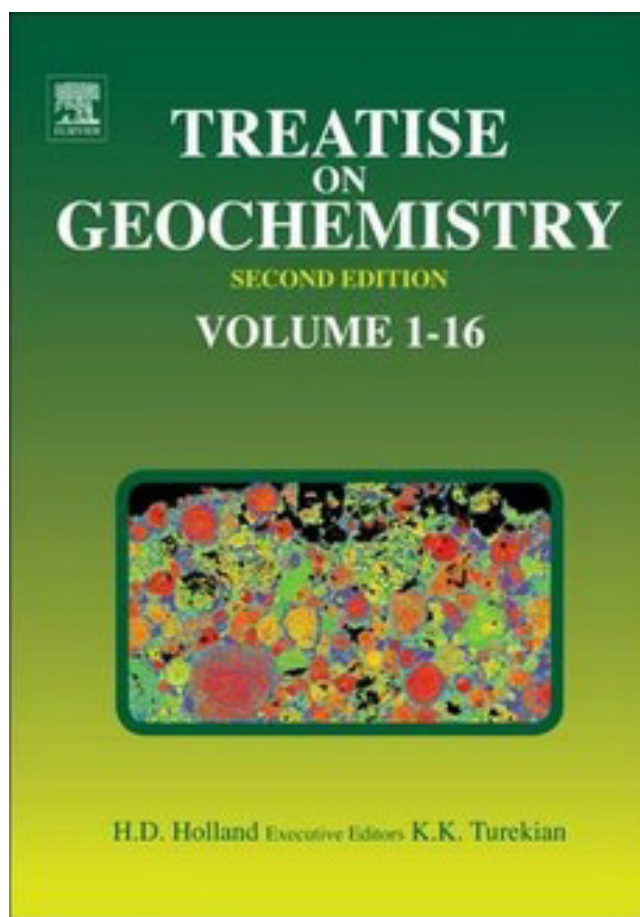


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8.14 Elemental and Isotopic Proxies of Past Ocean Temperatures

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8.14.1 Introduction

Determining the temperature evolution of the oceans is one of the most important problems in geosciences. Temperature is the most primary representation of the state of the climate system, and the temperature of the oceans is critical because the oceans are the dominant component of the Earth's internal climate system in terms of influencing climate change on time-scales of greater than a few hundred years. A set of isotopic and elemental proxies preserved in marine carbonate sediments and rocks provides earth scientists with a complementary set of approaches to determine past ocean temperatures. This is a

field with both a long history and a great deal of recent progress. Paleotemperature research has been at the forefront of geoscience research for over 50 years and, with our need to understand the global climate system heightened by modern climate change, it promises to remain a vibrant and important area well into the future.

The first edition of this chapter gave an overview of research in this field as of mid-2002. In the intervening decade, there has been a great deal of progress in a number of areas within the field of elemental and isotopic proxies of temperature, among them development of the clumped isotope approach in biogenic carbonates, refinements of the foraminiferal Mg/Ca

proxy, and application of both oxygen isotopes and Mg/Ca to high-resolution paleoclimate sequences of the last few millennia. This second edition preserves the structure and content of the first edition while surveying some of these newer contributions.

This chapter begins by reviewing the history of the elemental and isotopic proxies and how that history shapes research priorities today. The state of our knowledge at present is then reviewed, including areas that are well developed (i.e., oxygen isotopes in coral aragonite), areas that are presently experiencing phenomenal growth (i.e., Mg/Ca in foraminifer shells), and areas that are just starting to develop (i.e., Ca isotopes and clumped isotopes in carbonates). An estimation of the uncertainty in each of these techniques and areas, including aspects that particularly need to be addressed, is included. The question of overlap and confirmation between proxies and, in particular, how information from one proxy can augment a second proxy is also addressed (Table 1).

8.14.2 A Brief History of Early Research on Geochemical Proxies of Temperature

Geologists have been interested in establishing the temperature history of the oceans for as long as they have documented historical variations in marine sediments. Probably the first realization that geochemical variations might reflect temperatures can be traced to the great American geochemist Frank Wigglesworth Clarke (1847–1931), the namesake of the Geochemical Society's Clarke award. Aside from his voluminous contributions to establishing precise atomic weights, the composition of the Earth's crust, and natural waters, Clarke found time to document a provocative relationship between the Mg content of biogenic carbonates and their growth temperature (Clarke and Wheeler, 1922). The authors speculated that this relationship had a definite cause and could possibly be useful: "This rule, or rather tendency, we are inclined to believe is general, although we must admit that there are probably exceptions to it." Clarke and Wheeler recognized that the Mg-to-Ca ratio of present-day seawater is nearly constant from ocean to ocean, and that the relationship therefore had to have some cause other than compositional variations: "That warmth favors the assimilation of magnesia by marine invertebrates seems to be reasonably certain, but why it should be so is not clear. The relation is definite but as yet unexplained. *We hope it is not inexplicable*" (italics added for emphasis). Further along in the same paragraph, Clarke and Wheeler presaged the field of geochemical paleoceanography and paleoclimatology: "Attempts will likely be made to use our data in studies of climatology, but are such attempts likely to be fruitful?" The authors envisioned researchers using the bulk Mg content of ancient rocks to determine past temperatures, an approach they deemed doubtful because it would depend on the ratios of particular organisms in rocks. Of course, Clarke and Wheeler did not envision the powerful analytical techniques available to the present-day analyst, where the trace element content of individual chambers of plankton shells can be readily analyzed. Such single species analysis is what eventually enabled the useful application of Clarke and Wheeler's original insight to paleothermometry (see below). However, it was not until the late 1990s that the observed

Mg relationship became both explicable and fruitful for climatology.

The next great step forward came after the Second World War, when Harold Urey (1893–1981), a 1934 Nobel Laureate for his discovery of deuterium, the heavy isotope of hydrogen, took up a professorship at the University of Chicago. There, he became interested in the utilization of natural fractionations in stable isotope systems for geological purposes (Urey, 1947). He theorized that the effect of temperature on the partitioning of oxygen isotopes between water and carbonate might become a useful geological tool: "Accurate determinations of the O^{18} content of carbonate rocks could be used to determine the temperature at which they were formed." Interestingly, Urey did not envision that compositional variations in the ocean would complicate such determinations: "First, there is the large reservoir of oxygen in the oceans which *cannot have changed* in isotopic compositions during geological time" (italics added for emphasis). He of course recognized that if such variations occurred, they would complicate paleotemperature determinations, and he pointed out in the same paragraph that variations in the isotopic composition of calcium would hinder its potential use for paleotemperature analysis, a point relevant to present research (see below). Of course, Urey would not have known about or envisioned the considerable effects continental glaciation and crustal exchange would have on the oxygen isotopic composition of the oceans (Sturchio, 1999).

Urey pioneered the use of oxygen isotopes for paleotemperature determination when he applied the technique to belemnite fossils from the upper Cretaceous (Urey et al., 1951). However, it was left to Urey's students and postdoctoral scholars to fully exploit his original insights. Major advances came from the establishment of a so-called paleotemperature equation by Samuel Epstein (1919–2001), mainly based on calcite precipitated by molluscs in either controlled experiments or field-collected samples (Epstein et al., 1953). Analysis of this calcite yielded a paleotemperature equation that demonstrated a sensitivity of $\sim 0.2\text{‰}$ change in $\delta^{18}O$ per degree Celsius. It is important to note that during this time period, and, as shown above, from the conception of the original idea, the emphasis in using oxygen isotopes was to reconstruct paleotemperatures. A few years later, Cesare Emiliani (1922–95), a student and later a postdoctoral scholar with Urey, exploited these advances when he documented regular cyclic variations in the oxygen isotopic composition of planktonic foraminifera taken from eight sediment cores in the Caribbean (Emiliani, 1955b). Although Emiliani did allow for small variations in the isotopic composition of seawater, he largely interpreted the observed $\delta^{18}O$ variations as a reflection of recurring cold intervals in the past during which tropical surface waters cooled by 6–8 °C. Many of the questions raised by Emiliani's classic 1955 study are still relevant today and are addressed in detail below (Table 1).

During this same time period, scholars at Chicago examined the potential temperature dependence of trace elements in carbonates, focusing mainly on Mg and Sr incorporation (Chave, 1954). Although these studies provided some additional insights beyond Clarke and Wheeler's (1922) original findings, they failed to yield advances of the kind that were spurring research on isotopic variations. Samuel Epstein (personal communication, 1992) felt that the general sense in the

Table 1 Summary of major paleotemperature techniques

	Phases	Sensitivity (per °C)	Estimated SE	Major secondary effects	Timescale ^a
Oxygen isotopes	Foraminifera	0.18–0.27‰	0.5 °C if $\delta^{18}\text{O}_{\text{seawater}}$ is known	Effect of $\delta^{18}\text{O}_{\text{seawater}}$	0–100 Ma
	Corals	~0.2‰	0.5 °C if $\delta^{18}\text{O}_{\text{seawater}}$ is known	Kinetic effects	0–130 ka
	Opal			Effect of $\delta^{18}\text{O}_{\text{seawater}}$	0–30 ka
Mg/Ca	Foraminifera	~9%	~1 °C	Effect of $\delta^{18}\text{O}_{\text{seawater}}$ Dissolution, Salinity ($S > 35$) Secular Mg/Ca variations (>10 Ma)	0–100 Ma
	Ostracodes	~9%	~1 °C	Dissolution? Calibration	0–3.2 Ma
Sr/Ca	Corals	–0.4 to –1.0%	0.5 °C?	Growth effects Secular Sr/Ca changes (>5 ka)	0–130 ka
Ca isotopes	Foraminifera	0.02 to 0.24‰	unknown	Species effects, calcification	0–125 ka
Alkenone unsaturation index (Chapter 8.15)	Sediment organics	0.033 (0.023–0.037) in U_{37}^{K} (Müller et al., 1998; Pelejero and Calvo, 2003)	~1.5 °C (global calib.)	Transport, species variation	0–3 Ma
Faunal transfer functions (Imbrie and Kipp, 1971)	Foraminifera, Radiolaria, and Dinoflagellates	N/A	1.5 °C	Ecological shifts	0–?

^aTimescale over which the technique has been applied.

Chicago group was that elemental substitution was likely to be less regular than isotopic substitution, presumably because the individual activity coefficients of each element would introduce additional complexity beyond a simple temperature dependence.

Following Emiliani's (1955b) discovery, other laboratories established the capability to apply oxygen isotope variations to oceanic temperature history. It is worth a brief mention of two further major advances relevant to Urey's original conception. In 1967, Nicholas Shackleton (1937–2006) of Cambridge University reported the first systematic downcore variations in the oxygen isotopic composition of benthic foraminifera (Shackleton, 1967). He argued that benthic fauna, because they lived in the near-freezing bottom waters of the ocean, would mainly record the change in isotopic variation of seawater. By demonstrating that the observed benthic variations were of similar magnitude to those in planktics, he was able to demonstrate that the major portion of the isotopic signal recorded in marine sediments reflected oscillations in the oxygen isotopic composition of the ocean, which in turn occurred in response to the periodic transfer of isotopically depleted water onto continental ice sheets. Once this paradigm shift was in place, Shackleton and others were able to use oxygen isotopic variations as a stratigraphic and chronometric tool for marine sediments (Shackleton and Opdyke, 1973), an advance which led to the establishment of a precise timescale for the late Quaternary marine record and ultimately the verification of orbital variations as the pacemakers of the Pleistocene ice ages (Hays et al., 1976). Thus, from Urey's conception to Shackleton's insight, a tool originally envisioned as a paleothermometer found its most profound use as a recorder of the compositional variations in seawater that Urey considered to be an unlikely influence. Parallel advances in the utilization of elemental variations did not occur until the 1990s

(see below), but it is worth mentioning as a close to this historical summary that recent research indicates that the Mg/Ca content of foraminifera provides at least a partial solution to the 'Urey dilemma,' because it provides, in combination with oxygen isotopes, a simultaneous temperature and isotopic composition history for seawater (Elderfield et al., 2010, 2012; Lea et al., 2000; Lear et al., 2000; Pahnke et al., 2003; Sosdian and Rosenthal, 2009).

8.14.3 Oxygen Isotopes as a Paleotemperature Proxy in Foraminifera

8.14.3.1 Background

The use of oxygen isotope ratios as a paleotemperature indicator in carbonate minerals is based on the thermodynamic fractionation between ^{16}O and ^{18}O that occurs during precipitation (Urey, 1947). This fractionation, which offsets the $\delta^{18}\text{O}$ ($\delta^{18}\text{O} = [(^{18}/^{16}\text{O}_{\text{sample}} / ^{18}/^{16}\text{O}_{\text{standard}}) - 1]$) of carbonate minerals relative to seawater by $\sim +30\text{‰}$, is a logarithmic function of temperature with a slope, over the oceanic temperature range of -2 to 30 °C, of between -0.20 and -0.27‰ per degree Celsius, in agreement with thermodynamic predictions (Kim and O'Neil, 1997; O'Neil et al., 1969; Shackleton, 1974; Zhou and Zheng, 2003). Because the oxygen isotope proxy is based on a thermodynamic principle, it is expected to be robust and relatively unaffected by secondary kinetic factors. For foraminifera, unicellular zooplankton, and benthos that precipitate calcite and, less commonly, aragonite shells (sometimes called tests), oxygen isotopic ratios do appear to be quite robust, although there are clear indications of a secondary effect from factors such as ontogenetic variations and seawater carbonate ion (see below).

The most significant complication in using oxygen isotopes to determine both absolute temperatures and relative temperature changes is that the $\delta^{18}\text{O}$ of carbonate solids reflects both temperature fractionation and the $\delta^{18}\text{O}$ of the seawater from which the carbonate precipitated. The $\delta^{18}\text{O}$ of seawater in turn reflects two major factors: (1) the mean $\delta^{18}\text{O}$ of seawater (Adkins et al., 2002; Schrag et al., 1996), which is determined by the amount of continental ice, which varies on timescales of 10^4 – 10^5 years, and by the interaction between seafloor basalts and seawater, which varies on timescales of 10^7 – 10^8 years; and (2) the evaporation–precipitation (rainfall) balance (E–P) for that part of the ocean or, for subsurface waters, the balance that applied to the source waters of those deep waters. The second factor is often described as a ‘salinity effect’ because $\delta^{18}\text{O}$ tends to track with salinity variations because both respond to E–P. The relationship between $\delta^{18}\text{O}$ and salinity, however, varies considerably over the ocean because of the varying isotopic composition of freshwater (Schmidt et al., 2001). It is important to emphasize that both effects cast considerable uncertainty into the use of oxygen isotopic ratios for absolute and relative paleothermometry on essentially all timescales.

Despite these caveats, oxygen isotopic ratios are probably the most widely used climate proxy in ocean history research. Reasons for this widespread use relate to the history of oxygen isotopes in geological research (see Section 8.14.2): the fact that they can be measured quite precisely by mass spectrometry and are relatively immune, at least in younger deposits, to secondary effects, the fact that $\delta^{18}\text{O}$ records tend to be quite reproducible and clearly record climate variability, and finally, the fact that $\delta^{18}\text{O}$ records have proven to be so powerful for stratigraphic and chronological purposes (Lisiecki and Raymo, 2005).

An important aspect of the application of oxygen isotopic ratios in foraminifera is that planktonic forms occupy several ecological niches, including surface waters, shallow subsurface waters, and deeper thermocline waters. Along with their benthic counterparts, this makes it possible to recover oxygen isotopic records representative of different parts of the water column. A complication, however, is that many of the planktonic species migrate vertically, potentially compounding the signals they record.

8.14.3.2 Paleotemperature Equations

There are a number of calibrations in use for oxygen isotopes in foraminifera, some derived from other organisms (Epstein et al., 1953), some derived from culturing (Bemis et al., 1998; Erez and Luz, 1983), and some derived from core-top calibrations (Shackleton, 1974). These calibrations take the form of a polynomial paleotemperature equation:

$$T = a + b(\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}}) + c(\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}})^2 \quad [1]$$

where T = temperature ($^{\circ}\text{C}$), a = temperature when $\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}}$ (both on V-PDB scale) is 0, b is the slope, and c is the second-order term for curvature (not always included). The inverse of the slope b represents the change in $\delta^{18}\text{O}$ (in ‰) for a 1°C change in temperature. If the

second-order term c is included, then the slope is not constant. The value of the slope is predicted to increase with decreasing temperature because isotopic fractionation increases with decreasing temperature (Urey, 1947). Experimental evidence from inorganic calcite precipitation studies indicates that the slope ranges from 0.27‰ per degree Celsius at 0°C to 0.20‰ per degree Celsius at 25°C (Kim and O’Neil, 1997; O’Neil et al., 1969). Observational evidence from calibration of foraminiferal $\delta^{18}\text{O}$ indicates a similar or slightly larger range of values (Bemis et al., 1998). The status of oxygen isotope calibrations is extensively reviewed by Bemis et al. (1998). For warm-water studies, the low light *Orbulina universa* calibration of Bemis et al. (1998) appears to work well:

$$T = 16.5 - 4.80(\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}}) \quad [2]$$

For cold waters and certain benthics (e.g., *Uvigerina*), the Shackleton (1974) expression, which is a polynomial expansion of the equation of O’Neil et al. (1969), appears to work well:

$$T = 16.9 - 4.38(\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}}) + 0.1(\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}})^2 \quad [3]$$

The quantitative applicability of these equations is becoming more important with the growing interest in combining independent foraminiferal temperature estimates from Mg/Ca with $\delta^{18}\text{O}$ to calculate $\delta^{18}\text{O}_{\text{water}}$ (Elderfield and Ganssen, 2000; Elderfield et al., 2010; Lea et al., 2000; Lear et al., 2000; Mashiotta et al., 1999; Pahnke et al., 2003; Sosdian and Rosenthal, 2009).

8.14.3.3 Secondary Effects and Diagenesis

There has been a long discussion in the literature as to the extent to which foraminiferal shells are in oxygen isotopic equilibrium. The precise state of equilibrium cannot be defined with sufficient precision from theory, so the general practice is to compare observed foraminiferal calibrations to those from inorganic experiments (Bemis et al., 1998; Kim and O’Neil, 1997; Shackleton, 1974). Such comparisons suggest that foraminiferal shells can be offset from equilibrium for a number of reasons (Figure 1), including offsets from unknown vital effects in benthic species (Duplessy et al., 1970), offsets due to the effect of light on symbiotic algae (Bemis et al., 1998; Spero and Lea, 1993), offsets due to ontogeny (growth) (Spero and Lea, 1996), offsets due to carbonate ion concentration in seawater (Spero et al., 1997), and offsets due to the addition of gametogenic calcite at depth (Duplessy et al., 1981). All of these effects can complicate the use of oxygen isotopes for paleotemperature or paleo- $\delta^{18}\text{O}_{\text{water}}$ studies. Some of these effects, such as that due to gametogenic calcite (Hamilton et al., 2008), also apply to Mg/Ca paleothermometry (Dekens et al., 2002; Rosenthal et al., 2000), so it is likely that complementary studies will improve our understanding of the limitations these effects impose. Recent advances using ion microprobe analysis reveal unexpected intratest variability in oxygen isotopes (Kozdon et al., 2009); spatial studies of this kind promise to provide important insights into vital effects.

On Quaternary timescales, the main diagenetic concern is partial shell dissolution that takes place on the seafloor or within the sedimentary mixed layer. This effect has been

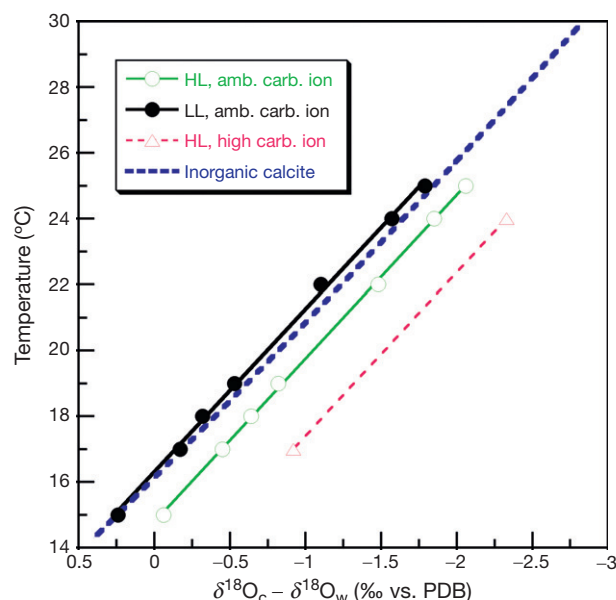


Figure 1 Comparison of oxygen isotope paleotemperature equations for *Orbulina universa*, a symbiont-bearing planktonic foraminifera, with values for inorganic calcite precipitation (Kim and O'Neil, 1997). These data demonstrate that the low light (LL) oxygen isotope equation at ambient carbonate ion concentration for *O. universa* is essentially indistinguishable from the inorganic equation. For high light conditions (HL), in which symbiont photosynthetic activity is maximized, $\delta^{18}\text{O}$ shifts to more negative values. For high-carbonate ion conditions, $\delta^{18}\text{O}$ shifts to even more negative values. These trends demonstrate the range of potential biological influences on foraminiferal $\delta^{18}\text{O}$. Modified from Bemis BE, Spero HJ, Bijma J, and Lea DW (1998) Reevaluation of the oxygen isotopic composition of planktonic foraminifera: Experimental results and revised paleotemperature equations. *Paleoceanography* 13: 150–160.

demonstrated to increase the $\delta^{18}\text{O}$ of shells by $\sim 0.2\text{‰ km}^{-1}$ in deeper, more dissolved sediments (Dekens et al., 2002; Wu and Berger, 1989), presumably through the loss of individual shells and/or shell material with more negative $\delta^{18}\text{O}$. Because this effect appears to be coincident for both oxygen isotopes and Mg/Ca (Brown and Elderfield, 1996; Dekens et al., 2002; Rosenthal et al., 2000), it is likely that complementary studies will allow a better assessment of the potential biases imposed by dissolution. On longer timescales, diagenetic effects multiply to include gradual replacement of the primary calcite (Schrage, 1999a; Schrage et al., 1995). Studies suggest that shells with unusually good levels of preservation, such as those preserved in impermeable clay-rich sediments, record much more negative $\delta^{18}\text{O}$ (and hence warmer temperatures) than shells from deeply buried open-ocean sequences (Pearson et al., 2001). Recent advances using ion microprobe analysis suggests that primary oxygen isotope ratios can be recovered by targeting areas of the test that are less susceptible to postdepositional alteration (Kozdon et al., 2011).

8.14.3.4 Results on Quaternary Timescales

The many important results achieved in paleoceanography and paleoclimatology using oxygen isotope ratios in foraminiferal shells are well known and have been reviewed and

summarized in many other places (e.g., Imbrie et al., 1992; Lisiecki and Raymo, 2005; Mix, 1992; Shackleton, 1987). Because of the outstanding geological importance of oxygen isotopic results, they take a central place in the history of proxy development, a subject discussed in Sections 8.14.2 and 8.14.3.1. As was emphasized in Section 8.14.2, the pioneers in utilization of oxygen isotopes envisioned them as a paleotemperature tool. With the realization that change in the isotopic composition of the ocean exceeded the temperature influence on foraminiferal calcite (Shackleton, 1967), emphasis shifted to the use of Quaternary oxygen isotopic variations as a tool for stratigraphy and chronology (Hays et al., 1976; Shackleton and Opdyke, 1973) and for calibration of the magnitude of past sea level and ice volume change (Chappell and Shackleton, 1986; Shackleton, 1987; Waelbroeck et al., 2002). With the advent of independent geochemical paleotemperature proxies, it became possible to deconvolve the isotopic signal into its temperature and compositional components (Elderfield and Ganssen, 2000; Mashiotto et al., 1999; Rostek et al., 1993). Current research (see Sections 8.14.7.4 and 8.14.7.5) is focused on the veracity of this approach and the separation of ice volume and hydrological influences in the extracted $\delta^{18}\text{O}_{\text{water}}$ records (Elderfield et al., 2010; Lea et al., 2000, 2002; Lear et al., 2000; Martin et al., 2002; Pahnke et al., 2003; Sosdian and Rosenthal, 2009). Another very fruitful approach is to utilize oxygen isotope records from semi-isolated basins such as the Red Sea, where the oxygen isotope signal is dominated by changes in sea level (Rohling et al., 2009; Siddall et al., 2003).

8.14.3.5 Results for the Neogene, Paleogene, and Earlier Periods

The Cenozoic benthic foraminiferal $\delta^{18}\text{O}$ record is one of the major successes of the geochemical approach to paleoclimate research (Zachos et al., 2001). Because it is a record of the combined influences of temperature and ice volume, which are evolving semi-independently over the course of the Cenozoic, it is more a record of earth system processes than of temperature (see Chapter 8.20). There has been a great deal of interest and controversy concerning the utilization of oxygen isotopes in low-latitude planktonic foraminifera to determine tropical ocean temperatures on longer timescales (Barron, 1987). Research suggests that diagenetic overprinting of primary foraminiferal $\delta^{18}\text{O}$ is a major influence (Pearson et al., 2001; Schrage, 1999a). Results from Pearson et al. (2001) suggest that low-latitude sea surface temperatures (SSTs) during the Late Cretaceous and Eocene epochs were at least 28–32 °C compared with previous estimates, based on less well-preserved material, of 15–23 °C. Obviously, such a large shift requires a reevaluation of Paleogene and Cretaceous climates, but it might also point the way toward a means of correcting less well-preserved samples for diagenesis, perhaps in combination with the Mg/Ca approach.

8.14.3.6 Summary of Outstanding Research Issues

Of the primary paleothermometric techniques reviewed in this chapter, oxygen isotopes in foraminifera have the longest

history of development and application. It is probably safe to say that oxygen isotopes are on the most secure ground in terms of known influences and inherent accuracy. Unexpected findings, such as a primary seawater carbonate ion influence (Spero et al., 1997) and secondary diagenetic overprints (Pearson et al., 2001; Schrag, 1999a), suggest that there is still major progress to be made in this area. New techniques such as ion probe analysis promise to improve our understanding of vital effects. The most outstanding research issues today certainly must include progress and prospects for combining Mg/Ca paleothermometry with oxygen isotopes on both Quaternary, Neogene, and Paleogene timescales, and the need for reevaluation of the integrity and interpretation of Paleogene oxygen isotope ratios in foraminifera.

8.14.4 Oxygen Isotopes as a Climate Proxy in Reef Corals

8.14.4.1 Background

Many of the factors described in Section 8.14.3 apply equally to oxygen isotopes in corals, which are dominantly composed of aragonite. Corals, however, have many unique aspects that require separate consideration. First, their oxygen isotopic composition is invariably depleted relative to equilibrium by ~1–6‰, presumably because of their different biochemical mechanisms of precipitation as well as the influence of symbiotic zooxanthellae (McConnaughey, 1989a,b). This offset from equilibrium actually discouraged early researchers, who assumed that corals would not be reliable temperature recorders (S. Epstein, Caltech, personal communication, 1998). Eventually, however, researchers began to investigate the prospect of attaining climate records from coral skeletons, and despite the offset from equilibrium, research revealed that the oxygen isotopic composition recorded subseasonal variations in seawater temperature and salinity (Cole and Fairbanks, 1990; Druffel, 1985; Dunbar and Wellington, 1985; Emiliani et al., 1978; Fairbanks and Dodge, 1979; McConnaughey, 1989a; Shen et al., 1992; Weber and Woodhead, 1972). These early discoveries have been followed by a fantastic array of results from longer coral time series that have enabled researchers to establish coral climate records as the marine equivalent of tree ring records (Gagan et al., 2000). In general, coral $\delta^{18}\text{O}$ records are not interpreted directly as temperature records but rather as climate records whose variability reflects some combination of temperature and salinity effects.

Because aragonite is more susceptible to dissolution than calcite, especially under the influence of meteoric waters, and because most fossil corals are recovered from uplifted terrestrial deposits, diagenesis is an especially important limiting factor in recovering older coral records. This problem can be partly circumvented by drilling into submerged fossil deposits, but because of logistical difficulties, this has been accomplished in only a few key spots such as Barbados, Tahiti, and the Great Barrier Reef (GBR) (Asami et al., 2009; Bard et al., 1996; DeLong et al., 2010; Fairbanks, 1989). The recent International Ocean Drilling Program (IODP) expeditions targeted at Tahiti (Expedition 310) and the GBR (Expedition 325) should yield many new results from submerged, less-altered coral samples, including those that preserve seasonal variations.

8.14.4.2 Paleotemperature Equations

Weber and Woodhead (1972) first demonstrated that oxygen isotopes in corals respond to temperature but are offset to negative $\delta^{18}\text{O}$ values relative to equilibrium. Presently, the oxygen isotope paleotemperature equation is well calibrated for corals (Gagan et al., 2000). The systematic offset from the equilibrium or inorganic aragonite value is attributed to a biological or vital effect (McConnaughey, 1989a,b). This offset, however, appears to be stable over time in many different settings (Gagan et al., 2000), although researchers recognize that vital effects can offset coral $\delta^{18}\text{O}$ to varying degrees (Cohen et al., 2004; Corrège, 2006; McConnaughey, 1989a,b; Spero et al., 1997; Watanabe et al., 2003). The slope of the calibrations is variable and less than 0.23‰ per degree Celsius, the slope from inorganic aragonite experiments (Zhou and Zheng, 2003); the difference is attributed to variability in skeletal growth rate (Gagan et al., 2012).

Of course, the oxygen isotopic composition of carbonate is also a function of the $\delta^{18}\text{O}$ of seawater, which varies with the local E–P balance, and hence salinity. Because temperature and salinity often vary together in the tropics, researchers tend to use coral $\delta^{18}\text{O}$ variations as climate proxies rather than temperature proxies. This approach has been very successful (see Section 8.14.4.4), but it still leaves the problem of attributing the observed changes in $\delta^{18}\text{O}$ to some specific combination of temperature and $\delta^{18}\text{O}_{\text{water}}$ changes. One solution is to use an independent temperature proxy such as Sr/Ca (see Section 8.14.9) at the same time to separate the coral $\delta^{18}\text{O}$ signal into its components (Gagan et al., 1998; McCulloch et al., 1994). It is also possible that comparison of records of coral $\delta^{18}\text{O}$ from different areas with contrasting climatology could be used to separate temperature and $\delta^{18}\text{O}_{\text{water}}$ influence.

8.14.4.3 Secondary Effects and Diagenesis

The major secondary effect for oxygen isotopes in hermatypic reef corals is the negative offset from equilibrium (Emiliani et al., 1978). The degree to which this offset is stable in space and time (Cohen et al., 2004; Corrège, 2006; Linsley et al., 1999; McConnaughey, 1989a,b; Watanabe et al., 2003) is critical to the interpretation of observed $\delta^{18}\text{O}$ variations in terms of absolute temperature and salinity changes. Measurements of $\delta^{18}\text{O}$ in coral heads from a single reef do reveal up to 1‰ variability in absolute values from specimen to specimen. The biological factors that cause these differences obviously have the potential to affect the use of coral $\delta^{18}\text{O}$ for paleoclimate research, but this challenge can be overcome by stacking multiple coral datasets from common locations (Linsley et al., 2008; Tudhope et al., 1995).

There is some evidence that the buildup of aragonite cements in living coral skeletons can affect the fidelity of coral $\delta^{18}\text{O}$ and Sr/Ca (see Section 8.14.9.3) records (Müller et al., 2001; Sayani et al., 2011). This occurs as pore spaces in the older part of the coral heads fill with inorganic aragonite, which has a more enriched $\delta^{18}\text{O}$ relative to the original coral material. As a result, the recorded climate signal in the oldest part of the coral is shifted to systematically colder and/or higher salinity values. Müller et al. (2001) observed that both $\delta^{18}\text{O}$ and Sr/Ca were biased similarly by inorganic aragonite

precipitation, so cross-checks between proxies within the same coral do not alleviate the problem. Fortunately, however, it is possible to observe the precipitation of the secondary aragonite using petrography.

Because aragonite reverts to calcite when it interacts with meteoric water, subaerial exposure of fossil corals has the potential to change the $\delta^{18}\text{O}$ of the coral. Generally, diagenetically altered corals can be avoided by using X-ray crystallography to screen for the presence of calcite. One study suggests that small, restricted levels of aragonite alteration have minimal effects on coral $\delta^{18}\text{O}$ (McGregor and Gagan, 2003). A more recent study suggests that early diagenetic impacts on the $\delta^{18}\text{O}$ and Sr/Ca of 350–750-year-old corals are significant but can be circumvented by analysis of pristine skeletal elements (Sayani et al., 2011).

8.14.4.4 Results on Historical Timescales

Records of oxygen isotopic variations in coral heads have become important paleoclimatic archives of tropical climate change (Figure 2), and they have been incorporated into historical climate records used to assess global warming in the past century (Crowley, 2000a; Mann et al., 1998). Some of the outstanding findings from the coral records include the following: (1) most of the longer records show a secular shift to more negative $\delta^{18}\text{O}$ values starting in the nineteenth century; (2) a series of decadal or longer coherent shifts in the nineteenth century that might reflect regional to global cooling patterns; (3) shifts in the magnitude and frequency of the El Niño/Southern Oscillation (ENSO) phenomenon and Indian Ocean monsoon over the past two centuries (Cobb et al., 2001; Cole et al., 2000; Urban et al., 2000); and (4) records of ENSO behavior over the last 1000 years, using fossil corals deposited on Palmyra Island beaches by storms (Cobb et al., 2003).

These coral records have great value as 'generic' proxy climate records, in the same sense that tree ring records have been

used without an explicit attribution of the observed variations to temperature, precipitation, etc. Because these records are based on a geochemical parameter that follows thermodynamic rules, it should be possible eventually to extract true temperature and/or salinity records from the coral time series (e.g., Gorman et al., 2012). Another potential complication, however, is that the coral records might reflect biological effects such as gradual growth into shallower waters as coral heads grow (Gagan et al., 2000). Many coral heads show a secular shift to more negative $\delta^{18}\text{O}$ values in the most modern period of growth, a result generally attributed to warming of surface waters in response to anthropogenic factors (Gagan et al., 2000; Grottoli and Eakin, 2007). However, in at least some cases, this shift appears to be larger than can be explained by SST shifts recorded by instrumental records (the records in Urban et al., 2000, and Cobb et al., 2001 are good examples), so this trend either reflects a coincident decline in surface salinity or the aforementioned biological factors or perhaps undetected secondary aragonite precipitation in the oldest parts of the coral (Müller et al., 2001).

8.14.4.5 Results on Late Quaternary Timescales

With the realization that oxygen isotopes in coral heads record subannual ocean climate variations came the idea of using such records from fossil corals to reconstruct both absolute and relative climate change for past geological periods (Fairbanks and Matthews, 1978). Because fossil corals from emerging coastlines have been exposed to meteoric fluids and weathering, this approach requires consideration of the potential for diagenetic changes (see Section 8.14.4.3). Although the complications of using fossil corals as paleoclimate tools are greater, the information to be gained is of great importance because it applies to climate systems under different boundary conditions (Tudhope et al., 2001).

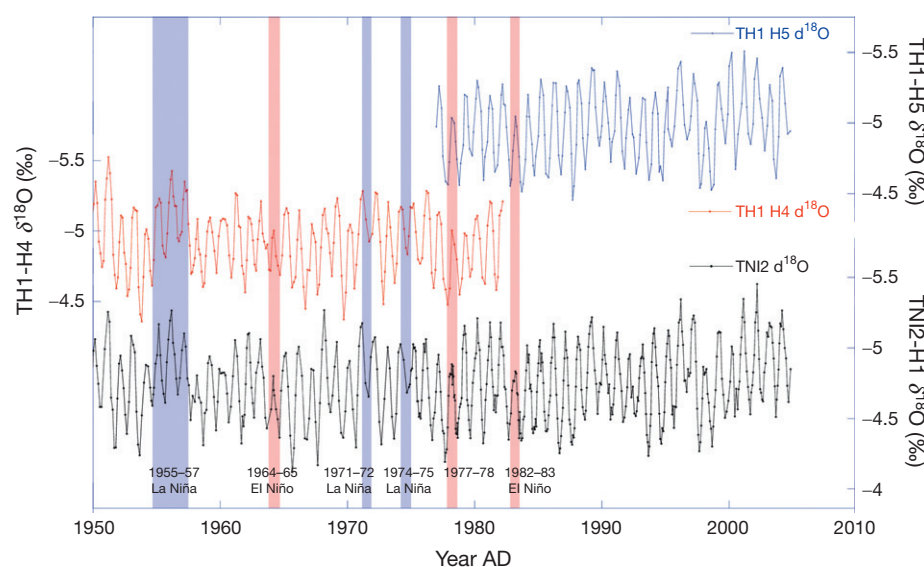


Figure 2 Comparison of three oxygen isotope records from coral cores taken in the Tonga Islands, South Pacific. The coral cores were sampled at ~ 1 mm resolution, equivalent to about 1 month of growth. The figure illustrates the correspondence between the three records, as highlighted for specific El Niño and La Niña events. Note that the mean values for each record are slightly different. Reproduced from Linsley BK, Zhang PP, Kaplan A, Howe SS, and Wellington GM (2008) Interdecadal-decadal climate variability from multicoral oxygen isotope records in the South Pacific Convergence Zone region since 1650 A.D. *Paleoceanography* 23: PA2219.

The first generation of studies on oxygen isotopes in fossil corals attempted to use absolute differences as a gauge of changes in mean ocean $\delta^{18}\text{O}$ in response to continental glaciation and mean SST changes. Early studies used coral $\delta^{18}\text{O}$ to better define the relationship between sea level change and mean ocean $\delta^{18}\text{O}$ changes (see [Section 8.14.3.4](#)) ([Fairbanks and Matthews, 1978](#)). A number of studies published in the 1990s use coral $\delta^{18}\text{O}$ to try to establish SST history for the tropics ([Guilderson et al., 1994, 2001](#); [McCulloch et al., 1999](#)). These studies suggest quite large glacial cooling of 4–6 °C for both tropical Atlantic and Pacific SSTs ([Gagan et al., 2012](#)). Such large cooling is generally not supported by other approaches ([Bard et al., 1997](#); [Lea et al., 2000](#); [Nürnberg et al., 2000](#)). Obviously, the coral $\delta^{18}\text{O}$ approach depends heavily on knowledge of the $\delta^{18}\text{O}$ of local seawater, which will shift with both ice volume and local changes in E versus P (see [Section 8.14.3.1](#)). Sr/Ca paleothermometry in corals provides a way around this problem, but this approach has its own set of limitations (see [Section 8.14.9.3](#)).

Some studies have focused instead on the climate variability encoded in annual and subannual fossil coral $\delta^{18}\text{O}$ ([Hughen et al., 1999](#); [Tudhope et al., 2001](#)). This approach does not require separating the oxygen isotope signal into its components, but rather uses the coral $\delta^{18}\text{O}$ signal as a climate proxy, with particular attention to the spectral characteristics of the time series. This approach is also less subject to diagenetic constraints, because corals that maintain distinct seasonal signatures are likely to be relatively unaltered. The results of these studies have been quite impressive in demonstrating that the nature of ENSO variability has been different under varying geological boundary conditions. [Tudhope et al. \(2001\)](#) documented coral climate proxy variability for seven different time slices. These records demonstrate that the amplitude of ENSO variability (2.5–7 year band) has generally been weaker in the geological past relative to the twentieth century. The amplitudes appear to have been weakest in the mid-Holocene (~6.5 ka) and during most of the cold glacial episodes ([Tudhope et al., 2001](#)). These records are by necessity fragmentary and comprise only a short window into ENSO variability in the past. These records also do not address the question of changes in ENSO frequency in the past, as have been suggested by studies of other climate proxies (e.g., [Rodbell et al., 1999](#)).

8.14.4.6 Summary of Outstanding Research Issues

Like the Cenozoic benthic foraminiferal record, high-resolution coral oxygen isotope records have been among the great successes of geochemistry applied to paleoclimate research. This is ironic given that early researchers were highly skeptical about the fidelity of coral $\delta^{18}\text{O}$ because corals are out of equilibrium ([Emiliani et al., 1978](#)). Although coral $\delta^{18}\text{O}$ is clearly a valuable indicator of climate history, many challenges remain in direct assignment of the observed trends to an absolute history of temperature and salinity. High priorities for future research include validating a coincident temperature proxy such as Sr/Ca (see [Section 8.14.9](#)) and determining the degree to which factors associated with the growth of large coral heads and early diagenesis influence longer term records.

8.14.5 Oxygen Isotopes as a Climate Proxy in other Marine Biogenic Phases

Oxygen isotopes have been used as temperature or climate proxies in a number of other marine biogenic phases, although far less widely than in foraminifera or reef corals. Probably, the most important work has been on oxygen isotopes in diatom opal ([Shemesh et al., 1992, 1994, 1995](#)). Because many sites in the Southern Ocean contain virtually no carbonate, opal $\delta^{18}\text{O}$ becomes critical for both stratigraphic and paleoclimatological purposes. Unfortunately, the systematics of oxygen isotopes in diatoms appears to be considerably more complex than for carbonates ([Juillet-Leclerc and Labeyrie, 1986](#); [Labeyrie and Juillet, 1982](#)). Oxygen isotopes have also been measured as temperature or climate proxies in ahermatypic solitary corals ([Smith et al., 1997](#)), in coralline sponges ([Zhou and Zheng, 2002](#)), in fish otoliths ([Andrus et al., 2002](#)), as well as in pteropods ([Grossman et al., 1986](#)) and other molluscs.

8.14.6 Clumped Oxygen Isotopes

The study of clumped isotope analogues has opened up new research avenues in the earth sciences ([Eiler, 2007](#)). This technique takes advantage of the fact that the clumping of the heavy isotopes ^{13}C and ^{18}O into bonds within calcium carbonate (i.e., $\text{Ca}^{13}\text{C}^{18}\text{O}^{16}\text{O}_2$) is temperature dependent. Clumped-isotope thermometry is based on analysis of $^{13}\text{C}^{18}\text{O}^{16}\text{O}$ produced by acid digestion of carbonates. This technique has recently been extended to corals, otoliths, and foraminifera, with promising early results ([Ghosh et al., 2006, 2007](#); [Tripathi et al., 2010](#)). A challenge for all forms of carbonate clumped isotope thermometry is the need for very large and clean samples, long analytical runs, and extensive replication to achieve results that translate into precise paleotemperature determination ([Ghosh et al., 2006](#)). The degree to which clumped isotope thermometry will become a useful proxy method in marine archives will likely depend on how well researchers can reduce these constraints in the future.

8.14.7 Magnesium as a Paleotemperature Proxy in Foraminifera

8.14.7.1 Background and History

Since the late 1990s, research in the use of Mg/Ca ratios in foraminifer shells has advanced as fast as any area in climate proxy research. As a result of these advances, researchers now have a good idea of the main advantages and limitations of this approach. It is fair to say that this new paleothermometry approach, perhaps more than any other, is revolutionizing the means by which paleoceanographers and paleoclimatologists unravel ocean and climate history. For this reason, the history of this development is more closely reviewed than for the other proxies.

As discussed in [Section 8.14.2](#), the observation that Mg was higher in marine carbonates precipitated in warmer waters dates to the early part of the twentieth century. Several studies confirmed these early observations for neritic foraminifer shells, which are composed of high-Mg calcite (>5% MgCO_3)

(Chave, 1954; Chilingar, 1962). Another study suggested that pelagic foraminifera, which are composed of low-Mg calcite (<1% MgCO_3), might also follow this pattern (Savin and Douglas, 1973). Several studies demonstrated that inorganic carbonates follow this pattern as well (Chilingar, 1962; Katz, 1973). This latter point is important because it indicates that the temperature influence cannot be entirely biological.

Another important milestone in this research came with the recognition that dissolution on the seafloor or within the sediments could significantly alter the Mg/Ca ratio of foraminifer shells (Bender et al., 1975; Hecht et al., 1975; Lorens et al., 1977). Lorens et al. (1977) went so far as to state that “*diagenesis rules out* using Mg/Ca ratios of whole tests as growth temperature indicators” (italics added for emphasis). Despite this clear hindrance, studies documenting systematic downcore variations (Cronblad and Malmgren, 1981) and possible links to growth temperature (Delaney et al., 1985) kept interest in the possibility of this proxy's usefulness alive. Several studies in the 1990s confirmed the early observations of a dissolution effect and species rankings (Brown and Elderfield, 1996; Rosenthal and Boyle, 1993; Russell et al., 1994). It was not until Dirk Nürnberg, a German doctoral student at Bremen University, used electron microprobe determinations on shell surfaces to document more convincing Mg/Ca–temperature relationships in cultured and natural core-top and downcore planktonic foraminifera (Nürnberg, 1995; Nürnberg et al., 1996a,b) that the international community recognized the potential of this new tool. Confirmation of a response of Mg in benthic foraminifera to bottom water temperatures, a result presaged by Scot Izuka's (University of Hawaii) pioneering study of Mg in *Cassidulina* (Izuka, 1988), occurred at about the same time (Rathburn and De Deckker, 1997; Rosenthal et al., 1997; Russell et al., 1994). The Rosenthal et al. (1997) paper is notable for its broad calibration and for being the first to point out that the relationship of Mg to temperature is predicted, albeit with a smaller slope, by thermodynamic calculations.

Progress has been rapid since these initial findings, in part because of improvements in analytical instrumentation and methods. Milestones include the first attempt to deduce glacial tropical SSTs using Mg/Ca (Hastings et al., 1998), the first calibrations made on cultured whole shells (Lea et al., 1999), the first attempt to combine Mg/Ca paleotemperatures with oxygen isotopic ratios to deduce variations in $\delta^{18}\text{O}_{\text{seawater}}$ (Elderfield and Ganssen, 2000; Mashiotta et al., 1999), the first long tropical SST and $\delta^{18}\text{O}_{\text{water}}$ records (Lea et al., 2000), the first application of benthic Mg to Cenozoic climate evolution (Lear et al., 2000), the first detailed late Quaternary benthic Mg records (Martin et al., 2002), and the first detailed sediment trap calibrations (Anand et al., 2003).

The following sections detail the most important of these findings and research priorities for the future.

8.14.7.2 Calibration and Paleotemperature Equations

The underlying basis for Mg paleothermometry is that the substitution of Mg in calcite is endothermic and therefore is favored at higher temperatures. The enthalpy change for the reaction based on the most recent thermodynamic data is 21 kJ mol^{-1} (Koziol and Newton, 1995), which equates to an exponential increase in Mg/Ca of 3% per degree Celsius using

the van't Hoff equation (Lea et al., 1999). The thermodynamic prediction of an exponential response is one of the reasons that Mg paleotemperature calibrations are generally parameterized this way. Available inorganic precipitation data generally follow the thermodynamic prediction (Burton and Walter, 1987; Chilingar, 1962; Katz, 1973; Mucci, 1987), with the most extensive dataset (Oomori et al., 1987) yielding a $3.1 \pm 0.4\%$ per degree Celsius increase in D_{Mg} for calcites precipitated in seawater over $10\text{--}50^\circ\text{C}$ (all responses given as percentages are calculated as exponentials, with 95% CI).

Foraminiferal shells differ from the thermodynamic prediction in two fundamental ways. First, foraminifera contain 5–10 times lower Mg than predicted from thermodynamic calculations (Bender et al., 1975). Second, the response of shell Mg to temperature is about three times larger than the thermodynamic prediction and inorganic observation, averaging $9 \pm 1\%$ per degree Celsius (Lea et al., 1999), for reasons that are unknown but which have important implications for Mg paleothermometry. First, this threefold increase in response increases the sensitivity of the approach, which is critical in determining its real error, which depends in large part on the relative magnitude of the temperature response versus that of all the combined sources of error, including measurement error, population variability, and secondary effects. Second, it raises the question of why the response is so much greater in foraminifera, and whether its augmentation depends on secondary factors that might change over geological time. One possibility is that the much smaller Mg content of foraminiferal shells increases the thermodynamic response (Figure 3). Data from Toyofuku et al. (2000), who

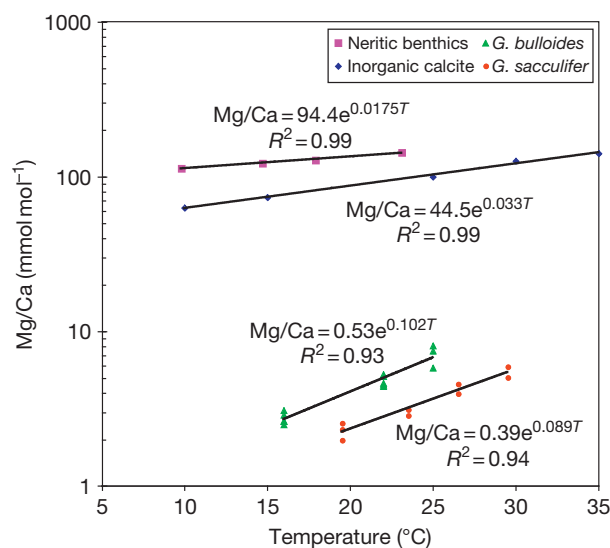


Figure 3 Comparison of Mg/Ca–temperature relationships for inorganic calcite precipitation (Oomori et al., 1987), neritic benthic foraminifera (Toyofuku et al., 2000), a tropical spinose symbiont-bearing planktonic foraminifera, *G. sacculifer* (Nürnberg et al., 1996a,b), and a subpolar spinose symbiont-barren planktonic foraminifera, *G. bulloides* (Lea et al., 1999). All of the foraminifera results are from culturing. Mg/Ca is plotted on a log scale because of the wide range of values. All of the relationships are fit with an exponential. Note that high-Mg inorganic and benthic calcite have a shallower slope and much smaller exponential constant (2–3%); the low-Mg foraminiferal calcite has a steeper slope and higher exponential constant (9–10%). Low-Mg benthic foraminifera have exponential constants of $\sim 10\%$ (Rosenthal et al., 1997).

calibrated two neritic high-Mg benthic species in culturing experiments, suggest that Mg/Ca in these species increases by between 1.8 and 2.6% per degree Celsius, a far smaller increase than is observed for low-Mg foraminifera. The Mg response to temperature found by Toyofuku et al. (2000) is actually much closer to the ~3% per degree Celsius observed for inorganic calcite (Oomori et al., 1987), which has Mg contents similar to neritic benthics. This correspondence suggests the Mg response to temperature might scale with the Mg content of calcite.

In the first generation of studies, three planktonic species, *Globigerinoides sacculifer*, *Globigerina bulloides*, and *O. universa*, were calibrated by culturing and fit with equations of the form:

$$\text{Mg/Ca (mmol mol}^{-1}\text{)} = be^{mT} \quad [4]$$

where b is the preexponential constant, m the exponential constant, and T the temperature (Lea et al., 1999). Fitting Mg/Ca–temperature data with an equation of this form has the dual advantage of allowing for an exponential response while also parameterizing, by the use of the natural logarithm e , the exponential constant as the change in Mg/Ca per degree Celsius. It should be noted that it is the exponential constant that determines the magnitude of temperature change calculated from downcore variations in Mg/Ca and the preexponential constant that determines the absolute temperature. Calibration results for these three species indicate exponential constants between 0.085 and 0.102, equivalent to 8.5–10.2% increase in Mg/Ca per degree Celsius (Lea et al., 1999; Nürnberg et al., 1996a,b). Subsequent culturing studies have largely confirmed the early results, but with significant refinements, especially with respect to the impact of salinity and calcite saturation on Mg uptake (Duenas-Bohorquez et al., 2009; Kisakürek et al., 2008; Russell et al., 2004; von Langen et al., 2005).

A study utilizing planktonic foraminifera from a sediment-trap time series off Bermuda extended calibration to seven species, which in aggregate have a temperature response of $9.0 \pm 0.3\%$, in remarkable agreement with the culturing studies (Anand et al., 2003; Figure 4). The preexponential constant b in this study ranges between 0.3 and 0.5, with the exception of higher values for *O. universa*, which appears to be unique in many aspects of its shell geochemistry (Anand et al., 2003; Lea et al., 1999; Nürnberg et al., 1996a,b). More recent sediment trap studies support the earlier results while providing alternate calibrations that extend to different species (McConnell and Thunell, 2005; Mohtadi et al., 2009; Pak et al., 2004).

Core-top calibrations are in general agreement with the culturing results and include calibrations of multiple planktonic species (Dekens et al., 2002; Elderfield and Ganssen, 2000; Lea et al., 2000; Regenberg et al., 2009; Rosenthal and Lohmann, 2002). The Dekens et al. (2002) calibrations, which include a second term to account for dissolution in the form of a water depth or saturation effect, are discussed in Section 8.14.7.3.

Calibration for benthic species is somewhat more uncertain. The first comprehensive calibration was carried out by Yair Rosenthal, then at MIT, who used *Cibicides* spp. from shallow sediments on the Bahamas outer bank to calibrate benthic Mg between 5 and 18 °C (Rosenthal et al., 1997). When this calibration is augmented with *C. wuellerstorfi* data

from deeper sites and adjusted for an analytical offset between atomic absorption spectrophotometry and ICP-MS (Martin et al., 2002), the calibration yields

$$\text{Mg/Ca} = 0.85e^{0.11T} \quad [5]$$

The value of the exponential constant, 0.109 ± 0.007 (95% CI), overlaps with estimates from planktonic species, suggesting that Mg response to temperature of this magnitude is a common factor among foraminifera. It should be noted that the Martin et al. (2002) dataset suggests that the Mg response might be steeper at bottom water temperatures <4 °C, possibly due to lower carbonate ion concentration in the deepest Atlantic and Pacific waters. Subsequent calibrations extended to multiple species and settings suggest that different species respond differently, with varying degrees of influence of seawater carbonate ion and/or calcite saturation (Bryan and Marchitto, 2008; Elderfield et al., 2006; Kristjansdottir et al., 2007; Lear et al., 2002; Marchitto et al., 2007; Rathmann and Kuhnert, 2008; Rosenthal et al., 2006; Toyofuku et al., 2011; Yu and Elderfield, 2008). Resolving the calibration for benthic Mg at the coldest temperatures is an important research priority because there is a great deal of research interest in establishing the temperature evolution of cold bottom waters. Establishing calibrations for other species is also a high priority, in part, because of the insight this provides into the basis for Mg paleothermometry.

8.14.7.3 Effect of Dissolution

It has been known since the 1970s that the Mg content of foraminiferal shells, as well as other carbonates, is susceptible to change via dissolution (Hecht et al., 1975; Lorens et al., 1977). As mentioned previously, this factor was one of the main reasons that little hope was held out for the usefulness of foraminiferal Mg as a paleotemperature proxy. At present, researchers accept that dissolution alters the Mg/Ca content of foraminiferal shells and instead are investigating the degree to which such changes occur, how dissolution can be assessed and whether correction factors are possible, and the degree to which dissolution affects Mg/Ca and oxygen isotopes similarly or dissimilarly.

In the mid-1990s, a number of groups measured Mg/Ca in planktonic foraminifera from oceanic depth transects, mostly as support for studies of other metals (F, U, and V) in the shells (Brown and Elderfield, 1996; Hastings et al., 1996; Rosenthal and Boyle, 1993; Russell et al., 1994). The advantage of the depth transect approach is that one can assume that shells with similar compositions rain down from overlying surface waters to all the sites, and that observed differences must be due to postdepositional processes. These studies demonstrated, to a greater or lesser degree, that Mg/Ca in the shells declines with water depth and the increased dissolution inferred. Rosenthal and Boyle (1993) in particular documented both the general relationship between Mg/Ca and $\delta^{18}\text{O}$ as well as the drop in Mg/Ca with water depth in both spinose and nonspinose species. In general, these studies indicated that the drop in Mg/Ca is more pronounced for nonspinose species such as *Globorotalia tumida*, a result that was interpreted to reflect

preferential dissolution of Mg-rich chamber calcite over Mg-poor keel calcite (Brown and Elderfield, 1996). One of these studies also revived the idea, first suggested by Savin and Douglas (1973), that the Mg content of the shells influenced their solubility (Brown and Elderfield, 1996). Calculations suggest that the saturation horizon for ontogenetic calcite with Mg/Ca of 10 mmol mol⁻¹, about twice the value found in typical tropical shells, could be 300 m shallower. Mg loss presumably occurs when shells are on the seafloor and/or when they pass through the sediment mixed layer where metabolic CO₂ is available to hasten dissolution. The fact that surface dwelling *Globigerinoides ruber* indicate decreasing Mg/Ca with water depth in the western equatorial Pacific (Dekens et al., 2002; Lea et al., 2000), an area with minimal temporal and spatial variation in mixed-layer temperatures, suggests that Mg loss might occur via preferential dissolution of Mg-rich portions of the shell (Brown and Elderfield, 1996; Lohmann, 1995). It is also quite possible, however, that the progressive loss of the less robust individuals, which might have preferentially calcified in the warmest waters, shifts the mean Mg/Ca to lower values in deeper sediments.

An obvious complexity in utilizing shell Mg/Ca for paleotemperature is that many species migrate vertically and/or add gametogenic calcite at depths significantly deeper than their principal habitat depth (Bé, 1980). This complicates the dissolution question because these different shell portions are likely to have slightly different solubilities and Mg/Ca ratios. An innovative approach to this problem was suggested by Rosenthal et al. (2000), who argued that the relationship between size-normalized shell mass and dissolution loss could be used to correct shell Mg/Ca. This approach, which relies on a constant relationship between shell mass changes and Mg/Ca changes, has yet to be validated in downcore studies, although Rosenthal and Lohmann (2002) demonstrated that this approach can yield consistent glacial–interglacial SST changes from cores both above and below the lysocline.

Other studies have attempted to use water depth transects to assess dissolution (Dekens et al., 2002; Lea et al., 2000; Regenberg et al., 2006). Dekens et al. (2002) quantified the Mg/Ca loss in depth transects as a percentage loss per kilometer water depth, thus allowing direct comparison of the magnitude of potential dissolution loss versus the magnitude of the temperature effect. If independent estimates of past shifts in lysocline depth are available, it is then possible to estimate the magnitude and direction of dissolution bias downcore. Dekens et al. (2002) found, based on core tops from the tropical Atlantic and Pacific, that Mg/Ca loss ranged from 3% per km water depth for *G. sacculifer*, 5% for *G. ruber*, and 22% for *N. dutertrei*, a nonspinose thermocline dweller. This equates to a bias in Mg paleothermometry of 0.4, 0.6, and 2.8 °C per km effective shift, respectively, in foraminiferal lysocline, or depth of effective dissolution. Given that evidence for late Quaternary lysocline shifts is generally between 0.2 and 0.8 km (Farrell and Prell, 1989), this approach suggests that downcore dissolution biases in Mg paleothermometry will be less than 0.5 °C for spinose surface dwellers. Calibration equations derived from the Dekens et al. (2002) calibration set are also parameterized using Δ carbonate ion (the difference between in situ and saturation values) to account for differences in dissolved carbonate ion between basins.

Alternative approaches have been developed to account for the influence of dissolution. Martin and coworkers are using temporal changes in Mg/Ca within oceanic depth transects to reconstruct changes in deepwater carbonate chemistry (Fehrenbacher and Martin, 2011; Fehrenbacher et al., 2006). They are also utilizing electron microprobe studies to assess shell heterogeneity and response to dissolution. Another approach centers on developing dissolution indexes from X-ray tomography of foraminiferal shells (Johnstone et al., 2011) or bulk sedimentological parameters (Lea et al., 2006; Mekik et al., 2007). Sediment trap studies that compare samples from different water depths can also provide insights into dissolution (Huang et al., 2008).

The evidence for dissolution effects on Mg in benthic foraminifera is less certain. For one, it is more difficult to discern a dissolution trend because benthic Mg/Ca decreases with increasing water depth and decreasing bottom water temperature. Data from a depth transect on the Ontong Java Plateau for Sr/Ca, Ba/Ca, and Cd/Ca have been used to infer a dissolution effect on these elements (McCorkle et al., 1995), although alternative interpretations such as carbonate ion or pressure effects on biomineralization have also been suggested (Elderfield et al., 1996). Martin et al. (2002) suggested that the steeper trend of benthic Mg/Ca in the coldest waters, estimated at ~20 versus 11% per degree Celsius, might reflect dissolution and Mg loss in the deepest, most undersaturated waters. Alternatively, this difference might reflect the influence of other factors, such as carbonate ion saturation. Regardless, this will be a critical issue in validating benthic Mg/Ca for use in the coldest bottom waters.

8.14.7.4 Other Secondary Effects on Mg/Ca

Mg is a trace component of foraminiferal shells, occurring at abundances of 125–2500 ppm, and therefore shells are subject to contamination and overprinting when they are deposited in marine sediments. This fact was first recognized by Cesare Emiliani (Emiliani, 1955a), but its importance for Mg paleothermometry was not fully appreciated until the pioneering study of Barker et al. (2003). Other studies have highlighted the importance of suitable sample purification (Bian and Martin, 2010; Martin and Lea, 2002) and in particular have demonstrated that for certain sites, such as those subject to the influence of Mg-rich volcanic shards (Lea et al., 2005), Mn–Mg-rich overgrowths (Pena et al., 2005), or Mg-rich carbonate overgrowths (Regenberg et al., 2007), sample purification is a formidable challenge. One novel approach to sample purification is a flow-through procedure that attempts to separate the primary and secondary signals (Benway et al., 2003; Haley and Klinkhammer, 2002; Klinkhammer et al., 2004).

Primary factors other than temperature also influence Mg/Ca in planktonic shells. Based on culturing, there is clear evidence for differences in uptake between species (Anand et al., 2003; Lea et al., 1999), with as much as a factor of 2 variation. For this reason, species-specific calibrations are necessary, although it is difficult to do this by any means other than culturing because of the complication of habitat depth. It is also clear that there are large spatial heterogeneities in foraminiferal shells, as revealed by the application of spatial mapping techniques (Eggins et al., 2003, 2004; Sadekov et al.,

2008, 2009). These heterogeneities, which are larger than can be explained by vertical migration, clearly indicate that ontogenetic growth affects shell Mg/Ca.

The impact of salinity variations on Mg/Ca is an interesting question that goes back to one of the early studies on Mg uptake (Nürnberg et al., 1996a). Because the Mg/Ca ratio is nearly constant across the ocean salinity range for present-day seawater, one would not predict a large effect. In the first edition (Lea, 2003), it was stated that salinity appears to exert a small effect on shell Mg/Ca, with an observed increase of between $6 \pm 4\%$ for *O. universa* (Lea et al., 1999) and $8 \pm 3\%$ for *G. sacculifer* (Nürnberg et al., 1996a) per salinity unit (SU) increase, based on culturing results. (Note: this and all other relationships of this kind are quoted as the exponential constant, with 95% confidence intervals, for an exponential fit to the observational data; the original published data were not always fit this way. An exponential fit has the advantage of giving the response in terms of a constant percentage, which then can be easily related to the exponential constant in the temperature response equation.) Assuming a Mg/Ca temperature response of 10% per degree Celsius (see Section 8.14.7.2), a salinity influence of 6–8% is equivalent to a positive bias of between 0.6 and 0.8 °C per SU increase.

Since the first edition, there has been a major focus on the effect of salinity on Mg/Ca. This focus has been driven by several core-top studies that argue for a large salinity effect, most notably Ferguson et al. (2008) and Arbuszewski et al. (2010). Ferguson et al. (2008) were the first to argue for a large salinity effect (15–59% per SU), on the basis of elevated Mg/Ca values in core tops from the Mediterranean. Subsequent studies have demonstrated that at least some of the elevated values reported by Ferguson et al. (2008) were due to early diagenesis, via the buildup of Mg-rich carbonate phases in the shells (Boussetta et al., 2011; Hoogakker et al., 2009; Kontakiotis et al., 2011; van Raden et al., 2011). Other core-top studies, however, present compelling evidence that a primary salinity effect of 15–27% per SU does indeed exist (Arbuszewski et al., 2010; Mathien-Blard and Bassinot, 2009). All of this evidence must be weighed against new culturing studies that support a salinity effect of only 4–6% per SU (Dissard et al., 2010b; Duenas-Bohorquez et al., 2009; Kisakürek et al., 2008).

At this point, there is no easy resolution to this conflict. Some of the core-top studies have suggested that culturing does not capture the full environmental response because it only partially simulates natural conditions. However, the problem with this argument is that the temperature dependence of foraminiferal Mg was first confirmed by culturing. Why would cultured foraminifera respond to temperature and not salinity? A solution perhaps lies in systematic studies of plankton tow and sediment trap samples, which bypass some of the inherent problems of core tops (e.g., diagenesis and bioturbation) while preserving the full natural life cycle. Regardless, researchers in this area need to solve this conflict because of the uncertainty it introduces into Mg/Ca paleothermometry.

The first investigation of the effect of seawater pH suggested that pH has a significant effect on Mg uptake, with an observed decrease of $-6 \pm 3\%$ per 0.1 pH unit increase for *G. bulloides* and *O. universa* (Lea et al., 1999). Subsequent studies have refined these results, suggesting that any pH effect might vary

between species and over the pH range of consideration (Dissard et al., 2010a; Duenas-Bohorquez et al., 2009; Russell et al., 2004). Again assuming a Mg/Ca temperature response of 10% per degree Celsius (Section 8.14.7.2), a pH influence of 6% per 0.1 pH unit is equivalent to a bias of -0.6 °C per 0.1 pH unit increase. Past variability in oceanic pH (Sanyal et al., 1996) and water column variability in pH could therefore both exert significant biases on Mg paleothermometry.

Over the last decade, there has been some progress in elucidating the impact of changing seawater Mg/Ca ratios on Mg/Ca paleothermometry (Broecker and Yu, 2011; Fantle and DePaolo, 2006; Medina-Elizalde et al., 2008). On timescales longer than the residence time of Ca (~ 1 My), Mg/Ca paleothermometry is likely to be influenced by changing seawater Mg/Ca. Over the entire Cenozoic, seawater Mg/Ca is estimated to have changed between two and fivefold. An additional consideration is that the partition coefficient for Mg incorporation likely depends on seawater Mg/Ca.

8.14.7.5 Results over the Last Few Millennia

A new area of investigation using Mg paleothermometry is the analysis of high-resolution marine sequences that span the last few millennia (Black et al., 2007; Kuwaes et al., 2009; Lund and Curry, 2006; Newton et al., 2006; Oppo et al., 2009; Richey et al., 2007; Saenger et al., 2011). Such sequences are found in settings where rapidly accumulating sediments remain undisturbed, such as in the anoxic Cariaco Basin on the Venezuelan shelf. The challenge in these studies is the low signal-to-noise ratio, due to the small temperature signal relative to the compound paleothermometry error. Regardless, major progress has been made, most notably in the western tropical Pacific, where Oppo et al. (2009) demonstrated that SST change in this region strongly resembles global records while also revealing patterns of tropical Pacific climate change over the last two thousand years.

8.14.7.6 Results on Quaternary Timescales

The first generation of Mg paleothermometry studies led to a number of important and unprecedented findings for paleoceanographic and paleoclimatic research. These include documenting the history of subpolar Antarctic SST variations (Mashiotto et al., 1999; Rickaby and Elderfield, 1999), tropical Atlantic and Pacific SST changes (Elderfield and Ganssen, 2000; Hastings et al., 1998; Lea et al., 2000; Nürnberg et al., 2000), and changes in bottom water temperature in the Atlantic and Pacific (Martin et al., 2002). These studies also established $\delta^{18}\text{O}_{\text{seawater}}$ records for the subpolar Antarctic (Mashiotto et al., 1999), equatorial Pacific (Lea et al., 2000, 2002), and, for five different planktonic species in one core, the tropical Atlantic (Elderfield and Ganssen, 2000). Subsequently, a number of high-resolution records from the tropical Pacific have been published (Koutavas et al., 2002; Lea et al., 2006; Rosenthal et al., 2003; Stott et al., 2002), including records of thermocline dwellers (Xu et al., 2006, 2008). Important Mg/Ca records have also been published from the tropical Atlantic (Lea et al., 2003; Schmidt et al., 2004; Weldeab et al., 2006, 2007) and tropical Indian Ocean (Levi et al., 2007; Naidu and Govil, 2010; Saraswat et al., 2005). There

have also been a number of important high latitude studies, especially in the southern hemisphere (Pahnke et al., 2003).

Among these Mg/Ca results, perhaps the most important are those that are available for the tropics. Past SST changes in the tropics have been a contentious issue (Crowley, 2000b), mostly because the actual glacial–interglacial changes are relatively small ($<5^{\circ}\text{C}$) and therefore more difficult to detect unambiguously using either faunal or geochemical methods. The faunal approach in particular is hampered by the fact that glacial tropical assemblages in the warm pools are not very different from their interglacial counterparts (Crowley, 2000b). Even with reexamination and major refinements, the faunal approach does not yield significant cooling in the tropical warm pools (Mix et al., 1999; Trend-Staid and Prell, 2002). The Mg/Ca approach works especially well in the tropics because the calibration curve at warm temperatures shows the largest absolute change in Mg/Ca per degree Celsius (Figures 3 and 4). Oligotrophic tropical sites, which are poor candidates for the alkenone unsaturation paleotemperature approach, generally contain abundant specimens of *G. ruber* and *G. sacculifer*, which are well calibrated for Mg/Ca. These low-productivity sites also have minimal potential for diagenetic changes, which removes one confounding factor for trace element work.

In the first edition, it was stated that application of Mg/Ca paleothermometry in a series of studies from the early 2000s had “cracked the problem of glacial cooling of the tropical warm pools” by establishing a $2.8 \pm 0.7^{\circ}\text{C}$ level of glacial cooling, relative to late Holocene conditions, especially for the western Pacific warm pool (Lea et al., 2000; Rosenthal et al., 2003; Stott et al., 2002; Visser et al., 2003). This statement is supported by the compatibility of a $\sim 3^{\circ}\text{C}$ cooling with oxygen isotope results, by the fact that Mg/Ca results fall in the middle of the range of cooling inferred from a range of proxies applied to the Last Glacial Maximum (LGM), and by support from modeling and statistical studies (Ballantyne et al., 2005; Greene et al., 2002). In the last decade, many Mg/Ca and alkenone unsaturation studies have confirmed this level of cooling (Barker et al., 2005; de Garidel-Thoron et al., 2007;

Naidu and Govil, 2010; Stott et al., 2007; Visser et al., 2003; Xu et al., 2008, 2010). Results from other proxies, however, still give contradictory results for the LGM as well other chronozones such as the Younger Dryas (Asami et al., 2009; Corrège et al., 2004; DeLong et al., 2010; Waelbroeck et al., 2009). Controversy about a recent climate sensitivity study (Schmittner et al., 2011) that utilizes the MARGO LGM compilation (Waelbroeck et al., 2009) – which averages $<2^{\circ}\text{C}$ of cooling in the low latitudes, perhaps because of the preponderance of faunal results – highlights the importance of resolving remaining conflicts in this research area.

One aspect of the Mg/Ca data that supports the accuracy of the paleotemperature data is how systematic deep tropical records are in the time domain. Records from the western Pacific warm pool reaching back over a million years indicate that Pleistocene glacial episodes were systematically $\sim 3^{\circ}\text{C}$ cooler than modern conditions (de Garidel-Thoron et al., 2005; Lea et al., 2000; Medina-Elizalde and Lea, 2005). Results from many tropical Pacific and Indian Ocean studies spanning the last few climate cycles support these results (Bolliet et al., 2011; Pena et al., 2008; Russon et al., 2011; Saraswat et al., 2005).

One of the strengths of the Mg/Ca approach is that the recorded paleotemperature is recorded simultaneously with the $\delta^{18}\text{O}$ composition of the shell. Combining these factors using an oxygen isotope paleotemperature equation yields the $\delta^{18}\text{O}_{\text{water}}$ at the time of shell precipitation. Early studies using this approach suggested it was likely to yield important results on shifts in global ice volume as well as regional salinity shifts (Elderfield and Ganssen, 2000; Lea et al., 2000, 2002; Mashiotta et al., 1999; Rosenthal et al., 2003; Stott et al., 2002). A paleosalinity proxy has always been a difficult prospect, but it appears now that comparison of extracted $\delta^{18}\text{O}_{\text{water}}$ will make it possible to reconstruct patterns of salinity change in the past (Schmidt and Lynch-Stieglitz, 2011; Schmidt et al., 2004; Stott et al., 2002, 2004). A recent application of this approach to Gulf of Guinea sediments demonstrates its utility in reconstructing high-resolution changes in $\delta^{18}\text{O}_{\text{water}}$ over the last climate cycle (Weldeab et al., 2007). The reconstructed $\delta^{18}\text{O}_{\text{water}}$ record demonstrates millennial-scale shifts

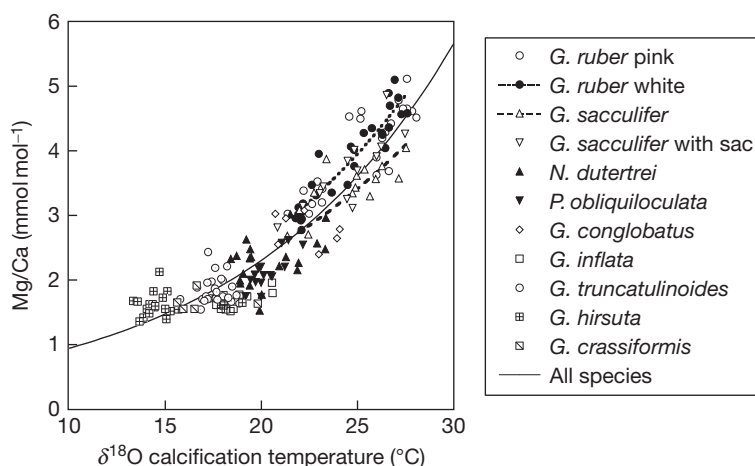


Figure 4 Mg/Ca of different planktonic foraminifera from a Bermuda sediment trap time series, plotted versus calcification temperatures calculated from the oxygen isotopic composition of the shells (Anand et al., 2003). The aggregate fit to all the data in the plot is $\text{Mg/Ca} = 0.38\exp(0.09T)$, very similar to relationships derived from culturing and core-top studies.

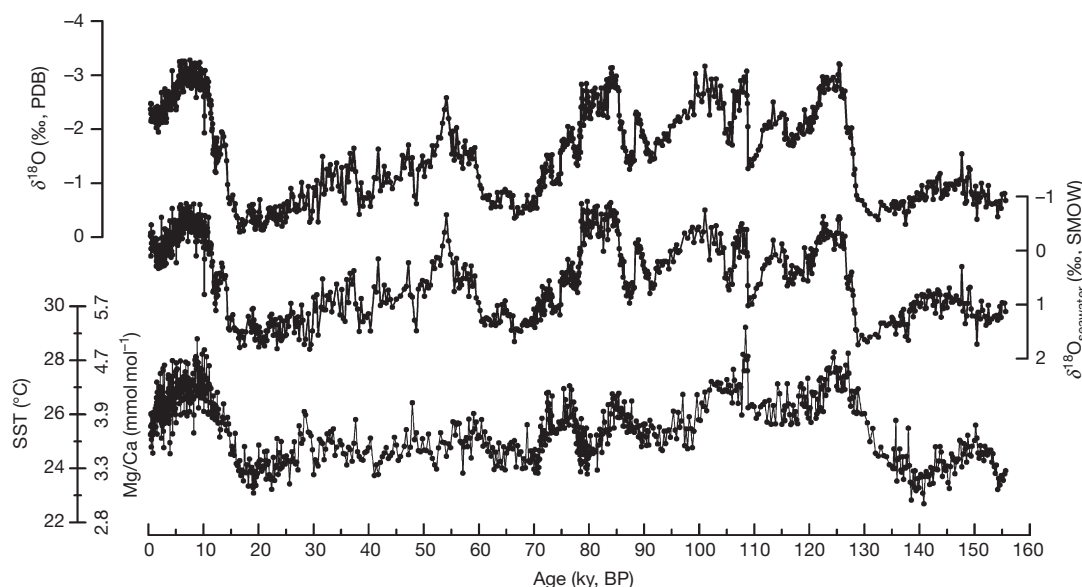


Figure 5 Downcore records of Mg/Ca-based SSTs, $\delta^{18}\text{O}$, and $\delta^{18}\text{O}_{\text{water}}$ derived from the surface dwelling planktonic foraminifera *G. ruber* in a core from the Gulf of Guinea, off West Africa. This study demonstrates how Mg/Ca paleothermometry and oxygen isotopes can be combined to reconstruct high-resolution records of surface $\delta^{18}\text{O}_{\text{water}}$, which in this case are thought to reflect rapid shifts in the West African monsoon. The average sample resolution is 150 years. Modified from Weldeab S, Lea DW, Schneider RR, and Andersen N (2007) 155,000 years of West African monsoon and ocean thermal evolution. *Science* 316: 1303–1307.

that are interpreted as a rainfall and runoff response to the West African monsoon (Figure 5).

Another strength of Mg paleothermometry is that it can be applied to benthic fauna, including ostracode shells (see Section 8.14.7). There are no other techniques that provide direct estimates of bottom water temperatures. The first published study focused on the late Quaternary presented detailed records of benthic foraminiferal Mg/Ca variations, from the eastern tropical Atlantic and Pacific, in the late Quaternary (Martin et al., 2002). These records indicate the great promise of this approach in elucidating deepwater temperature variations, which appear to have been on the order of 2–3 °C. However, there are also considerable challenges. The absolute magnitude of the Mg/Ca change is much smaller in the cold temperature region, and therefore other influences, such as vital effects, dissolution, or calcification effects (Elderfield et al., 1996), can exert significant biases. Recent benthic Mg work has extended bottom water temperature records beyond 3 Ma BP (Sosdian and Rosenthal, 2009) and has also added new insights into how benthic Mg responds to bottom water temperatures and other variables (Elderfield et al., 2010, 2012). Other work has demonstrated that benthic Mg can be used to reveal millennial-scale fluctuations in bottom water temperature (Skinner and Shackleton, 2006; Skinner et al., 2003).

8.14.7.7 Results for the Neogene, Paleogene, and Beyond

One of the most exciting prospects for Mg paleothermometry is combining this approach with the benthic oxygen isotope curve for the Cenozoic (Zachos et al., 2001) to separate the influence of temperature and ice volume. Several early studies suggested the great potential of this approach (Billups and Schrag, 2002; Lear et al., 2000). Lear et al. (2000) presented a dataset extending back to the Eocene. Their data revealed that

benthic Mg/Ca records the gradual ~12 °C cooling of bottom waters during the Cenozoic that had been inferred from oxygen isotopes. Combining the Mg/Ca-based temperatures with measured $\delta^{18}\text{O}$ allows calculation of the $\delta^{18}\text{O}$ evolution of seawater, which can be traced to the expansion and contraction of ice sheets. Comparison of Mg temperature trends with $\delta^{18}\text{O}$ over the Eocene–Oligocene boundary suggests that $\delta^{18}\text{O}$ shifts are dominated by global ice volume shifts. Subsequent studies have focused in on more restricted time intervals (Creech et al., 2010; Lear et al., 2010; Pusz et al., 2011; Shevenell et al., 2008). A recent compilation of Cenozoic benthic Mg reveals a coherent picture of progressive warming of bottom waters throughout the Cenozoic (Cramer et al., 2011; Katz et al., 2010).

Mg/Ca paleothermometry has been successfully applied to planktonic records over the Pliocene (Karas et al., 2011; Medina-Elizalde and Lea, 2010; Wara et al., 2005), the Miocene (Shevenell et al., 2004), across the Paleocene/Eocene boundary (Zachos et al., 2003) and to the early Paleogene (Tripathi et al., 2003). Some studies have even extended Mg/Ca to Cretaceous sediments, with startling evidence for very high tropical SST (Bice et al., 2006). Whether utilizing benthic or planktonic foraminifera, uncertainties such as calibration for extinct species, diagenesis, and changes in seawater Mg/Ca become more challenging when Mg paleothermometry is extended to longer timescales, but there are also great prospects for major discoveries.

8.14.7.8 Summary of Outstanding Research Issues

Mg paleothermometry has been enjoying a period of phenomenal growth, and it has quickly taken its place as one of the most useful means paleoceanographers have to study past climates. Many questions, such as ecological bias, species

offsets, environmental influences other than temperature, dissolution, and diagenetic overprinting, must be addressed before the ultimate reliability of Mg paleothermometry is known. One inherent advantage is the enormous amount already known about foraminiferal ecology and geochemistry, much of which applies equally to oxygen isotopes and Mg/Ca. At this stage, the most fundamental issues are (1) resolving how much salinity influences Mg uptake; (2) establishing the extent to which dissolution biases downcore Mg/Ca records; and (3) establishing the degree to which benthic Mg variations record temperature variations versus calcite saturation in the coldest part of the bottom water temperature range ($<4^{\circ}\text{C}$).

8.14.8 Magnesium as a Paleotemperature Proxy in Ostracoda

Mg paleothermometry applied to ostracode shells has proved to be an important means of discerning past variations in bottom water temperatures (Corrège and De Deckker, 1997; Cronin et al., 1996, 2000; Dwyer et al., 1995). This approach is based on the same principle as Mg paleothermometry in foraminifera, although ostracode calibrations have been fit linearly. These linear calibrations suggest that the increase in Mg/Ca in ostracodes is $\sim 9\%$ per degree Celsius, similar to the foraminiferal calibrations (see Section 8.14.7.2). Dwyer et al. (1995) demonstrate that ostracode Mg/Ca can be used quite effectively to separate bottom water temperature and $\delta^{18}\text{O}_{\text{water}}$ influences in both the Quaternary and Pliocene. In light of subsequent discoveries, it is interesting to note that Dwyer et al. (1995) documented a lead in their late Quaternary ostracode Mg/Ca record of 3500 years over benthic $\delta^{18}\text{O}$. Similarly, a study of Mg in benthic foraminifera in a tropical Atlantic core saw a lead of ~ 4000 years in benthic Mg over benthic $\delta^{18}\text{O}$ over the last 200 ky (Martin et al., 2002). These results highlight the importance of independent paleothermometers.

8.14.9 Strontium as a Climate Proxy in Corals

8.14.9.1 Background

The use of Sr/Ca in corals as a paleothermometer was attempted in the late 1960s but did not come to fruition until the early 1990s, with the application of more precise analytical techniques. Early studies indicated that there was an inverse relationship between seawater temperature and Sr content of both inorganically precipitated and coral aragonite, with a relatively small inverse temperature dependence of just under 1% per degree Celsius (Kinsman and Holland, 1969; Lea et al., 1989; Smith et al., 1979; Weber, 1973). The breakthrough study for coral Sr/Ca, led by Warren Beck, then at the University of Minnesota (Beck et al., 1992), utilized extremely precise isotope dilution thermal ionization mass spectrometric (ID-TIMS) determinations to establish the relationship between Sr/Ca and temperature. Their calibration data indicated a 0.6% decrease in Sr/Ca per degree Celsius, and with determinations of $\pm 0.03\%$ (2SD) possible by ID-TIMS, Beck et al.'s (1992) approach indicated a possible paleotemperature determination of a remarkable $\pm 0.05^{\circ}\text{C}$! Along with their calibration data, Beck et al. (1992) presented Sr/Ca data from a fossil

coral from Vanuatu that had been dated to the late Younger Dryas/early Holocene period. These data indicated a 5.5°C cooling of SST in this region and were among the first strong evidence challenging the CLIMAP (1981) view of relatively unchanged tropical SST during glacial episodes.

Following the Beck et al. (1992) publication, a number of laboratories undertook more detailed studies of the calibration and also investigated the application of this approach to paleoceanography and paleoclimatology (de Villiers et al., 1994, 1995; Gagan et al., 1998; Guilderson et al., 1994; McCulloch et al., 1994). Generally, these studies have supported Beck et al.'s (1992) original insights, although two major problems with the Sr/Ca approach have been identified: (1) it appears that growth rate and symbiont activity have a marked influence on coral Sr/Ca (Cohen et al., 2001, 2002; de Villiers et al., 1994), and (2) there is fairly strong evidence for a secular shift in seawater Sr/Ca on glacial–interglacial timescales, with generally higher values during glacial episodes (Martin et al., 1999; Stoll and Schrag, 1998; Stoll et al., 1999). Another major step forward came with the development of a very rapid but still precise atomic absorption spectrophotometry method (Schrag, 1999b); this technique enables researchers to generate the large datasets required for long, high-resolution climate records (Linsley et al., 2000).

8.14.9.2 Paleotemperature Equations

The relationship between coral Sr/Ca and seawater temperature is parameterized as a linear function of the form:

$$\text{Sr/Ca}_{\text{coral}} (\text{mmol mol}^{-1}) = b + m(\text{SST}) \quad [6]$$

The thermodynamic prediction for Sr substitution in aragonite is actually an exponential response with an inverse temperature dependence, a consequence of the negative enthalpy (exothermic) nature of the reaction in which Sr substitutes for Ca in aragonite. The observed exponential constant for inorganic aragonite precipitation is quite small: 0.45% per degree Celsius (Kinsman and Holland, 1969). Therefore, over the small range of coralline Sr paleothermometry, the relationship can be quite adequately expressed as a linear relationship. The single inorganic aragonite precipitation study indicates a slope m of 0.039 and an intercept b of $10.66 \text{ mmol mol}^{-1}$ (Kinsman and Holland, 1969). Calibrations are available for a number of coral species, but mostly for species of *Porites* (Beck et al., 1992; Cohen et al., 2001, 2002; de Villiers et al., 1994; Gagan et al., 1998; Mitsuguchi et al., 1996; Shen, 1996; Sinclair et al., 1998; Smith et al., 1979). Values of the intercept b , which determines the absolute Sr/Ca for a particular temperature, range from 10.3 to 11.3; values of the slope m , which determines the temperature sensitivity, range from 0.036 to 0.086. The variability in the slope is a critical problem for coral Sr paleothermometry because the cited slopes equate to variability in temperature dependence of -0.4 to -1.0% per degree Celsius. Therefore, a recorded change of Sr/Ca in corals of 1% can imply between a 1 and 2.5°C shift in paleotemperature. Of course, in practice, it is possible to narrow this uncertainty by conducting local calibrations (e.g., Corrège et al., 2000).

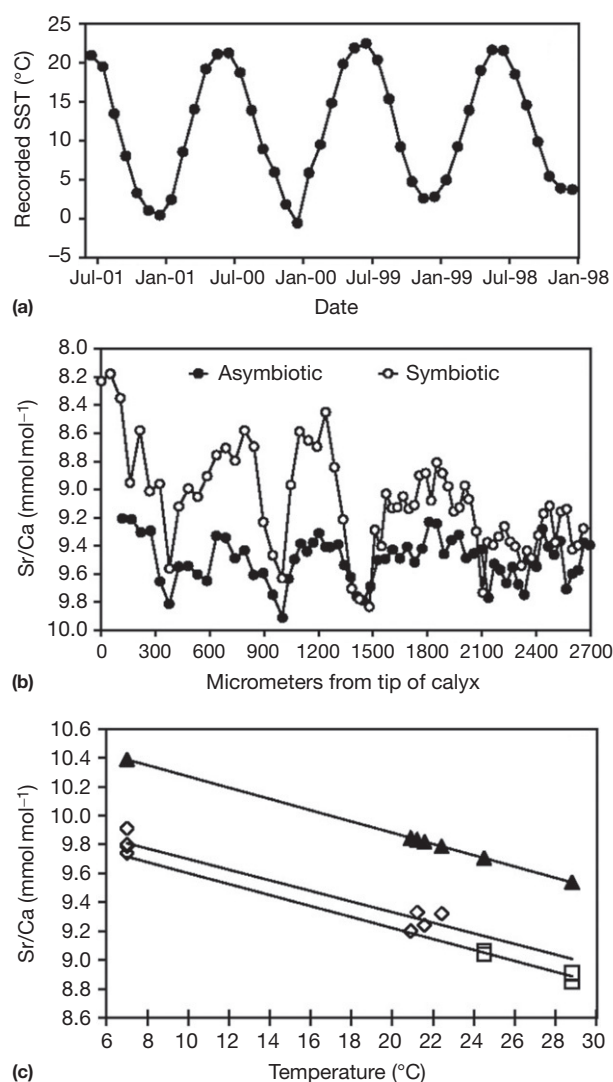


Figure 6 Comparison of Sr/Ca records in symbiont-bearing and symbiont-barren ahermatypic corals (Cohen et al., 2002). (a) Average monthly SST at 12 ft (4 m) depth in the Woods Hole harbor, the coral collection site, between January 1998 and July 2001. (b) Life history Sr/Ca profiles from symbiotic (open circles) and asymbiotic (solid circles) skeleton of *Astrangia poculata* colonies collected in Woods Hole in July 2001. Skeletal Sr/Ca in the first year of life is the same in both samples, but the similarities decrease as the corallites mature, a divergence caused by a progressive decrease in summertime Sr/Ca in the symbiotic skeleton. (c) The Sr/Ca–SST relationship in the asymbiotic *Astrangia* skeleton ($= -0.036 \times +10.065$) is compared with the nighttime skeleton of the tropical reef coral *Porites* ($= -0.038 \times +9.9806$) and inorganic aragonite precipitated at equilibrium ($= -0.039 \times +10.66$). The slopes of the regression equations, indicative of the temperature sensitivity of Sr/Ca uptake into the coral skeleton, are similar for all three precipitates (-0.036 , -0.038 , and -0.039 , respectively). This agreement establishes temperature as the primary control of Sr/Ca in the asymbiotic skeleton. Reproduced from Cohen AL, Owens KE, Layne GD, and Shimizu N (2002) The effect of algal symbionts on the accuracy of Sr/Ca paleotemperatures from coral. *Science* 296: 331–333. With permission from the American Association for the Advancement of Science.

The key question is the degree to which the relationship between coral Sr/Ca and SST stays constant in time and space. There have been a number of investigations of this question (Alibert and McCulloch, 1997; Cahyarini et al., 2009; Cohen

et al., 2001, 2002, 2004; Corrège, 2006; de Villiers et al., 1994; Fallon et al., 2003; Gagan et al., 2012; Inoue et al., 2007; Mitsuguchi et al., 2003; Sinclair et al., 2006), and the answer seems to be that growth and environmental factors clearly do affect eqn [2]. A study based on ahermatypic solitary corals indicates that algal symbionts might be the main influence on the slope, with an enhancement of 65% associated with enhanced calcification during periods of strong symbiotic photosynthesis (Cohen et al., 2002; Figure 6). If this result applies generally, it will have important implications for the use of corals in paleoclimate research, because most of the long records are based on the symbiont-bearing reef coral *Porites* (Schrug and Linsley, 2002). However, there is a lot of evidence that coral Sr paleothermometry works remarkably well, and the key question appears to be ascertaining the meaningfulness of long-term secular shifts on both historical and prehistoric timescales (see Sections 8.14.9.4 and 8.14.9.5).

8.14.9.3 Secondary Effects and Diagenesis

The main secondary effects on Sr/Ca paleothermometry appear to be related to growth rate and symbiosis (see Section 8.14.9.2). It is not yet known how these effects might influence the use of coral Sr/Ca for paleoclimate studies, but one imagines that the effects could be important if the growth conditions are changing over the lifetime of the coral. One of the most impressive long-term Sr/Ca records, from Rarotonga in the South Pacific (Linsley et al., 2000), implies a large cooling in ~ 1760 , early in the coral head's life history. This cooling does not appear in some other climate records (Cane and Evans, 2000) and could therefore reflect secondary effects.

The effect of diagenesis has been widely studied for the Sr/Ca paleothermometer. For young corals growing during historical times, there is clear evidence that precipitation of inorganic aragonite in the pores of the oldest parts of the coral heads can affect the bulk coral Sr/Ca (Dalbeck et al., 2011; Enmar et al., 2000; Hendy et al., 2007; Müller et al., 2001). This secondary aragonite has a higher Sr/Ca ratio than the original coral material, and it therefore biases Sr/Ca paleotemperatures to colder values. It also affects other geochemical proxies, including stable isotopes, in corals (Hendy et al., 2007). The effect on oxygen isotopes, however, is likely to be smaller than for Sr/Ca (Dalbeck et al., 2011).

As subaerially exposed corals interact with meteoric waters, they are altered to calcite. This alteration results in a loss of Sr from the skeleton and will obviously have strong effects on Sr/Ca paleothermometry. To avoid this problem, researchers routinely screen for the presence of calcite in fossil corals. One study (McGregor and Gagan, 2003) demonstrates that local diagenesis can have marked effects on coral Sr/Ca, with a very large positive bias on reconstructed SST. This occurs because of the large drop in Sr/Ca that accompanies conversion of aragonite to calcite. Interestingly, the bias on oxygen isotopes is much smaller, mainly because the absolute difference in aragonite and calcite end-member compositions is much smaller for $\delta^{18}\text{O}$ (see Section 8.14.4.3). McGregor and Gagan (2003) suggest that such localized low-level diagenesis can be detected through a combination of X-ray diffraction techniques, thin section analysis, and high-resolution spatial sampling of the coral skeleton.

A unique secondary complication for Sr/Ca is the potential influence of small changes in seawater Sr/Ca (Sun et al., 2005). Although spatial variability in seawater Sr/Ca in the present ocean is very small ($\leq 2\%$) (Brass and Turekian, 1974; de Villiers et al., 1994), the small sensitivity of the coral Sr/Ca paleothermometer makes it sensitive to these variations. For example, an observed 2% variation in coralline Sr/Ca, which equates to the maximum seawater variation, is equivalent to between a 2 and 5 °C temperature change, depending on the slope of the calibration (see Section 8.14.9.2). In practice, it is likely that most locations do not experience variations of more than 0.5% in seawater Sr/Ca (de Villiers et al., 1994), but on historical timescales, it is at least possible that larger shifts have taken place.

On geological timescales, there is evidence that shifts in seawater Sr/Ca large enough to affect Sr/Ca paleothermometry have taken place. Such shifts were first hypothesized by Dan Schrag's group at Harvard, who recognized that changes in sea level associated with changing continental ice volume had the potential to change seawater Sr/Ca because calcium carbonate deposition on the continental shelves is dominated by aragonite, which contains ~5 times more Sr than calcite, which dominates deep-sea carbonate deposition (Stoll and Schrag, 1998). Lowered sea level during continental glaciation favors deposition in the deep sea, which therefore raises the Sr/Ca of seawater. Stoll and Schrag (1998) calculated that this change could result in a 1–2% enrichment of seawater Sr/Ca during or just after sea-level lowstands, which, depending on which calibration is used, would result in a –1 to –5 °C bias in Sr/Ca paleothermometry.

Subsequently, Pamela Martin (UCSB) and coworkers demonstrated that systematic glacial–interglacial variations in foraminiferal Sr/Ca as large as and even somewhat larger than those predicted by Stoll and Schrag (1998) are indeed preserved in deep-sea records (Martin et al., 1999). Several studies have confirmed this observation (Elderfield et al., 2000; Shen et al., 2001; Stoll et al., 1999). These studies indicate foraminiferal shells record variations of up to 6% on glacial–interglacial timescales. Some of this variation is undoubtedly due to secondary (kinetic) effects on foraminiferal Sr/Ca, such as temperature, pH, and salinity, all of which are known to have small influences on shell Sr/Ca (Lea et al., 1999). But comparison of benthic records from different ocean basins suggests that there is a strong common signal in these records, with a common glacial–interglacial amplitude of up to 3% (Martin et al., 1999). Comparison of this stacked benthic record with coral Sr/Ca ratios of fossil corals suggests that up to half of the observed coral Sr/Ca variation might be attributable to seawater Sr/Ca variation (Martin et al., 1999). This might explain why drops in tropical SST during glacial episodes based on fossil coral Sr/Ca (Beck et al., 1992; Guilderson et al., 1994; McCulloch et al., 1996, 1999) are typically twice that suggested by other geochemical proxies (Lea et al., 2000). Regardless of the exact details, it is clear that secular changes in seawater Sr/Ca have the potential to influence the Sr/Ca paleothermometer on longer timescales.

8.14.9.4 Results on Historical Timescales

The first long time series of Sr/Ca were published from Rarotonga and the GBR in the South Pacific (Hendy et al., 2002; Linsley et al., 2000). These records show clear interannual

variability as well as distinct secular trends. For example, the GBR records (Hendy et al., 2002), which are an average of eight different coral cores, indicate a secular shift to warmer SST in the youngest part of the records (after ~1950). This shift is corroborated by $\delta^{18}\text{O}$ and U/Ca measurements in the same corals and appears to track well with instrumental records. This is quite important because of the question of attribution for the prominent trend toward more negative $\delta^{18}\text{O}$ observed in many large corals (see Section 8.14.4.4). Combining the metal paleotemperature records with the $\delta^{18}\text{O}$ record yields a residual $\delta^{18}\text{O}_{\text{water}}$ record that suggests that GBR waters have become progressively less salty since the mid-nineteenth century. Results from the Rarotonga site (Linsley et al., 2000) are somewhat different and suggest a prominent cooling in ~1750 followed by a series of decadal oscillations that correlate in the twentieth century with the Pacific Decadal Oscillation (Mantua et al., 1997). The warm period recorded in the mid-eighteenth century at the Rarotonga site appears to be corroborated in the GBR sites, although with a reduced magnitude. Because this time interval was cold in much of the northern hemisphere, the warm South Pacific SSTs and high salinities might be an important clue to the source of what is known as the Little Ice Age in the northern hemisphere (Hendy et al., 2002).

8.14.9.5 Results on Geological Timescales

The first detailed Sr/Ca results published for well-dated fossil corals (Beck et al., 1992) were interpreted as indicating a 6 °C cooling of tropical SST in the region of Vanuatu in the South Pacific during the latest Younger Dryas/earliest Holocene. Although the degree of cooling was probably exaggerated, presumably because of a secular increase in seawater Sr/Ca (Lea et al., 2000; Martin et al., 1999; Stoll and Schrag, 1998), Beck et al. (1992) were among the first to seriously challenge the prevailing view of warm tropical oceans during glacial episodes. Subsequently, Sr/Ca data from sites in the Caribbean (Guilderson et al., 1994) and western Pacific (McCulloch et al., 1999), apparently supported by coincident shifts in $\delta^{18}\text{O}$, were published to indicate 5–6 °C cooling of tropical SSTs during glacial episodes. Holocene changes in SST have also been reconstructed using Sr/Ca (Beck et al., 1997; Gagan et al., 1998). In retrospect, it appears that the estimates of glacial cooling were too large, in part, because they would have rendered large parts of the tropical sea inhospitable to massive reef corals (Crowley, 2000b). In addition, terrestrial shifts such as the well-known drop in snow lines during the Last Glacial Maximum are compatible with tropical SST drops of ~3 °C (Greene et al., 2002; Pierrehumbert, 1999). Pinpointing the exact cause of why coral Sr/Ca appears to give an excess cooling signature of glacial episodes is obviously an important research problem (Gagan et al., 2012), but regardless of the exact causes of that offset, the tropical cooling results from coral Sr/Ca were a very important initial part of the motivation that led to a growing focus on the paleoclimatic role of the tropics.

The spectral characteristics of Sr/Ca records in fossil corals can, like oxygen isotopes, provide insight into changes in interannual climate change such as ENSO without requiring conversion into absolute SSTs (Corrège et al., 2000; Hughen et al., 1999). The results of Hughen et al. (1999) are notable for providing evidence, in the form of interannual variations in

Sr/Ca and $\delta^{18}\text{O}$, of ENSO-like variability in a fossil coral from Sulawesi, Indonesia, dated to the last interglacial sea level high stand at 124 ky BP.

8.14.9.6 Summary of Outstanding Research Issues

In only a decade, the coral Sr/Ca paleothermometer has grown to be a fundamental tool for paleoclimate research on historical and geological timescales. Optimal use of this tool requires a better understanding of the coral Sr/Ca temperature calibration in both space and time. The most critical current question is the degree to which symbiosis and other kinetic factors influence the sensitivity of the paleothermometer (Cohen et al., 2002). If the Sr/Ca of coral carbonate precipitated by hermatypic corals during the day is strongly biased by photosynthesis, as suggested by Cohen et al. (2002), it will place a severe limitation on both the usefulness and the accuracy of the Sr/Ca paleothermometer.

On geological timescales, how much secular change in seawater Sr/Ca occurred, as well as the extent of diagenetic influence on coral Sr/Ca, require further investigation. Foraminiferal Sr 'stacks' of seawater Sr/Ca change (Martin et al., 1999) could be improved by adding more cores and improving the precision of the analyses (Shen et al., 2001). It might also be possible to correct for offsets between sites by taking into account environmental factors that also influence foraminiferal Sr/Ca. In this way it should be possible eventually to generate definite secular records of seawater Sr/Ca that can be suitably applied to coral Sr/Ca paleothermometry.

8.14.10 Magnesium and Uranium in Corals as Paleotemperature Proxies

The ratios of Mg/Ca and U/Ca in corals appear to serve as paleothermometers, although with apparently less fidelity than is found for Sr/Ca. The results for U/Ca (Min et al., 1995; Shen and Dunbar, 1995) and Mg/Ca (Fallon et al., 1999; Mitsuguchi et al., 1996; Sinclair et al., 1998) show convincing annual cycles, but with some complications; for example, Sinclair et al. (1998) observe, using laser ICP-MS analyses of coral surfaces, that there are high-frequency oscillations in Mg/Ca that range up to 50% of the total signal. In their comparative study, Sinclair et al. (1998) also observed differences in the seasonal profile of U/Ca and Sr/Ca, suggesting that other factors might be at play for uranium incorporation. Fallon et al. (1999) observed that Mg incorporation tracked with SST but also evinced variability not related to temperature, suggesting that Mg/Ca paleothermometry in corals is not going to be as simple as it appeared in the initial study (Mitsuguchi et al., 1996).

Two of these studies also looked at boron incorporation into the coral skeleton and observed that it also appears to be at least in part related to temperature (Fallon et al., 1999; Sinclair et al., 1998). The fact that at minimum, four elements follow a seasonal pattern related to temperature suggests that elemental incorporation in coral skeletons is linked to calcification and is not simply driven by a thermodynamic temperature effect. If this applies generally, then all of the coral metal paleothermometers will have to be applied with attention to the possibility of distortions caused by growth factors.

8.14.11 Calcium Isotopes as a Paleotemperature Proxy

The possibility of using calcium isotopes for paleothermometry is a relatively new idea that is based on the empirical observation of temperature-related fractionation between the isotopes ^{40}Ca and ^{44}Ca (reported as $\delta^{44}\text{Ca}$). Measurements of precise Ca isotopic variations are quite challenging (Russell et al., 1978), and this has limited investigations of this isotopic system to relatively small datasets. Zhu and Macdougall (1998) compared three pairs of warm and cold foraminifera and demonstrated a systematic difference. Subsequent studies focused on neritic benthic foraminifera (De La Rocha and DePaolo, 2000), a spinose tropical planktonic foraminifera (Näglér et al., 2000), and a subtropical planktonic foraminifera (Gussone et al., 2003). The most convincing evidence of the potential utility of the Ca isotope paleothermometer for foraminifera comes from Näglér et al. (2000), who demonstrated an increase of 0.24‰ in shell $\delta^{44}\text{Ca}$ per degree Celsius, based on three cultured points of *G. sacculifer*. Downcore measurements from a core in the tropical Atlantic indicate that shells from glacial intervals are about 0.5–1.0‰ depleted in $\delta^{44}\text{Ca}$, consistent with colder glacial temperatures. A more recent study using Ca isotopes determined that glacial temperatures in the tropical Atlantic were about 3 °C colder than the Holocene, in agreement with other proxies (Hippler et al., 2006). Although the results of Näglér et al. (2000) indicate that Ca isotope paleothermometry has promise, they are somewhat confounded by a subsequent study which shows a much weaker response of $\delta^{44}\text{Ca}$ to temperature ($\sim 0.02\text{‰}$ per degree Celsius) in a subtropical foraminifera, *O. universa*, calibrated over a wide temperature range by culturing (Gussone et al., 2003). The weaker response in *O. universa* is mirrored by a similar response in inorganically precipitated aragonite (Gussone et al., 2003). More recent studies (Gussone et al., 2009; Kisakürek et al., 2011) suggest that foraminifera follow a complex Ca isotope fractionation behavior that appears to be primarily driven by precipitation kinetics, suggesting limited utility for paleothermometry. Böhm et al. (2006), who investigated modern scleractinian corals, also concluded that Ca isotopes would most likely have only limited utility for paleothermometry.

8.14.12 Conclusions

In the 65 years since Harold Urey's pioneering paper (Urey, 1947), geochemists have come up with a remarkable array of paleotemperature proxies in marine carbonates. These proxies work in diverse oceanic settings, in different organisms, in different parts of the water column, and on varied timescales. Each proxy has different strengths and weaknesses, and some of the proxies, such as Mg/Ca and oxygen isotopes in foraminifera, reinforce each other when applied together.

Perhaps, the most remarkable is the amount of progress that has been made in the last two decades on three new or revived paleothermometric approaches, each of which works particularly well in the tropics: oxygen isotopes in corals, Mg/Ca in foraminifera, and Sr/Ca in corals. This progress, in

conjunction with advances in alkenone unsaturation paleothermometry (see [Chapter 8.15](#)), has not only expanded the importance of geochemistry in paleoclimate research but also changed its focus from a mainly chronostratigraphic and sea level tool (i.e., oxygen isotopes in foraminifera) to a series of proxies that can be used to gauge the temporal and spatial history of oceanic temperatures. This shift, and the general level of agreement between geochemical paleothermometers for such fundamental problems as the cooling of the glacial tropics, suggests that major breakthroughs in long-standing paleoclimatological issues are now within reach. Although many problems and challenges remain, and although none of the available proxies work perfectly, it is clear that recent progress has elevated geochemical paleothermometers to an even more fundamental role in quantitative paleoclimate research.

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