the platform by overproduction of bioclastic debris (Ogg et al. 1995). In addition, Cretaceous through Eocene equatorial upwelling zones were likely more nutrient-rich than similar regions in modern oceans (Fisher and Arthur 1977; Hallock and Schlager 1986; Hallock et al. 1991). Widespread phosphatic deposition in meridional upwelling zones of Cretaceous age (e.g., Cook and McElhinney 1979) supports this argument.

Halimeda bioherms in the northern lagoon of the Great Barrier Reef (Davies and Marshall 1985), along the western banks of the Nicaraguan Rise in the western Caribbean (Hine et al. 1987), and in the Makassar Straits of Indonesia (Roberts et al. 1988) provide examples of choralgal sedimentation under mesotrophic conditions. Characteristics that all three locations share include: (1) geographic settings in warm, tropical waters; (2) relatively clear surface waters that permit sufficient light to penetrate to 30–60 m to support prolific *Halimeda* photosynthesis and growth; (3) a physical oceanographic mechanism that periodically forces uppermost nutricline waters over the substratum where the *Halimeda* are growing; and (4) temperatures in uppermost nutricline waters that are only a degree or two cooler than surface waters, as maintenance of relatively warm temperatures over the banks is crucial to both rapid algal growth rates and geochemical factors that promote aragonite precipitation by photosynthetic mechanisms (Hallock 2001). Eutrophic conditions occur where sufficient runoff or upwelling elevates nutrient levels to support significant phytoplankton densities in the water column, and the consequent lack of light limits benthic algal growth so that bottom-dwelling communities are dominated by non-photosynthetic organisms (Fig. 2). If terrigenous sedimentation is limited, benthic carbonate production will continue to dominate, produced by members of the Heterozoan association (James 1997), especially oysters or other bivalves, predatory and detritus-feeding gastropods, grazing and burrowing echinoids, crinoids, bry-

ozoans, and azooxanthellate corals. Moreover, because these communities are not light dependent, they can produce carbonate sediments, and even buildups, at outer shelf and slope-depths where food is abundant and hemipelagic sedimentation is limited by currents. If found in tropical settings, this is the kind of carbonate sedimentation that is most likely to be confused with cool-water carbonates.

In a study of Oligo-Miocene carbonates from the Murray Basin (S. Australia), Lukasik et al. (2000) have recognized four bio-litological associations (large foraminifera-bryozoa, echinoid-bryozoa, mollusk and clay facies) and interpreted them to represent shallow water (<50 m) deposition under progressively higher trophic resources levels, from low mesotrophy to eutrophy. The shift from high to low mesotrophy conditions within these strata was interpreted to reflect a change in climate from wet to seasonally dry conditions and decreased influence of land-derived nutrient supply. Lower trophic resource levels during periods of dry climate resulted in deepening of the euphotic zone and widespread proliferation of larger foraminifera Photozoan fauna. Periods of wet climate led to increased trophic resources, shallowing of the euphotic zone, and widespread development of a Heterozoan fauna.

Oligo-Miocene ramp carbonates in the central Mediterranean are characterized by Heterozoan faunas (e.g., Mutti et al. 1997; Vecsei and Sanders 1999) with minor contributions from Photozoan assemblages (Brandano and Corda 2002). Faunal data in association with geochemical criteria (Mutti et al. 1997, 1999; Spezzaferrri et al. 2001) suggest that nutrient supply was a major factor in the control of facies development and variability. Recently, Mutti and Bernoulli (2003) have provided further evidence of the role of trophic resource control on the basis of a study of sea-floor lithification in non-tropical ramp carbonates from the Maiella (Italy). These authors have suggested that the occurrence of diagenetic features such as microbial micrite and phosphate microspherules, which precipitated in the absence of sedimentation near the seafloor, can be related to higher nutrient supply. Progressive intensification of upwelling on this carbonate margin, triggered by regional changes in water circulation and modulated by sea-level changes, delivered additional trophic resources on the ramp, and increased flux of

organic matter to the seafloor led to temporary formation of microbial biofilms. The regional occurrence of silica-rich marls and phosphate layers in age-equivalent, deep-water settings are consistent with this scenario.

Characteristic sediments in areas of hypertrophication include diatom-rich, organic-rich or phosphatic sediments. Because coral reefs are typically relatively shallow and exposed to wave and current action, hypertrophication is not likely to occur on a coral reef without human intervention, such as the installation of a sewage outfall or serious runoff from heavily fertilized fields. Even where sewage pollution profoundly affected reef communities in Kaneohe Bay, Hawaii, production of organic matter by plankton doubled the biomass of benthic heterotrophs but did not outpace oxygen supply (Smith et al. 1981).

Interpretation of nutrient gradients in pelagic settings

A separate line of research from what we have discussed in the previous paragraphs regards the reconstruction of paleoproductivity based on the study of pelagic sediments (see Elderfield 1990; Boyle 1993). The three major approaches involve the interpretation of biotic assemblages, measurement of a flux, such as organic matter (C_{org}) and opal, or the measurement of a proxy closely associated with nutrient concentrations within the waters, such as stable isotopes ($\delta^{13}C$ and $\delta^{15}N$) and trace metal chemistry (Ba, Cd, etc.).

Paleontological tools used to reconstruct past nutrient gradients

The spectrum of benthic communities along the nutrient and temperature gradients as just described are controlled largely by energetics. Comparable biotic spectra can be recognized among pelagic communities (Hallock et al. 1991; Aubry 1998; Boersma et al. 1998). Planktonic foraminifera and coccolithophorids are the dominant pelagic sediment producers in warm oligotrophic and mesotrophic waters, while diatoms and radiolaria dominate in high latitudes and beneath meridional upwelling zones (Table 1). A major difference is that, while

Table 1 Planktonic biota along nutrient gradients

Oligotrophic	Mesotrophic	Eutrophic	Hypertrophic
Diverse planktonic foraminifera and nannoplankton	Very diverse planktonic foraminifera and nannoplankton	Less diverse planktonic foraminifera and nannoplankton	Few if any planktonic foraminifera and nannoplankton
Low accumulation rates	High accumulation rates	Accumulation rates vary	Little or no accumulation rates
Some radiolarians, mostly fragile	Diverse radiolarians	Diverse radiolarian	Low radiolarian diversity
Minimal accumulation rates	Moderate accumulation rates	High accumulation rates	High accumulation rates
Relatively few diatoms	Moderate diatom diversity	High diatom diversity	Low diatom diversity
Minimal accumulation rates	Low accumulation rates	Moderate to high accumulation rates	High accumulation rates

shallow-water carbonates are largely autochthonous, the assemblage of microfossils that accumulates on the seafloor often consists primarily of what lived in waters, hundreds to thousands of meters above where they accumulated, minus what was dissolved prior to burial.

Furthermore, there can be at least three distinct habitats within the pelagic realm in oligotrophic regions. Trophic resources are very different among the three zones. Where solar energy for photosynthesis is abundant, the nutrients required for protein synthesis are limited. Coccolithophorids and spinose planktonic foraminifera with algal symbionts are among the organisms best adapted in oligotrophic surface waters of the subtropical gyres, and to a lesser extent, in temperate and tropical regions (Ryther 1969; Hallock et al. 1991). Despite their ability to live in such environments, their abundances (and therefore their carbonate production) is limited. In uppermost thermocline/nutricline waters that are sufficiently shallow for some photosynthesis, there is typically a zone known as the "chlorophyll maximum", in which trophic resources may be 3–5× higher than in overlying surface waters. Planktonic foraminifera that lack algal symbionts can live at these depths, but their abundances are also limited. Thus, oligotrophic waters are characterized by diverse assemblages of calcareous nano- and microfossils, but overall carbonate production is nutrient limited.

Equatorial upwelling zones and seasonally enriched (by upwelling or mixing) temperate to tropical waters represent the maximum in both diversity and productivity for the planktonic carbonate producers (Hallock et al. 1991; Boersma et al. 1998). Sedimentation beneath these areas may also be augmented by a diverse assemblage of radiolaria and, to a lesser extent, by diatoms. Microfossil assemblages beneath these zones are most diverse because assemblages characteristic of eutrophic to oligotrophic waters may be represented. They are also among the most productive with respect to calcium carbonate because nutrients are sufficiently abundant, at least seasonally, to support coccolithophorid and planktonic foraminiferal blooms, but not sufficiently high to favor domination of the plankton by siliceous plankton and to promote overproduction of organic matter to the degree that the calcium carbonate compensation depth is shoaled.

In coastal, meridional, and high-latitude upwelling zones, large chain-forming diatoms are most competitive and provide the base for short food chains. Coccolithophorids and planktonic foraminifera, having slower uptake and turnover rates, are less competitive. The waters are cool and rich in CO₂, which results in lower carbonate saturation or undersaturation, and this limits the preservation of whatever carbonates that are produced.

Obviously, these three descriptions represent distinct regions along the pelagic nutrient spectrum. Seasonal and interannual water mass changes can further complicate the sediment signal, as does differential preservation. Nevertheless, the assemblages of nano- and microfossils provide a useful starting point for interpreting paleoproductivity and have been successfully used by numerous

researchers (e.g., Aubry 1998; Boersma et al. 1998; Leckie 1989; Leckie et al. 2002). Geochemical evidence should always be compared with biotic evidence, since combined approaches can prevent misinterpretation of one or the other.

Flux and sediment measurements

Organic matter concentrations in marine sediments are controlled by rates of supply, extent of preservation, and degree of dilution by other sediment components (Pedersen and Calvert 1990). As organic matter is oxidized during settling, C_{org} is depth-dependant. Suess (1980) estimated that the settling flux of carbon decreases in proportion to the increase in water depth. To overcome the effect of dilution by other sediment components, all quantitative approaches to reconstruct past surface ocean primary productivity use mass accumulation rates (MARs) of carbonate and organic carbon (Müller and Suess 1979; Sarnthein et al. 1988; Berger et al. 1989).

Organic biochemical markers can also be used to distinguish different sources of organic matter. Biomarker concentrations reflect sedimentary input from specific marine sources, such as prymnesiophyte algae, dinoflagellates and chlorophyll (Boon et al. 1979; Marlowe et al. 1990).

Biogenic opal abundance in deep sea sediments is closely related to the production of diatoms and radiolarians in the overlying waters (Broecker and Peng 1982), and high rates of opal accumulation are found in sediments underlying upwelling areas. In contrast to C_{org}, biogenic opal shows no depth dependency due to oxidation. Fluctuations in biogenic opal and C_{org} tend to agree well, particularly in upwelling areas in the eastern Atlantic and Pacific oceans (Berger and Herguera 1992). However, high opal accumulation rates and very low C_{org} burial rates are noted in the highly productive regions around Antarctica and the North Pacific, indicating that changing conditions for preservation provide major uncertainties in trying to reconstruct paleoproductivity in a quantitative sense.

Geochemical proxies

The most commonly used stable isotope proxy for paleoproductivity is δ¹³C in benthic and planktonic foraminifera (Shackleton 1977; Broecker 1982; Curry et al. 1988). The δ¹³C of some benthic foraminifera (i.e., *Cibicides wuellerstorfi*) correlates with phosphate, becoming more negative (lighter) as phosphate increases during oxidation of organic matter, which is enriched in ¹²C (see Kroopnick 1985). The δ¹³C in planktonic foraminifera can be used as a proxy for surface-water nutrient concentrations: during photosynthesis, phytoplankton preferentially utilizes ¹²C (average phytoplankton δ¹³C value is −20‰; Broecker and Peng 1982); as a

result surface waters are enriched in ^{13}C and this signal is recorded by foraminiferal calcite (i.e., heavier $\delta^{13}\text{C}$ values reflect high surface productivity). However, as most photosynthesized organic matter is remineralized, particularly in upwelling areas, ^{12}C can be enriched, which can invert the signal (i.e., lighter $\delta^{13}\text{C}$ values reflect an enriched nutrients levels, particularly in the surface-dwelling species *Globigerinoides ruber* and *Globigerinoides sacculifer*) (Broecker and Peng 1982). This stresses how critical it is to interpret $\delta^{13}\text{C}$ values carefully, in particular if the oceanographic setting is not well understood or if the different components are not separated (e.g., bulk samples).

Nitrogen isotopes are another tracer of surface nutrient utilization (Francois et al. 1992; Calvert et al. 1992; Altabet and Francois 1993), the $^{15}\text{N}/^{14}\text{N}$ ratio of organic matter depending on the efficiency with which surface nitrate is utilized. Phytoplankton preferentially take up ^{14}N relative to ^{15}N so that where nutrient supply exceeds demand, the sinking organic matter has a lower $^{15}\text{N}/^{14}\text{N}$ ratio than the dissolved inorganic nitrate of the seawater. Further fractionation of $^{15}\text{N}/^{14}\text{N}$ occurs during early diagenesis, bacterial denitrification in the water column under anoxic conditions, and during nitrogen fixation of atmospheric N_2 by cyanobacteria.

Trace metal concentrations covary with parameters such as nutrients and alkalinity, and thus trace metal chemistry (e.g., Cd and Ba) of benthic foraminifera has proven to be a useful tool in reconstructing changes in ocean circulation throughout the Quaternary (Boyle 1988, 1990; Boyle and Keigwin 1982; Lea and Boyle 1990, 1993). Ba is a tracer of silicate and alkalinity and refractory nutrients with deep regeneration cycles. Cd covaries with phosphate in the modern ocean, and thus the Cd content of fossil foraminifera can infer phosphate concentrations in paleo-seawater. $\delta^{13}\text{C}$ and Cd/Ca in foraminiferal calcite have been used separately as indicators of surface nutrient concentrations (Boyle 1988; Keigwin and Boyle 1989; Layberie and Duplessy 1985; Charles and Fairbanks 1992). Changes in the habitat of foraminifera during their life-span and the depth at which they calcify, however, are potential complications to using trace metal concentrations as a proxy for past nutrient concentrations. Symbionts such as dinoflagellate algae affect the trace metal uptake of some foraminiferal species of Cd and possibly other bioactive trace metals such as Zn, Cu, Ni and Co (Mashiotta et al. 1997), and this must be taken into account when selecting the samples; it also underlines the importance of elaborate cleaning before the sample analysis.

Applicability of geochemical proxies to neritic settings

So far, the geochemical methods have been applied almost exclusively to open-ocean, pelagic sediments, and careful considerations must be made before applying

them to carbonate systems (see Fig. 4). Because most methods are component-specific, the applicability of each proxy is dependent on the environmental character of each particular setting, including facies types and lithologies, components present in the sediment, organic carbon content, and degree of preservation (Fig. 4). Flux proxies are most meaningful in open-ocean settings, where changes in concentration and sediment dilution linked to fluctuating rates of sediment supply are minimized. Conversely, stable isotopes ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) and trace metals potentially can be applied successfully to any environment, especially if focusing on specific components to isolate the record of processes within a distinct portion of the overlying water column.

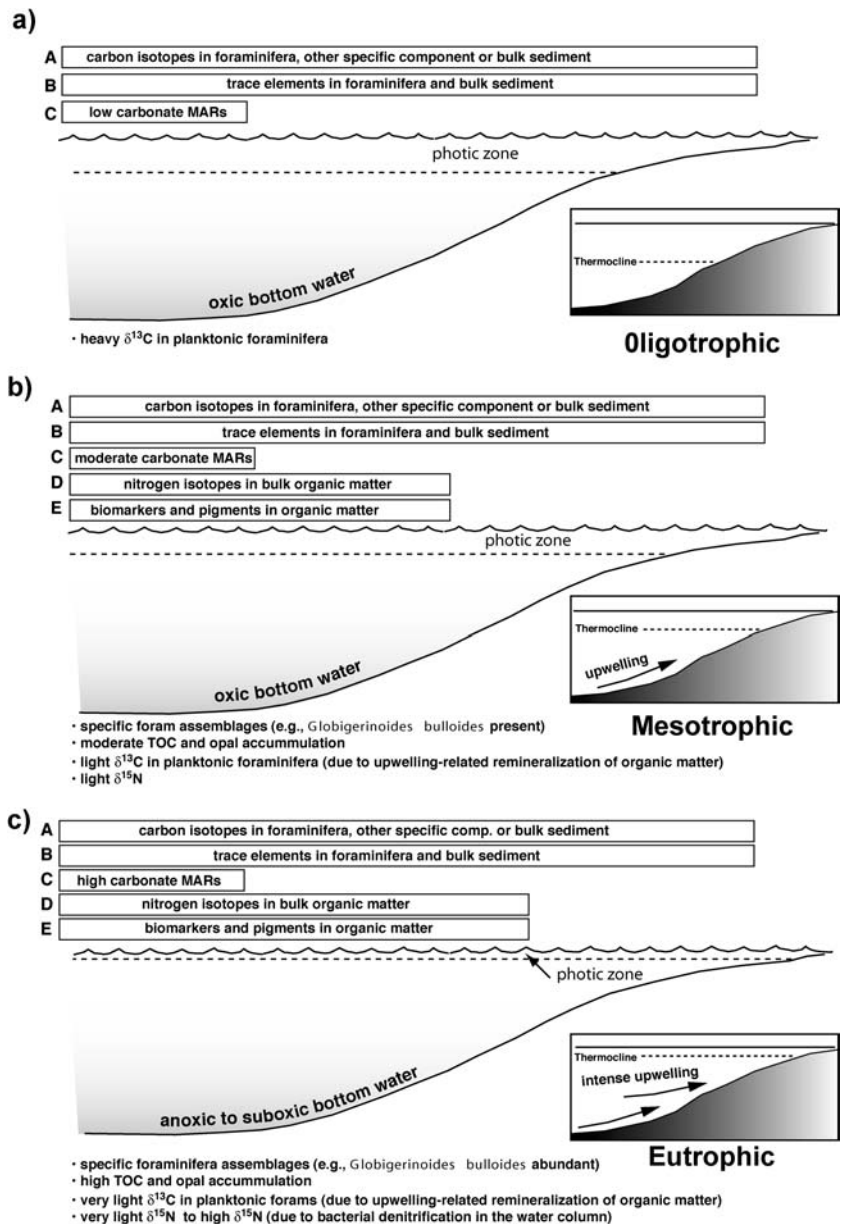
In Fig. 4 we have attempted to summarize which proxies can be applied under three different trophic states, and whether they can be applied only to the basin and slope sediments or also to the shelf. When it is not possible to make measurements directly on the platform sediments, in most cases productivity changes can be inferred primarily from deep-water sections, and carried to the shelf through integration of physical stratigraphy and development of high-resolution age models. For example, in a common geological situation where concentrations of organic matter and opal are high in the basin but low in the correlative shelf strata, an ideal strategy is to produce integrated high-resolution records of both neritic and pelagic strata to analyze the flux records using MAR of C_{org} and/or opal and biomarkers in the deeper water sections with which to reconstruct first-order biogenic fluxes, and then to infer the effects on time-equivalent platform strata.

Summary

To summarize, we have provided a short overview of two independent and very different approaches—a paleoecological/sedimentological approach and a geochemical approach—to recognize past variability in trophic resources. The perspective from which we write this paper is to elucidate the many factors controlling the nature and evolution of carbonate systems by providing criteria to interpret nutrient availability in ancient settings. Paleoecological approaches can be successfully applied to most Cenozoic settings, but become more uncertain with time and evolutionary changes. On the other hand, geochemical proxies can potentially be applied to both Cenozoic and Mesozoic settings. Their applicability to older time-slices is hindered by fundamental differences in pre-Mesozoic oceans, including lack of appropriate microfossils.

The integration of these two approaches should be used whenever possible, and particularly when results from one approach remain problematic. For example, when it is not possible to make geochemical analyses directly on the platform biota, productivity changes can be inferred primarily from deep-water sections, and carried to the shelf through integration of physical

Fig. 4 Use of proxies to reconstruct past nutrient concentrations under different oceanographic conditions. **a** Oligotrophic, **b** mesotrophic, and **c** eutrophic. Hypertrophic conditions are not illustrated because they do not support formation of neritic carbonates. *Boxes* labeled *A–D* correspond to the range in which the proxies can be used from shelf to basin. The *bulleted list* represents the most accurate proxies



stratigraphy and development of high-resolution age models. A common geological situation occurs when concentrations of organic matter and opal are high in the basin but low in the correlative shelf strata. In such a case, an ideal strategy would be to produce integrated high-resolution records of both neritic and pelagic strata, to analyze the flux records using MAR of C_{org} and/or opal and biomarkers in the deeper water sections with which to reconstruct first-order biogenic fluxes, and then to infer the effects on time-equivalent platform strata.

Clearly there is no single universal method to reconstruct the past nutrient availability in carbonate systems, but rather a variety of methods and approaches that need to be tailored to each specific geological situation. It should be stressed that no single tracer for productivity should be used alone, but rather a combined suite of

tracers should be used, in conjunction with biotic assemblages, to understand a carbonate system, particularly since different tracers can provide different insights into the system's paleo-ecology. More data and case studies are needed to integrate shallow and deep-water carbonate sequences, allowing us to better understand the links between changes in nutrient concentration and facies in carbonates sequences.

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