

6.14

Elemental and Isotopic Proxies of Past Ocean Temperatures

D. W. Lea

University of California, Santa Barbara, CA, USA

6.14.1	INTRODUCTION	000
6.14.2	A BRIEF HISTORY OF EARLY RESEARCH ON GEOCHEMICAL PROXIES OF TEMPERATURE	000
6.14.3	OXYGEN ISOTOPES AS A PALEOTEMPERATURE PROXY IN FORAMINIFERA	000
6.14.3.1	<i>Background</i>	000
6.14.3.2	<i>Paleotemperature Equations</i>	000
6.14.3.3	<i>Secondary Effects and Diagenesis</i>	000
6.14.3.4	<i>Results on Quaternary Timescales</i>	000
6.14.3.5	<i>Results for the Neogene, Paleogene, and Earlier Periods</i>	000
6.14.3.6	<i>Summary of Outstanding Research Issues</i>	000
6.14.4	OXYGEN ISOTOPES AS A CLIMATE PROXY IN REEF CORALS	000
6.14.4.1	<i>Background</i>	000
6.14.4.2	<i>Paleotemperature Equations</i>	000
6.14.4.3	<i>Secondary Effects and Diagenesis</i>	000
6.14.4.4	<i>Results on Historical Timescales</i>	000
6.14.4.5	<i>Results on Late Quaternary Timescales</i>	000
6.14.4.6	<i>Summary of Outstanding Research Issues</i>	000
6.14.5	OXYGEN ISOTOPES AS A CLIMATE PROXY IN OTHER MARINE BIOGENIC PHASES	000
6.14.6	MAGNESIUM AS A PALEOTEMPERATURE PROXY IN FORAMINIFERA	000
6.14.6.1	<i>Background and History</i>	000
6.14.6.2	<i>Calibration and Paleotemperature Equations</i>	000
6.14.6.3	<i>Effect of Dissolution</i>	000
6.14.6.4	<i>Other Secondary Effects: Salinity, pH, Gametogenesis, and Changes in Seawater Mg/Ca</i>	000
6.14.6.5	<i>Results on Quaternary Timescales</i>	000
6.14.6.6	<i>Results for the Neogene</i>	000
6.14.6.7	<i>Summary of Outstanding Research Issues</i>	000
6.14.7	MAGNESIUM AS PALEOTEMPERATURE PROXIES IN OSTRACODA	000
6.14.8	STRONTIUM AS A CLIMATE PROXY IN CORALS	000
6.14.8.1	<i>Background</i>	000
6.14.8.2	<i>Paleotemperature Equations</i>	000
6.14.8.3	<i>Secondary Effects and Diagenesis</i>	000
6.14.8.4	<i>Results on Historical Timescales</i>	000
6.14.8.5	<i>Results on Geological Timescales</i>	000
6.14.8.6	<i>Summary of Outstanding Research Issues</i>	000
6.14.9	MAGNESIUM AND URANIUM IN CORALS AS PALEOTEMPERATURE PROXIES	000
6.14.10	CALCIUM ISOTOPES AS A PALEOTEMPERATURE PROXY	000
6.14.11	CONCLUSIONS	000
	ACKNOWLEDGMENTS	000
	REFERENCES	000

6.14.1 INTRODUCTION

Determining the temperature evolution of the oceans is a fundamental problem in the 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 most important single component of the Earth's climate system. A suite of isotopic and elemental proxies, mostly preserved in marine carbonates, are the essential method by which earth scientists determine past ocean temperatures (see Table 1). 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 since 1950s, and, with our need to understand the global climate system heightened by the threat of global warming, it promises to remain a vibrant and important area well into the future.

In this chapter I begin by reviewing the history of the elemental and isotopic proxies and how that history shapes research priorities today. I then review the state of our knowledge at present (as of early 2000s), including areas that are well developed (i.e., oxygen isotopes in coral aragonite), areas that are experiencing phenomenal growth (i.e., Mg/Ca in foraminifer shells), and areas that are just starting to develop (i.e., Ca

isotopes in carbonates). In these reviews I include an estimation of the uncertainty in each of these techniques and areas, including aspects that particularly need to be addressed. I also address the question of overlap and confirmation between proxies, and in particular how information from one proxy can augment a second proxy.

6.14.2 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 magnesium content of biogenic carbonates and their growth temperature (Clarke and Wheeler, 1922). The authors speculated that this relationship had a definite cause and could

Table 1 Summary of major paleotemperature techniques.

	Phases	Sensitivity (per ‰)	Estimated SE	Major secondary effects	Time scale ^a
Oxygen Isotopes	Foraminifera	0.18–0.27‰	0.5 °C if $\delta^{18}\text{O}$ -sw is known	Effect of $\delta^{18}\text{O}$ -sw	0–100 Ma
	Corals	~0.2‰	0.5 °C if $\delta^{18}\text{O}$ -sw is known	Kinetic effects	0–130 ka
	Opal			Effect of $\delta^{18}\text{O}$ -sw	0–30 ka
Mg/Ca	Foraminifera	$9 \pm 1\%$	~1 °C	Dissolution Secular Mg/Ca variations (>10 Ma)	0–40 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	0.02–0.24‰	unknown	Species effects, calcification	0–125 ka
Alkenone unsaturation index ^b	Sediment organics	0.033 (0.023–0.037) in $U_{37}^{k'd}$	~1.5 °C (global calib.)	Transport, species variation	0–3 Ma
Faunal transfer functions ^c	Foraminifera, Radiolaria, Dinoflagellates	NA	1.5 °C	Ecological shifts	0–?

^a Timescale over which the technique has been applied. ^b Chapter 6.15. ^c (Imbrie and Kipp, 1971) ^d (Müller *et al.*, 1998 and Pelejero and Calvo, 2003).

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 magnesium to calcium ratio of the oceans was nearly constant, and that therefore the trend 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*” (quotations added for emphasis). Further along in this 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 magnesium 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 magnesium relationship became both explicable and fruitful for climatology.

The next great step forward came after World War II, 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).

It was left to Urey’s students and post-doctoral scholars to 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 mollusks 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 $^{\circ}C$. 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 reconstructing paleotemperatures. A few years later, Cesare Emiliani (1922–1995), a student and later a post-doctoral 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, 1955). 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 $^{\circ}C$. Many of the questions raised by Emiliani’s classic 1955 study are still relevant today and are addressed in detail below.

During this same period scholars at Chicago examined the potential temperature dependence of trace elements in carbonates, focusing mainly on magnesium and strontium 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 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 (1955) 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 of Cambridge University reported the first systematic down-core variations in benthic foraminifera (Shackleton, 1967). He argued that benthic fauna, because they lived in the near-freezing bottomwaters of the ocean, would mainly record

P0020

P0025

P0030

P0035

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). So 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 is the long-sought solution to the "Urey dilemma," because it provides, in combination with oxygen isotopes, a simultaneous temperature and isotopic composition history for seawater (Lea *et al.*, 2000; Lear *et al.*, 2000).

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 as well as 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: (i) the mean $\delta^{18}\text{O}$ of seawater (Schrag *et al.*, 1996), which is determined by the amount of continental ice, which varies on timescales of 10^4 – 10^5 yr, and by interaction between seafloor basalts and seawater, which varies on timescales of 10^7 – 10^8 yr and (ii) 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 6.14.2), 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, because $\delta^{18}\text{O}$ records have proven so useful for stratigraphic and chronological purposes.

An important aspect of the application of oxygen isotopic ratios in foraminifera is that the planktonic foraminifera 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 part of the water column. A complication, however, is that many of the planktonic species migrate vertically, potentially compounding the signals they record.

6.14.3.2 Paleotemperature Equations

There are a number of calibrations in use for oxygen isotopes in foraminifera, some derived

6.14.3 OXYGEN ISOTOPES AS A PALEOTEMPERATURE PROXY IN FORAMINIFERA

6.14.3.1 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 °C to 30 °C , of between -0.20‰ and -0.27‰ per °C , in agreement with thermodynamic predictions (O'Neil *et al.*, 1969; Shackleton, 1974; Kim and O'Neil, 1997; 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

P0045

P0050

P0055

S0025

P0060

from other organisms (Epstein *et al.*, 1953), some derived from culturing (Erez and Luz, 1983; Bemis *et al.*, 1998), 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 is temperature ($^{\circ}\text{C}$), a is 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 slope ranges from 0.27‰ per $^{\circ}\text{C}$ at 0°C to 0.20‰ per $^{\circ}\text{C}$ at 25°C (O'Neil *et al.*, 1969; Kim and O'Neil, 1997). 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 in 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 O'Neil (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 $\delta^{18}\text{O}_{\text{water}}$ (Mashiotta *et al.*, 1999; Elderfield and Ganssen, 2000; Lea *et al.*, 2000; Lear *et al.*, 2000).

6.14.3.3 Secondary Effects and Diagenesis

There has been a long discussion in the literature as to the extent to which foraminifera 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 inorganic experiments (Shackleton,

1974; Kim and O'Neil, 1997; Bemis *et al.*, 1998). Such comparisons suggest that foraminifera shells can be offset from equilibrium for a number of reasons (Figure 1), ranging from unknown vital effects that offset benthic species (Duplessy *et al.*, 1970), offsets due to the effect of light on symbiotic algae (Spero and Lea, 1993; Bemis *et al.*, 1998), offsets due to ontogeny (growth) (Spero and Lea, 1996), offsets due to carbonate ion concentration of seawater (Spero *et al.*, 1997), and offsets due to the addition of gametogenic calcite at depth (Duplessy and Blanc, 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 the effect of gametogenic calcite, also apply for Mg/Ca paleothermometry (Rosenthal *et al.*, 2000; Dekens *et al.*, 2002), so it is likely that complimentary studies will improve our understanding of the limitations these effects impose.

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 demonstrated to increase the $\delta^{18}\text{O}$ of shells by $\sim 0.2\text{‰}$ per km in deeper, more dissolved sediments (Wu and Berger, 1989; Dekens *et al.*, 2002), presumably through the loss of individual shells and/or shell material with more negative $\delta^{18}\text{O}$. Because this

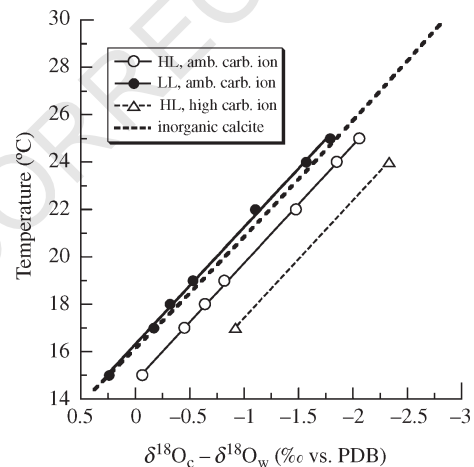


Figure 1 Comparison of oxygen-isotope paleotemperature equations for *O. universa*, a symbiont-bearing planktonic foraminifera, with values for inorganic calcite precipitation (Kim and O'Neil, 1997). These data demonstrate that the low light (LL) oxygen isotope equation at ambient carbonate ion concentration for *O. universa* is essentially indistinguishable from the inorganic equation. For high light (HL) conditions, 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 $\delta^{18}\text{O}$ (after Bemis *et al.*, 1998).

S0030

P0065

P0070

Q1 F0005

effect appears to be coincident for both oxygen isotopes and Mg/Ca (Brown and Elderfield, 1996; Rosenthal *et al.*, 2000; Dekens *et al.*, 2002), it is likely that complimentary 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 (Schrag *et al.*, 1995; Schrag, 1999a). Recent 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).

(Zachos *et al.*, 2001). Because it is a record of the combined influences of temperature and ice volume influence, 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 6.20). 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). Recent research suggests that diagenetic overprinting of the primary foraminiferal $\delta^{18}\text{O}$ is a major influence (Schrag, 1999a; Pearson *et al.*, 2001). Results from the Pearson *et al.* (2001) study suggest that low-latitude sea surface temperatures (SSTs) during the Late Cretaceous and Eocene epochs were at least 28–32 °C compared to 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 towards a means of correcting less well preserved samples for diagenesis, perhaps in combination with the Mg/Ca approach.

6.14.3.6 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 firm ground in terms of known influences and inherent accuracy. New results, such as a primary seawater carbonate ion influence (Spero *et al.*, 1997) and secondary diagenetic overprints (Schrag, 1999a; Pearson *et al.*, 2001), suggest that there is still major progress to made in this area. 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.

6.14.4 OXYGEN ISOTOPES AS A CLIMATE PROXY IN REEF CORALS

6.14.4.1 Background

Many of the factors described in Section 6.14.3.1 apply equally to oxygen isotopes in corals, which are dominantly composed of aragonite. Corals, however, have many unique aspects which require separate consideration. First, their oxygen isotopic composition is invariably depleted relative to equilibrium by

6.14.3.4 Results on Quaternary Timescales

The many important results achieved in paleoceanography and paleoclimatology using oxygen isotope ratios in foraminifera shells are well known and have been reviewed in many other places: e.g., Shackleton (1987), Imbrie *et al.* (1992), and Mix (1992). 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 Section 6.14.2 and 6.14.3.1. As was emphasized in Section 6.14.2, the pioneers in the 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 (Shackleton and Opdyke, 1973; Hays *et al.*, 1976) and for calibration of the magnitude of past sea-level and ice volume change (Chappell and Shackleton, 1986; Shackleton, 1987). With the advent of independent geochemical paleotemperature proxies, it became possible to deconvolve the isotopic signal into its temperature and compositional components (Rostek *et al.*, 1993; Mashiotta *et al.*, 1999; Elderfield and Ganssen, 2000). Current research (see Sections 6.14.6.4 and 6.14.6.5) is focused on the veracity of this approach and the separation of ice volume and hydrological influences in the extracted $\delta^{18}\text{O}$ -water records (Lea *et al.*, 2000, 2002; Lear *et al.*, 2000; Martin *et al.*, 2002).

6.14.3.5 Results for the Neogene, Paleogene, and Earlier Periods

The Cenozoic benthic foraminiferal $\delta^{18}\text{O}$ record is one of the major success of the geochemical approach to paleoclimate research

S0035

P0075

S0040

P0080

S0045

P0085

S0050

S0055

P0090

~1–6‰, presumably because of their different biochemical mechanisms of precipitation as well as the influence of symbiotic zooxanthellae (McConnaughey, 1989a; McConnaughey, 1989b). 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 (Weber and Woodhead, 1972; Emiliani *et al.*, 1978; Fairbanks and Dodge, 1979; Druffel, 1985; Dunbar and Wellington, 1985; McConnaughey, 1989a; Cole and Fairbanks, 1990; Shen *et al.*, 1992). These early discoveries have been followed by a fantastic array of results from longer coral time series that have enabled researchers to elevate coral climate records to the same level of importance as 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 circumvented by drilling into submerged fossil deposits, but because of logistical difficulties, so far this has been accomplished in only a few key spots such as Barbados and Tahiti (Fairbanks, 1989; Bard *et al.*, 1996).

6.14.4.2 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. 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 (McConnaughey, 1989a,b; Spero *et al.*, 1997). The slope of the calibrations, however, appears to be nearly constant at ~0.2‰ per °C, in general agreement with the slope from inorganic experiments (Zhou and Zheng, 2003); the constancy of the slope suggests

that historical changes in temperature will be accurately recorded.

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 $E-P$, 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 6.14.4.4), 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 6.14.8) at the same time to separate the coral $\delta^{18}\text{O}$ signal into its components (McCulloch *et al.*, 1994; Gagan *et al.*, 1998). 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.

6.14.4.3 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 (McConnaughey, 1989a,b) 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.

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 6.14.8.3) records (Muller *et al.*, 2001). 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 more salty 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 does 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

P0095

S0060

P0100

P0105

S0065

P0110

P0115

P0120

crystallography to screen for the presence of calcite. A recent study suggests that small, restricted levels of aragonite alteration have minimal effects on coral $\delta^{18}\text{O}$ (Mcgregor and Gagan, 2003).

have been incorporated into historical climate records used to assess global warming in the past century (Mann *et al.*, 1998; Crowley, 2000a). Some of the outstanding findings from the coral records include: (i) most of the longer records show a secular shift to more negative $\delta^{18}\text{O}$ values starting in the nineteenth century; (ii) a series of decadal or longer coherent shifts in the nineteenth century that might reflect regional to global cooling patterns; and (iii) shifts in the magnitude and frequency of the El Niño/Southern Oscillation (ENSO) phenomenon and Indian Ocean monsoon over the past two centuries (Cole *et al.*, 2000; Urban *et al.*, 2000; Cobb *et al.*, 2001).

6.14.4.4 Results on Historical Timescales

Measurement of oxygen isotopic variations in coral heads up to 500 yr old has to be counted among the great success of the geochemical approach to paleoclimate research (Figure 2). These records have become important paleoclimatic archives of tropical climate change, and they

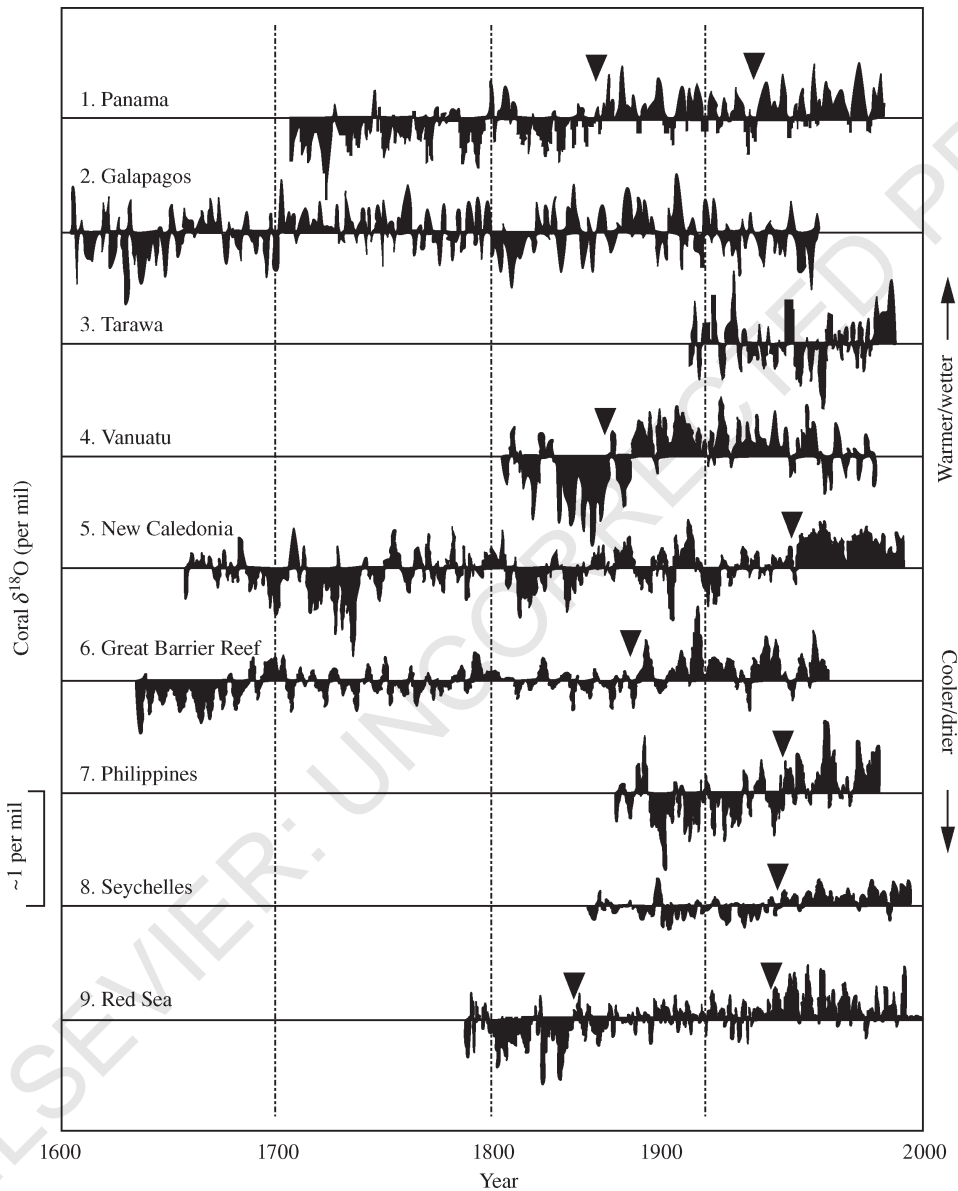


Figure 2 Comparison of annual mean coral oxygen isotope records in the Pacific and Indian Ocean region extending back more than 100 yr (Gagan *et al.*, 2000). These records demonstrate the considerable potential of this approach for documenting historical climate variation in the tropical oceans.

P0130 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 to eventually extract true temperature and/or salinity records from the coral time series. 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). But in at least some cases, this shift appears to be larger than can explained by SST shifts recorded by instrumental records (the records in Urban *et al.*, 2000; 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 (Muller *et al.*, 2001).

S0075 6.14.4.5 Results on Late Quaternary Timescales

P0135 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 6.14.4.3). 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).

P0140 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 6.14.3.4) (Fairbanks and Matthews, 1978). A number of studies published during 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 SST. 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 6.14.3). Sr/Ca paleothermometry in corals provides a way around this problem, but this approach appears to have its own set of limitations (see Section 6.14.8.3).

More recent studies are focusing 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. The Tudhope *et al.* (2001) study documented coral climate proxy variability for seven different time slices. These records demonstrate that the amplitude of ENSO variability (2–7 yr 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 only comprise 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 has been suggested by studies of other climate proxies (e.g., Rodbell *et al.*, 1999).

6.14.4.6 Summary of Outstanding Research Issues

S0080 P0150 High-resolution coral oxygen isotope records have to be counted among the great successes of the geochemical approach to paleoclimate research. This is ironic given that early researchers were highly skeptical about the fidelity of coral $\delta^{18}\text{O}$ because of the clear lack 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 establishing a coincident temperature proxy such as Sr/Ca (see Section 6.14.8) and determining the degree to which factors associated with the growth of large coral heads might influence longer-term records.

S0085 **6.14.5 OXYGEN ISOTOPES AS A CLIMATE
PROXY IN OTHER MARINE
BIOGENIC PHASES**

P0155 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 (Labeyrie and Juillet, 1982; Juillet-Leclerc and Labeyrie, 1986). Oxygen isotopes have also been measured as temperature or climate proxies in ahermatypic solitary corals (Smith *et al.*, 1997), in coralline sponges (Böhm *et al.*, 2000), in fish otoliths (Andrus *et al.*, 2002), as well as in pteropods (Grossman *et al.*, 1986) and other mollusks.

S0090 **6.14.6 MAGNESIUM AS A
PALEOTEMPERATURE
PROXY IN FORAMINIFERA**

S0095 **6.14.6.1 Background and History**

P0160 At the time of this writing (Spring 2002), research in the use of Mg/Ca ratios in foraminifer shells is probably advancing as fast as any area in climate proxy research. As a result of these advances since the late 1990s, 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, I review the history of this development more closely than for the other proxies.

P0165 As discussed in Section 6.14.2, the observation that magnesium was higher in marine carbonates precipitated in water warmers dates to the early part of the twentieth century. Several studies confirmed these early observations for neritic foraminifer shells, which are composed of high magnesium calcite (>5% MgCO_3) (Chave, 1954; Chilingar, 1962). Another study suggested that pelagic foraminifera, which are composed of low-magnesium calcite (<1% MgCO_3), might also follow this pattern (Savin and Douglas, 1973). Several studies also demonstrated that inorganic carbonates followed the same pattern (Chilingar, 1962; Katz, 1973). This latter point is

important, because it indicates that the temperature influence could not be entirely biological.

P0170 Another important milestone in research in this area 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 down-core 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 (Rosenthal and Boyle, 1993; Russell *et al.*, 1994; Brown and Elderfield, 1996). It was not until Dirk Nürnberg, a doctoral student at Bremen University, Germany, used electron microprobe determinations on shell surfaces to document more convincing Mg/Ca–temperature relationships in cultured, core-top and down-core planktonic foraminifera (Nürnberg, 1995; Nürnberg *et al.*, 1996a,b), that the international community recognized the potential importance of this new tool. Progress on documenting a potential response of magnesium in benthic foraminifera to bottomwater temperatures, a result presaged by Scot Izuka’s (University of Hawaii) pioneering study of magnesium in *Cassidulina* (Izuka, 1988), occurred at about the same time (Russell *et al.*, 1994; Rathburn and Deckker, 1997; Rosenthal *et al.*, 1997). The Rosenthal *et al.* (1997) paper is notable for its broad calibration and for being the first to point out that the magnesium relationship to temperature is predicted, albeit with a smaller slope, by thermodynamic calculations.

P0175 Progress has been very 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 culturing calibrations made on whole shells (Lea *et al.*, 1999), the first attempt to combine Mg/Ca paleotemperatures with oxygen isotopic ratios to deduce variations in $\delta^{18}\text{O}$ -seawater (Mashiotta *et al.*, 1999; Elderfield and Ganssen, 2000), the first long tropical SST and $\delta^{18}\text{O}_{\text{water}}$ records (Lea *et al.*, 2000), the first application of benthic magnesium to Cenozoic climate evolution (Lear *et al.*, 2000), and the first detailed Late Quaternary benthic magnesium records (Martin *et al.*, 2002). The following sections detail the most important of these findings and research priorities for the future.

6.14.6.2 Calibration and Paleotemperature Equations

The underlying basis for magnesium paleothermometry is that the substitution of magnesium in calcite is endothermic and therefore is favored at higher temperatures. The enthalpy change for the reaction based on the more recent thermodynamic data is 21 kJ mol^{-1} (Koziol and Newton, 1995), which can be shown, using the van't Hoff equation, to equate to an exponential increase in Mg/Ca of 3% per °C (Lea et al., 1999). The thermodynamic prediction of an exponential response is one of the reasons that magnesium paleotemperature calibrations are generally parameterized this way. Available inorganic precipitation data generally follows the thermodynamic prediction (Chilingar, 1962; Katz, 1973; Burton and Walter, 1987; Mucci, 1987), with the most extensive data set (Oomori et al., 1987) yielding a $3.1 \pm 0.4\%$ per °C increase in D_{Mg} for calcites precipitated in seawater over 10–50 °C (all responses given as percentages are calculated as exponentials, with 95% CI).

Foraminifera shells differ from the thermodynamic prediction in two fundamental ways.

First, foraminifera contain 5–10 times lower magnesium than predicted from thermodynamic calculations (Bender et al., 1975). Second, the response of shell magnesium to temperature is ~ 3 times larger than the thermodynamic prediction and inorganic observation, averaging $9 \pm 1\%$ per °C (Lea et al., 1999). Why the latter effect is so is not known, but it has several important implications for magnesium paleothermometry. First, it increases the sensitivity of this approach, which is critical in determining its real error, which depends on 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 if the augmentation of the response depends on secondary factor(s) that might change over geological time. One possibility is that the much smaller magnesium content of foraminifer shells increases the thermodynamic response (Figure 3). Data from a recent study (Toyofuku et al., 2000), which calibrated two neritic high-magnesium benthic species in culturing

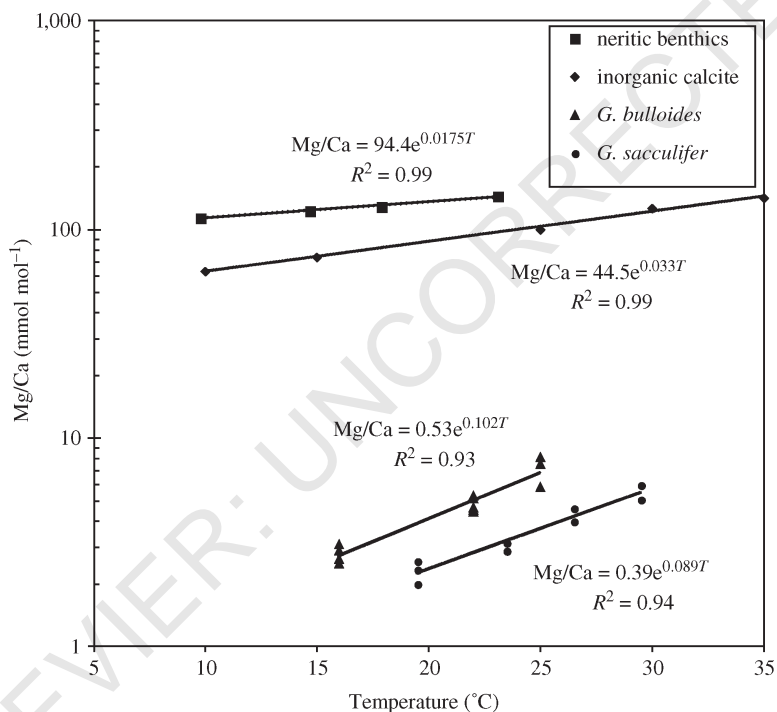


Figure 3 Comparison of Mg/Ca–temperature relationships for inorganic calcite precipitation (Oomori et al., 1987), neritic benthic foraminifera (Toyofuku et al., 2000), a tropical spinose symbiont bearing planktonic foraminifera, *G. sacculifer* (Nürnberg et al., 1996a,b), and a subpolar spinose symbiont 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 has 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 $\sim 10\%$ (source Rosenthal et al., 1997).

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

P0190 At present, three planktonic species, *Globigerinoides sacculifer*, *Globigerina bulloides*, and *O. universa*, have been 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 pre-exponential 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 parametrizing, by the use of the natural logarithm e , the exponential constant as the change in Mg/Ca per °C. It should be noted that it is the exponential constant that determines the magnitude of temperature change calculated from down-core variations in Mg/Ca and the pre-exponential constant that determines the absolute temperature. Calibration results for these three species indicates exponential constants between 0.085 and 0.102, equivalent to 8.5% to 10.2% increase in Mg/Ca per °C (Nürnberg *et al.*, 1996a,b; Lea *et al.*, 1999). A recent study utilizing planktonic foraminifera from a sediment trap time series off Bermuda extends calibration to seven other species, which in aggregate have a temperature response of $9.0 \pm 0.3\%$ (Anand *et al.*, 2003). The pre-exponential constant b 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 (Nürnberg *et al.*, 1996a,b; Lea *et al.*, 1999; Anand *et al.*, 2003). Core-top calibrations are in general agreement with the culturing results, and include calibrations of eight planktonic species (Elderfield and Ganssen, 2000; Lea *et al.*, 2000; Dekens *et al.*, 2002; 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 6.14.7.3.

P0195 Calibration for benthic species is somewhat more uncertain. The first comprehensive calibration was carried out by Yair Rosenthal, then at MIT, who used *Cibicidoides* spp. from shallow sediments on the Bahamas outer bank to calibrate benthic magnesium between 5 °C 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 a magnesium response to temperature of this magnitude is a common factor among foraminifera. It should be noted that the Martin *et al.* (2002) data set suggests that the magnesium response might be steeper at bottomwater temperatures, <4 °C. Resolving the calibration for benthic magnesium 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 bottomwaters. Establishing calibrations for other species is also a high priority, in part because of the insight this provides into the basis for magnesium paleothermometry.

6.14.6.3 Effect of Dissolution

P0105
P0200 It has been known since the 1970s that the magnesium content of foraminifer 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 magnesium as a paleotemperature proxy. At present, researchers accept that dissolution alters the Mg/Ca content of foraminifera 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.

P0205 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 (Rosenthal and Boyle, 1993; Russell *et al.*, 1994; Brown and Elderfield, 1996; Hastings *et al.*, 1996). 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 post-depositional processes. These studies demonstrated, to a greater or lesser degree, that Mg/Ca in the shells decreased with water depth and inferred increasing dissolution. The Rosenthal and Boyle (1993) study 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 was more pronounced for nonspinose species such as *Globorotalia tumida*, a result

that was interpreted to reflect preferential dissolution of magnesium-rich chamber calcite over magnesium-poor keel calcite (Brown and Elderfield, 1996). One of these studies also revived the idea, first suggested by Savin and Douglas (1973), that the magnesium 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. Magnesium loss presumably occurs when shells are on the seafloor and/or when they pass through the sediment mixed layer where metabolic CO₂ is available for dissolution. The fact that surface dwelling *Globigerinoides ruber* indicates decreasing Mg/Ca with water depth in the western equatorial Pacific (Lea et al., 2000; Dekens et al., 2002), an area with minimal temporal and spatial variation in mixed layer temperatures, suggests that magnesium loss might occur via preferential dissolution of magnesium-rich portions of the shell (Lohmann, 1995; Brown and Elderfield, 1996). It is also 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.

A clear 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 down-core studies, although a new study (Rosenthal and Lohmann, 2002), demonstrates that this approach can yield consistent glacial–interglacial SST changes from cores both above and below the lysocline.

A somewhat different approach has been taken by others (Lea et al., 2000; Dekens et al., 2002). They 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 down-core. 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 nonspinoso thermocline dweller. These terms equate to a bias on magnesium paleothermometry of 0.4 °C per km, 0.6 °C per km, 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 km and 0.8 km (Farrell and Prell, 1989), this approach suggests that down-core dissolution biases on magnesium 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.

The evidence for dissolution effects on magnesium in benthic foraminifera is less certain. For one, it is more difficult to discern a dissolution trend because benthic Mg/Ca is decreasing 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% per °C versus 11% per °C, might reflect dissolution and magnesium loss in the deepest, most undersaturated waters. Alternatively, it 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 on the coldest bottomwaters.

6.14.6.4 Other Secondary Effects: Salinity, pH, Gametogenesis, and Changes in Seawater Mg/Ca

Factors other than temperature and dissolution also appear to influence Mg/Ca in planktonic shells. Based on culturing, there is clear evidence for differences in uptake between species (Lea et al., 1999), with as much as a factor of two variations. 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. Salinity appears to exert a small effect on shell Mg/Ca, with an observed increase of between 6 ± 4% for *O. universa* (Lea et al., 1999) and 8 ± 3% for *G. sacculifer* (Nürnberg et al., 1996a) per salinity unit (SU) increase. (Note: this and all other

P0210

P0215

P0220

S0110

P0225

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 was 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 an Mg/Ca temperature response of 10% per °C (see Section 6.14.6.2), the salinity influence is equivalent to a positive bias of between 0.6–0.8 °C per SU increase. More extensive culturing data is needed; however, before such an influence can be accepted as likely to apply for salinity differences of <3.

Investigation of the effect of seawater pH indicates that pH has a significant effect on magnesium uptake, with an observed decrease of $-6 \pm 3\%$ per 0.1 pH unit increase for *G. bulloides* and *O. universa*. Again assuming an Mg/Ca temperature response of 10% per °C (Section 6.14.7.3), pH influence is equivalent to a bias -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.

A bias that applies equally to any foraminifera-based proxy is the problem of gametogenic calcite addition in the subsurface, as well as other vertical migration effects. For magnesium, one early study claimed that gametogenic calcite from *G. sacculifer* cultures is highly enriched in magnesium (Nürnberg *et al.*, 1996a), but this observation has not confirmed by studies of shells from sediments (Elderfield and Ganssen, 2000; Nürnberg *et al.*, 2000; Rosenthal *et al.*, 2000; Dekens *et al.*, 2002). The observation that Mg/Ca in *G. sacculifer*, a species known to add ~30% gametogenic calcite (Bé, 1980), is generally lower (Elderfield and Ganssen, 2000; Lea *et al.*, 2000; Dekens *et al.*, 2002) than in *G. ruber*, a species that adds little or no gametogenic calcite (Caron *et al.*, 1990), suggests that the addition of gametogenic calcite takes place in cold, subsurface waters and reduces Mg/Ca and inferred temperatures for those species that add significant shell calcite this way.

6.14.6.5 Results on Quaternary Timescales

Although magnesium paleothermometry has only been used for ~5 yr, it has already led to a number of important and unprecedented findings for paleoceanographic and paleoclimatic research. These include documenting the history of sub-polar Antarctic SST variations (Mashiotto *et al.*, 1999; Rickaby and Elderfield, 1999), tropical Atlantic and Pacific SST changes (Hastings *et al.*, 1998; Elderfield and Ganssen, 2000; Lea *et al.*, 2000; Nürnberg *et al.*, 2000), and changes in

bottomwater temperature in the Atlantic and Pacific (Martin *et al.*, 2002). Secondary products include $\delta^{18}\text{O}$ -seawater records for the sub-polar Antarctic (Mashiotto *et al.*, 1999), equatorial Pacific (Lea *et al.*, 2000; Lea *et al.*, 2002), and, for five different planktonic species in one core, the tropical Atlantic (Elderfield and Ganssen, 2000). Several other high-resolution records from the tropical Pacific have been published (Koutavas *et al.*, 2002; Stott *et al.*, 2002; Rosenthal *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 °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 re-examination 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 °C (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.

From this vantage point, it appears that Mg/Ca paleothermometry has cracked the problem of glacial cooling of the tropical warm pools (Hastings *et al.*, 1998; Lea *et al.*, 2000), although it must be said that the modest but systematic degree of cooling recorded by Mg/Ca was presaged by earlier results from the alkenone unsaturation technique (Lyle *et al.*, 1992; Bard *et al.*, 1997; Pelejero *et al.*, 1999). But the Mg/Ca results put the ~3 °C level of glacial cooling, relative to modern conditions, on a very firm footing, especially for the western Pacific warm pool (Lea *et al.*, 2000; Stott *et al.*, 2002; Visser *et al.*, 2003; Rosenthal *et al.*, 2003), which is the largest and warmest tropical water mass in the oceans. Results from a core on the Ontong Java Plateau, which lies on the equator in the center of the western Pacific warm pool, span the last 500 kyr and indicate that glacial cooling was systematically ~3 °C cooler than modern conditions and that this cooling occurred during each

P0230

P0235

S0115

P0240

P0245

P0250

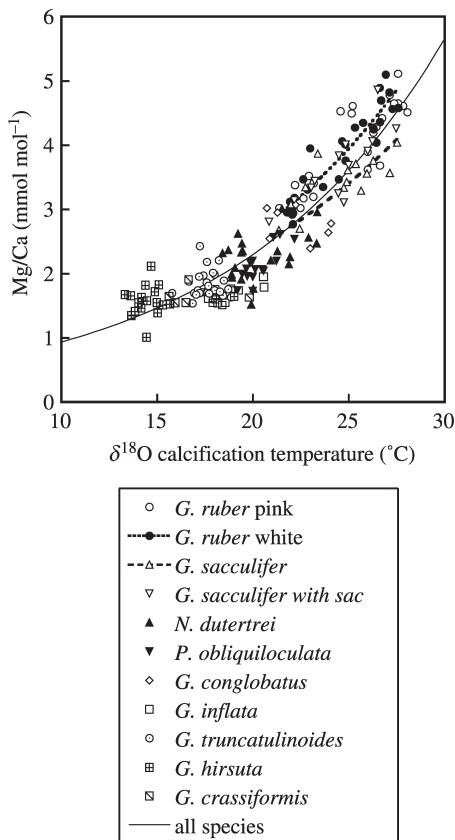


Figure 4 Mg/Ca of different planktonic foraminifera from a Bermuda sediment trap time series, plotted versus calcification temperatures calculated from the oxygen isotopic composition of the shells (Anand *et al.*, 2003). The aggregate fit to all the data in the plot is: $\text{Mg/Ca} = 0.38 \exp(0.09T)$,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

of the last five major glacial episodes (Figure 5). Of great interest is the fact that glacial warming appears to lead ice sheet demise by ~ 3 kyr (Lea *et al.*, 2000). This unanticipated SST lead, which suggests a prominent role for the tropics in pacing ice age cycles, has now also been observed in high-resolution records of the last deglaciation (Stott *et al.*, 2002; Rosenthal *et al.*, 2003).

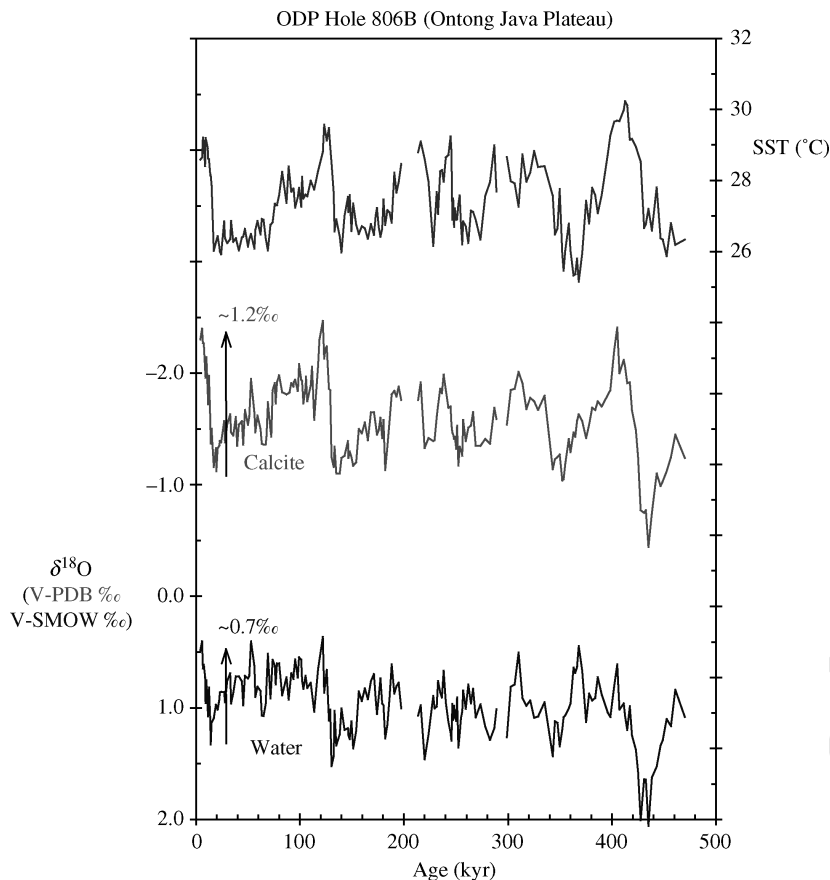
The Mg/Ca approach has also led to a number of other important findings. One of the strengths of this approach is that the recorded paleotemperature is recorded simultaneously with the $\delta^{18}\text{O}$ composition of the shell. Combining these factors using an oxygen-isotope paleotemperature equation yields the $\delta^{18}\text{O}$ -water at the time of shell precipitation. The limited number of studies using this approach already suggests that it is likely to yield important results on shifts in global ice volume as well as regional salinity shifts (Mashiotta *et al.*, 1999; Elderfield and Ganssen, 2000; Lea *et al.*, 2000, 2002; Stott *et al.*, 2002; Rosenthal *et al.*, 2003). A paleosalinity

proxy has always been a difficult prospect, but it appears now that comparison of extracted $\delta^{18}\text{O}$ -water will make it possible to reconstruct patterns of salinity change in the past (Lea, 2002). Such reconstructions will be invaluable in understanding paleoclimate shifts in the tropics.

Another strength of the magnesium paleothermometry is that it can be applied to benthic fauna, including ostracode shells (see Section 6.14.7). There are no other techniques that provide direct estimates of bottomwater temperatures. There is only one published study which contains detailed records of benthic foraminiferal Mg/Ca variations, from the eastern tropical Atlantic and Pacific, in the Quaternary (Martin *et al.*, 2002). These two records indicate the great promise of this approach in elucidating deep-water temperature variations, which appear to have been $\sim 2\text{--}3$ °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. Separating these effects will undoubtedly be a major research area in the future.

6.14.6.6 Results for the Neogene

One of the most exciting prospects for magnesium 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. Two studies already suggest the great potential of this approach (Lear *et al.*, 2000; Billups and Schrag, 2002). The Lear *et al.* (2000) study, which is based on a data set extending back to the Eocene, reveals that benthic Mg/Ca records the gradual ~ 12 °C cooling of bottomwaters that occurred during the Cenozoic and 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 magnesium temperature trends with $\delta^{18}\text{O}$ over the Eocene–Oligocene boundary reveals that the $\delta^{18}\text{O}$ shifts are dominated by global ice volume shifts. There are significant uncertainties, such as species offsets, diagenesis, and changes in seawater Mg/Ca, in extending magnesium paleothermometry to longer time-scales, but there are also great prospects for major discoveries. One can only await with anticipation the revelations yet to come when high-resolution benthic and planktonic Mg/Ca Neogene and Paleogene records are available from a number of sites!



F0025 **Figure 5** Down-core 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 ODP Hole 806B on the Ontong Java Plateau in the western equatorial Pacific (Lea *et al.*, 2000). Glacial marine isotope stages (MIS) are indicated. Note the reduction, from 1.2‰ to 0.7‰, in glacial–interglacial $\delta^{18}\text{O}$ amplitude when the temperature portion of the signal is removed. The fact that the $\delta^{18}\text{O}_{\text{water}}$ amplitude in the WEP is smaller than the oceanic mean change is attributed to a hydrological shift to less saline surface waters during glacial episodes (Lea *et al.*, 2000; Rosenthal *et al.*, 2003; Oppo *et al.*, 2003). Note the lead of Mg/Ca over $\delta^{18}\text{O}$, especially prominent on the MIS 12 to 11 transition.

S0125 6.14.6.7 Summary of Outstanding Research Issues

P0270 Magnesium paleothermometry is in the midst of a period of phenomenal growth, and it has quickly taken its place as one of the most useful means paleoceanographers have at their disposal 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 magnesium 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: (i) establishing the spatial and temporal stability of magnesium temperature calibrations for the important paleoceanographic species; (ii) establishing the extent to which dissolution biases

down-core Mg/Ca records; and (iii) establishing the degree to which benthic magnesium variations record temperature variations in the coldest part of the bottomwater temperature range (<4 °C).

S0130 6.14.7 MAGNESIUM AS PALEOTEMPERATURE PROXIES IN OSTRACODA

P0275 Magnesium paleothermometry applied to ostracode shells has proved to be an important means of discerning past variations in bottomwater temperatures (Dwyer *et al.*, 1995; Cronin *et al.*, 1996, 2000; Corregge and Deckker, 1997). This approach is based on the same principle as magnesium paleothermometry in foraminifera, although ostracode calibrations have been fit with linear calibrations. These calibrations suggest that the increase in Mg/Ca in ostracodes is ~9% per °C, and therefore similar to

the foraminiferal calibrations (see Section 6.14.6.2). The results in Dwyer *et al.* (1995) indicate that ostracode Mg/Ca can be used quite effectively to separate bottomwater 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) saw a lead of temperature over benthic $\delta^{18}\text{O}$ in their Late Quaternary ostracode Mg/Ca record of 3,500 yr. Similarly, a study of magnesium in benthic foraminifera in a tropical Atlantic core saw a lead of $\sim 4,000$ yr in benthic magnesium of temperature over benthic $\delta^{18}\text{O}$ over the last 200 kyr (Martin *et al.*, 2002). These results highlight the importance of independent paleothermometers.

1994; Gagan *et al.*, 1998). Generally these studies have supported the Beck *et al.* (1992) original insights, although two major problems with the Sr/Ca approach have been identified: (i) it appears that growth rate and symbiont activity have a marked influence on coral Sr/Ca (de Villiers *et al.*, 1994; Cohen *et al.*, 2001, 2002) and (ii) there is evidence for a secular shift in seawater Sr/Ca on glacial–interglacial timescales, with generally higher values during glacial episodes (Stoll and Schrag, 1998; Martin *et al.*, 1999; Stoll *et al.*, 1999). Another major step forward in the application of the Sr/Ca paleothermometer 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 data sets required for long, high-resolution climate records (Linsley *et al.*, 2000).

S0135 6.14.8 STRONTIUM AS A CLIMATE PROXY IN CORALS

S0140 6.14.8.1 Background

P0280 The idea of using Sr/Ca in corals as a paleothermometer goes back to the early 1970s, but it is one that that 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 strontium content of both inorganically precipitated and coral aragonite, with a relatively small inverse temperature dependence of just under 1% per °C (Kinsman and Holland, 1969; Weber, 1973; Smith *et al.*, 1979; Lea *et al.*, 1989). The breakthrough study for coral Sr/Ca, led by Warren Beck, then at 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 °C, and with determinations of $\pm 0.03\%$ (2 SD) possible by ID-TIMS, the Beck *et al.* (1992) approach indicated a possible paleotemperature determination of a remarkable ± 0.05 °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 it must be counted among the first strong evidence challenging the CLIMAP (1981) view of relatively unchanged tropical SST during glacial episodes.

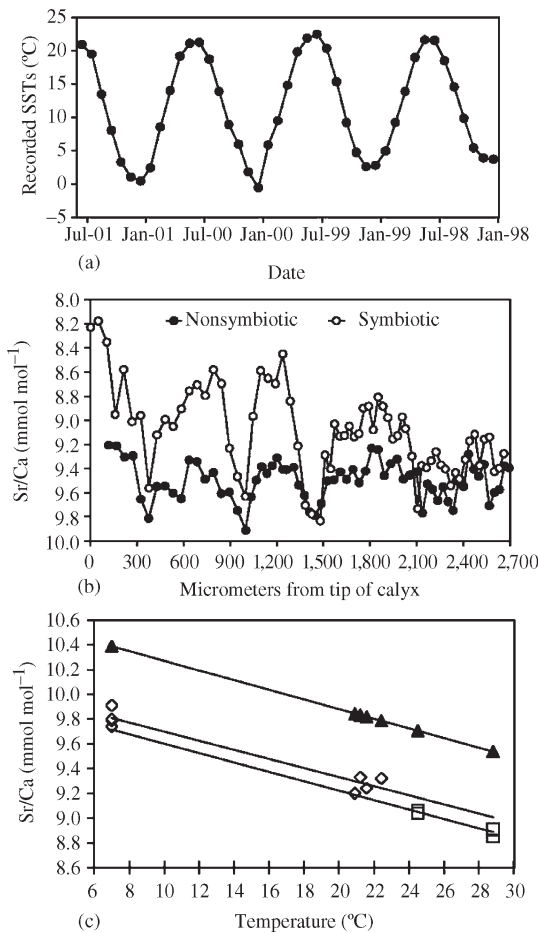
P0285 Following the Beck *et al.* (1992) publication, a number of laboratories undertook more detailed studies of the calibration and also investigated the application of this approach to paleoceanography and paleoclimatology (de Villiers *et al.*, 1994, 1995; Guilderson *et al.*, 1994; McCulloch *et al.*,

6.14.8.2 Paleotemperature Equations

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

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

P0295 The thermodynamic prediction for strontium 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 strontium substitutes for calcium in aragonite. The observed exponential constant for inorganic aragonite precipitation is quite small: -0.45% per °C (Kinsman and Holland, 1969). Therefore, over the small range of coralline strontium 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* (Smith *et al.*, 1979; Beck *et al.*, 1992; de Villiers *et al.*, 1994; Mitsuguchi *et al.*, 1996; Shen, 1996; Gagan *et al.*, 1998; Sinclair *et al.*, 1998; Cohen *et al.*, 2001, 2002). 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 (Figure 6). The variability in the slope is a critical problem for coral strontium paleothermometry, because the cited slopes equate to a variability in temperature dependence of -0.4% per °C to -1.0% per °C. Therefore, a recorded change of Sr/Ca in corals of 1% can imply between a 1 °C and 2.5 °C shift in paleotemperature. Of course, in practice, it is



F0030

Figure 6 Comparison of Sr/Ca records in symbiont-bearing and symbiont barren ahermatypic corals (Cohen *et al.*, 2002). (a) Average monthly SSTs 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 *A. 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 asymbiotic *Astrangia* skeleton ($= -0.036x + 10.065$) is compared with nighttime skeleton of the tropical reef coral *Porites* ($= -0.038x + 9.9806$) and inorganic aragonite precipitated at equilibrium ($= -0.039x + 10.66$). The slope 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 (source Cohen *et al.*, 2002).

possible to narrow this uncertainty by conducting local calibrations (e.g., Corregge *et al.*, 2000).

P0300

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 (de Villiers *et al.*, 1994; Alibert and McCulloch, 1997; Cohen *et al.*, 2001, 2002), and the answer seems to be that growth and environmental factors clearly do affect Sr uptake. The more recent of these studies, 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). 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* (Schrag and Linsley, 2002). However, there is a lot of evidence that coral strontium 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 6.14.8.4 and 6.14.8.5) Figure 6.

6.14.8.3 Secondary Effects and Diagenesis

S0150

P0305

The main secondary effects on Sr/Ca paleothermometry appear to be related to growth rate and symbiosis (see Section 6.14.8.2). 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.

P0310

The effect of diagenesis has not 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 (Enmar *et al.*, 2000; Muller *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.

P0315

As subaerially exposed corals interact with meteoric waters, they are altered to calcite. This alteration results in a loss of strontium 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. A new 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 6.14.4.3). 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.

P0320 A unique secondary complication for Sr/Ca is the potential influence of small changes in seawater Sr/Ca. 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 °C and 5 °C temperature change, depending on the slope of the calibration (see Section 6.14.8.2). 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 might have taken place.

P0325 On geological timescales, there is growing evidence that shifts in seawater Sr/Ca large enough to affect Sr/Ca paleothermometry have taken place. Such shifts were first hypothesized by a 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 strontium 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 of just after sea-level lowstands, which, depending on which calibration is used, would result in a -1 °C to -5 °C bias in Sr/Ca paleothermometry.

P0330 Subsequently, Pamela Martin (UCSB) and co-workers demonstrated that systematic glacial–interglacial variations in foraminiferal Sr/Ca similar to and even somewhat larger than those predicted by the Stoll and Schrag (1998) study are indeed preserved in deep-sea records (Martin *et al.*, 1999). Several studies have confirmed this observation (Stoll *et al.*, 1999; Elderfield *et al.*, 2000; Shen *et al.*, 2001). These studies indicate foraminifer 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 $\sim 3\%$ (Martin *et al.*, 1999). Comparison of this stacked benthic record with coral Sr/Ca values 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 tropical SST drops 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.

6.14.8.4 Results on Historical Timescales

S0155
P0335 A few long time series of Sr/Ca have been published, from Rorotonga and the Great Barrier Reef (GBR) in the South Pacific (Linsley *et al.*, 2000; Hendy *et al.*, 2002). These records show clear interannual variability as well as distinct secular trends. For example, the GBR (Hendy *et al.*, 2002) records, 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 towards more negative $\delta^{18}\text{O}$ observed in many large corals (see Section 6.14.4.4). Combining the metal paleotemperature records with the $\delta^{18}\text{O}$ record yields a residual $\delta^{18}\text{O}$ -water record that suggests that GBR waters have become progressively less salty since the mid-nineteenth century. Results from the Rorotonga 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 Rorotonga 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 NH (Hendy *et al.*, 2002).

6.14.8.5 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 Vanuatu region of the South Pacific during the latest Younger Dryas/earliest Holocene. Although the degree of cooling has not been supported by other data, presumably because of a secular increase in seawater Sr/Ca (Stoll and Schrag, 1998; Martin *et al.*, 1999; Lea *et al.*, 2000), the Beck *et al.* (1992) result was one of 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 glacial estimates of 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 snowlines during the last glacial maximum are compatible with tropical SST drops of ~3 °C (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, 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 inter annual climate change such as ENSO without requiring conversion into absolute SSTs (Hughen *et al.*, 1999; Corregge *et al.*, 2000). The Hughen *et al.* (1999) results 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 highstand, 124 ka.

6.14.8.6 Summary of Outstanding Research Issues

During the 1990s, 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 how the coral Sr/Ca temperature calibration is in both space and time. The most critical 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 material 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, the question of secular change in seawater Sr/Ca as well as diagenetic influence 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 to eventually generate definite secular records of seawater Sr/Ca that can be suitably applied to coral Sr/Ca paleothermometry.

6.14.9 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 (Mitsuguchi *et al.*, 1996; Sinclair *et al.*, 1998; Fallon *et al.*, 1999) 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 magnesium 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 (Sinclair *et al.*, 1998; Fallon *et al.*, 1999). The fact that at least 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.

S0175 **6.14.10 CALCIUM ISOTOPES AS A
PALEOTEMPERATURE PROXY**

P0370 The possibility of using calcium isotopes for paleothermometry is a very 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 calcium-isotopic variations are quite challenging (Russell *et al.*, 1978), and this has limited investigations of this isotopic system to relatively small data sets. This potential paleothermometer has been calibrated in neritic benthic foraminifera (De La Rocha and DePaolo, 2000), a spinose tropical planktonic foraminifera (Nägler *et al.*, 2000), and a subtropical planktonic foraminifera (Gussone *et al.*, 2003). In addition, Zhu and Macdougall (1998) compared three pairs of warm and cold foraminifera and demonstrated a systemic difference. The most convincing evidence of the potential utility of this new paleothermometer comes from the study of Nägler *et al.* (2000), which demonstrates an increase of 0.24‰ in shell $\delta^{44}\text{Ca}$ per °C, based on three cultured points of *G. sacculifer*. Down-core measurements from a core in the tropical Atlantic indicate that shells from glacial intervals are ~0.5–1.0‰ depleted in $\delta^{44}\text{Ca}$, consistent with colder glacial temperatures. Although the results in Nägler *et al.* (2000) indicate that calcium isotope paleothermometry has great promise, they are somewhat confounded by the fact a new study shows a much weaker response of $\delta^{44}\text{Ca}$ to temperature (~0.02‰ per °C) 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). Given a measurement precision of ~0.12‰ for replicate samples (Gussone *et al.*, 2003), the slope for *G. sacculifer* allows for a resolution of ~0.5 °C in paleothermometry, whereas the slope for *O. universa* allows for a resolution of only ~5 °C. Obviously, the utility of this approach will rely heavily on which slope is more generally representative, and if that slope is stable in space and time.

S0180 **6.14.11 CONCLUSIONS**

P0375 Geochemists have, since the 1950s, already come up with a remarkable array of paleo-temperature 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 most remarkable is the amount of progress that has been made since the mid-1980s on three new or revived paleothermometric approaches, each of which work 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 6.15), has not only expanded the importance of geochemistry in paleoclimate research, but changed its focus from mainly a 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, for example, the general level of agreement between geochemical paleothermometers for such fundamental problems as the cooling of the glacial tropics, suggests that major breakthroughs to 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 research progress has elevated geochemical paleothermometers to an even more fundamental role in quantitative paleoclimate research.

ACKNOWLEDGMENTS

The author thanks A. Cohen for sharing her compilation of coral strontium calibrations, and J. Cole, J. Clark, D. Schrag, and H. Spero for discussions. Some of this material is based upon work supported by the US National Science Foundation, more recently under grant OCE-0117886.

REFERENCES

- Alibert C. and McCulloch M. T. (1997) Strontium/calcium ratios in modern porites corals from the Great Barrier Reef as a proxy for sea surface temperature: calibration of the thermometer and monitoring of ENSO. *Paleoceanography* **12**(3), 345–363.
- Anand P., Elderfield H., and Conte M. H. (2003) Calibration of Mg/Ca thermometry in planktonic foraminifera from a sediment trap time series. *Paleoceanography* **18**(2), 1050, doi: 10.1029/2002PA000846.
- Andrus C. F. T., Crowe D. E., Sandweiss D. H., Reitz E. J., and Romanek C. S. (2002) Otolith $\delta^{18}\text{O}$ record of Mid-Holocene sea surface temperatures in Peru. *Science* **295**(5559), 1508–1511.
- Bard E., Hamelin B., Arnold M., Montaggioni L., Cabioch G., Faure G., and Rougerie F. (1996) Deglacial sea-level record from Tahiti corals and the timing of global meltwater discharge. *Nature* **382**, 241–244.
- Bard E., Rostek F., and Sonzogni C. (1997) Interhemispheric synchrony of the last deglaciation inferred from alkenone palaeothermometry. *Nature* **385**, 707–710.

P0380

Q3

S0185

- Barron E. J. (1987) Eocene equator-to-pole surface ocean temperatures: a significant climate problem? *Paleoceanography* **2**, 729–739.
- Bé A. W. H. (1980) Gametogenic calcification in a spinose planktonic foraminifer, *Globigerinoides sacculifer* (Brady). *Mar. Micropaleontol.* **5**, 283–310.
- Beck J. W., Edwards R. L., Ito E., Taylor F. W., Recy J., Rougerie F., Joannot P., and Henin C. (1992) Sea-surface temperature from coral skeletal strontium/calcium ratios. *Science* **257**(5070), 644–647.
- Beck J. W., Recy J., Taylor F. W., Edwards R. L., and Cabloh G. (1997) Abrupt changes in early Holocene Tropical sea surface temperature derived from coral records. *Nature* **385**(20 February 1997), 705–707.
- Bemis B. E., Spero H. J., Bijma J., and Lea D. W. (1998) Reevaluation of the oxygen isotopic composition of planktonic foraminifera: experimental results and revised paleotemperature equations. *Paleoceanography* **13**(2), 150–160.
- Bender M. L., Lorens R. B., and Williams D. F. (1975) Sodium, magnesium, and strontium in the tests of planktonic foraminifera. *Micropaleontology* **21**, 448–459.
- Billups K. and Schrag D. P. (2002) Paleotemperatures and ice volume of the past 27 Myr revisited with paired Mg/Ca and $^{18}\text{O}/^{16}\text{O}$ measurements on benthic foraminifera. *Paleoceanography* 10.1029/2000PA000567.
- Böhm F., Joachimski M. M., Dullo W. C., Eisenhauer A., Lehnert H., Reitner J., and Wörheide G. (2000) Oxygen isotope fractionation in marine aragonite of coralline sponges. *Geochim. Cosmochim. Acta* **64**(10), 1695–1703.
- Brass G. W. and Turekian K. K. (1974) Strontium distribution in GEOSECS oceanic profiles. *Earth Planet. Sci. Lett.* **23**, 141–148.
- Brown S. and Elderfield H. (1996) Variations in Mg/Ca and Sr/Ca ratios of planktonic foraminifera caused by postdepositional dissolution—evidence of shallow Mg-dependent dissolution. *Paleoceanography* **11**(5), 543–551.
- Burton E. A. and Walter L. M. (1987) Relative precipitation rates of aragonite and Mg calcite from seawater: temperature or carbonate ion control? *Geology* **15**, 111–114.
- Cane M. A. and Evans M. (2000) Do the tropics rule? *Science* **290**, 1107–1108.
- Caron D. A., Anderson O. R., Lindsey J. L., Faber J. W. W., and Lin Lim E. (1990) Effects of gametogenesis on test structure and dissolution of some spinose planktonic foraminifera and implications for test preservation. *Mar. Micropaleontol.* **16**, 93–116.
- Chappell J. and Shackleton N. J. (1986) Oxygen isotopes and sea level. *Nature* **324**, 137–140.
- Chave K. E. (1954) Aspects of the biogeochemistry of magnesium: I. Calcareous marine organisms. *J. Geol.* **62**, 266–283.
- Chilingar G. V. (1962) Dependence on temperature of Ca/Mg ratio of skeletal structures of organisms and direct chemical precipitates out of sea water. *Bull. Soc. CA Acad. Sci.* **61**(part 1), 45–61.
- Clarke F. W. and Wheeler W. C. (1922) The inorganic constituents of marine invertebrates. *USGS Prof. Pap.* **124**, 55.
- CLIMAP. (1981) Seasonal reconstructions of the Earth's surface at the last glacial maximum. In *The Geological Society of America Map and Chart Series MC-36*.
- Cobb K. M., Charles C. D., and Hunter D. E. (2001) A central tropical Pacific coral demonstrates Pacific, Indian, and Atlantic decadal climate connections. *Geophys. Res. Lett.* **V28**(N11), 2209–2212.
- Cohen A., Layne G., Hart S., and Lobel P. (2001) Kinetic control of skeletal Sr/Ca in a symbiotic coral: implications for the paleotemperature proxy. *Paleoceanography* **V16**(N1), 20–26.
- Cohen A. L., Owens K. E., Layne G. D., and Shimizu N. (2002) The effect of algal symbionts on the accuracy of Sr/Ca paleotemperatures from coral. *Science* **296**(5566), 331–333.
- Cole J. E. and Fairbanks R. G. (1990) The southern oscillation recorded in the $\delta^{18}\text{O}$ of corals from Tarawa Atoll. *Paleoceanography* **5**(5), 669–683.
- Cole J. E., Dunbar R. B., McClanahan T. R., and Muthiga N. A. (2000) Tropical Pacific forcing of decadal SST variability in the western Indian Ocean over the past two centuries. *Science* **287**, 617–619.
- Correge T. and Deckker P. D. (1997) Faunal and geochemical evidence for changes in intermediate water temperature and salinity in the western Coral Sea (northeast Australia) during the late quaternary. *Palaeogeogr. Palaeoclimat. Palaeoecol.* **313**, 183–205.
- Correge T., Delcroix T., Recy J., Beck W., Cabioch G., and Le Cornec F. (2000) Evidence for stronger El Niño-southern oscillation (ENSO) events in a Mid-Holocene massive coral. *Paleoceanography* **15**(4), 465–470.
- Cronblad H. G. and Malmgren B. A. (1981) Climatically controlled variation of Sr and Mg in quaternary planktonic foraminifera. *Nature* **291**, 61–64.
- Cronin T. M., Raymo M. E., and Kyle K. P. (1996) Pliocene (3.2–2.4 Ma) ostracode faunal cycles and deep ocean circulation, North Atlantic Ocean. *Geology* **24**(8), 695–698.
- Cronin T. M., Dwyer G. S., Baker P. A., Rodriguez-Lazaro J., and DeMartino D. M. (2000) Orbital and suborbital variability in North Atlantic bottom water temperature obtained from deep-sea ostracod Mg/Ca ratios. *Palaeogeogr. Palaeoclimat.* **162**(1–2), 45–57.
- Crowley T. J. (2000a) Causes of climate change over the past 1000 years. *Science* **289**(5477), 270–277.
- Crowley T. J. (2000b) CLIMAP SSTs re-visited. *Clim. Dyn.* **16**(4), 241–255.
- De La Rocha C. L. and DePaolo D. J. (2000) Isotopic evidence for variations in the marine calcium cycle over the Cenozoic. *Science* **289**(5482), 1176–1178.
- de Villiers S., Shen G. T., and Nelson B. K. (1994) The Sr/Ca-temperature relationship in coralline aragonite: influence of variability in $(\text{Sr}/\text{Ca})_{\text{seawater}}$ and skeletal growth parameters. *Geochim. Cosmochim. Acta* **58**(1), 197–208.
- de Villiers S., Nelson B. K., and Chivas A. R. (1995) Biological controls on coral Sr/Ca and $\delta^{18}\text{O}$ reconstructions of sea surface temperatures. *Science* **269**, 1247–1249.
- Dekens P. S., Lea D. W., Pak D. K., and Spero H. J. (2002) Core top calibration of Mg/Ca in tropical foraminifera: refining paleo-temperature estimation. *Geochem. Geophys. Geosys.* **3**, 1022, 10.1029/2001GC000200.
- Delaney M. L., Bé A. W. H., and Boyle E. A. (1985) Li, Sr, Mg, and Na in foraminiferal calcite shells from laboratory culture, sediment traps, and sediment cores. *Geochim. Cosmochim. Acta* **49**, 1327–1341.
- Druffel E. R. M. (1985) Detection of El Niño and decade timescale variations of sea surface temperature from banded coral records: implications for the carbon dioxide cycle. In *The Carbon Cycle and Atmospheric CO₂: Natural Variations Archean to Present*. American Geophysical Union, Washington, DC, pp. 111–122.
- Dunbar R. B. and Wellington G. M. (1985) Stable isotopes in a branching coral monitor seasonal temperature variation. *Nature* **293**, 453–455.
- Duplessy J.-C. and Blanc P.-L. (1981) Oxygen-18 enrichment of planktonic foraminifera due to gametogenic calcification below the euphotic zone. *Science* **213**, 1247–1250.
- Duplessy J. C., Lalou C., and Vinot A. C. (1970) Differential isotopic fractionation in benthic foraminifera and paleotemperatures reassessed. *Science* **168**, 250–251.
- Dwyer G. S., Cronin T. M., Baker P. A., Raymo M. E., Buzas J. S., and Correge T. (1995) North Atlantic deepwater temperature change during late pliocene and late quaternary climatic cycles. *Science* **270**, 1347–1351.
- Elderfield H. and Ganssen G. (2000) Past temperature and $\delta^{18}\text{O}$ of surface ocean waters inferred from foraminiferal Mg/Ca ratios. *Nature* **405**, 442–445.
- Elderfield H., Bertram C., and Erez J. (1996) Biomineralization model for the incorporation of trace elements into

- foraminiferal calcium carbonate. *Earth Planet. Sci. Lett.* **142**(3–4), 409–423.
- Elderfield H., Cooper M., and Ganssen G. (2000) Sr/Ca in multiple species of planktonic foraminifera: implications for reconstructions of seawater Sr/Ca. *Geochem. Geophys. Geosys.* **1**, paper no. 1999GC00031.
- Emiliani C. (1955) Pleistocene temperatures. *J. Geol.* **63**, 538–578.
- Emiliani C., Hudson J., Shinn E., and George R. (1978) Oxygen and carbon isotopic growth record in a reef coral from the Florida keys and a deep-sea coral from Blake Plateau. *Science* **202**, 627–628.
- Enmar R., Stein M., Bar-Matthews M., Sass E., Katz A., and Lazar B. (2000) Diagenesis in live corals from the Gulf of Aqaba: I. The effect on paleo-oceanography tracers. *Geochim. Cosmochim. Acta* **64**(18), 3123–3132.
- Epstein S., Buchsbaum R., Lowenstam H. A., and Urey H. C. (1953) Revised carbonate-water isotopic temperature scale. *Geol. Soc. Am. Bull.* **64**, 1315–1325.
- Erez J. and Luz B. (1983) Experimental paleotemperature equation for planktonic foraminifera. *Geochim. Cosmochim. Acta* **47**, 1025–1031.
- Fairbanks R. G. (1989) A 17,000-year glacio-eustatic sea level record: influence of glacial melting rates on the Younger Dryas event and deep-ocean circulation. *Nature* **342**, 637–642.
- Fairbanks R. G. and Dodge R. E. (1979) Annual periodicities in $^{16}\text{O}/^{18}\text{O}$ and $^{13}\text{C}/^{12}\text{C}$ ratios in the coral *Montrastrea annularis*. *Geochim. Cosmochim. Acta* **43**, 1009–1020.
- Fairbanks R. G. and Matthews R. K. (1978) The marine oxygen isotope record in Pleistocene coral, Barbados, West Indies. *Quat. Res.* **10**, 181–196.
- Fallon S. J., McCulloch M. T., Woesik R. v., and Sinclair D. J. (1999) Corals at their latitudinal limits: laser ablation trace element systematics in *Porites* from Shirigai Bay, Japan. *Earth Planet. Sci. Lett.* **172**, 221–238.
- Farrell J. W. and Prell W. L. (1989) Climatic change and CaCO_3 preservation: an 800,000 year bathymetric reconstruction from the central equatorial Pacific ocean. *Paleoceanography* **4**(4), 447–466.
- Gagan M. K., Ayliffe L. K., Hopley D., Cali J. A., Mortimer G. E., Chappell J., McCulloch M. T., and Head M. J. (1998) Temperature and surface-ocean water balance of the Mid-Holocene tropical western Pacific. *Science* **279**(13 February 1998), 1014–1018.
- Gagan M. K., Ayliffe L. K., Beck J. W., Cole J. E., Druffel E. R. M., Dunbar R. B., and Schrag D. P. (2000) New views of tropical paleoclimates from corals. *Quat. Sci. Rev.* **19**(1–5), 45–64.
- Grossman E., Betzer P. R., Walter C. D., and Dunbar R. B. (1986) Stable isotopic variation in pteropods and atlantids from North Pacific sediment traps. *Mar. Micropaleontol.* **10**, 9–22.
- Guilderson T. P., Fairbanks R. G., and Rubenstone J. L. (1994) Tropical temperature variations since 20,000 years ago: modulating interhemispheric climate changes. *Science* **263**, 663–665.
- Guilderson T., Fairbanks R., and Rubenstone J. (2001) Tropical Atlantic coral oxygen isotopes: glacial-interglacial sea surface temperatures and climate change. *Mar. Geol.* **172**(N1–2), 75–89.
- Gussone N., Eisenhauer A., Heuser A., Dietzel M., Bock B., Böhm F., Spero H. J., Lea D. W., Bijma J., and Nägler T. F. (2003) Model for kinetic effects on calcium isotope fractionation ($\delta^{44}\text{Ca}$) in inorganic aragonite and cultured planktonic foraminifera. *Geochim. Cosmochim. Acta* **67**(7), 1375–1382.
- Gussone N., Eisenhauer A., Heuser A., Dietzel M., Bock B., Böhm F., Spero H., Lea D. W., Bijma J., Zeebe R., and Nägler T. F. (2003) Model for kinetic effects on calcium isotope fractionation ($\delta^{44}\text{Ca}$) in inorganic aragonite and cultured planktonic foraminifera. *Geochim. Cosmochim. Acta* **67**(7), 1375–1382.
- Hastings D. W., Emerson S. R., and Nelson B. K. (1996) Vanadium in foraminifera calcite: evaluation of a method to determine paleo-seawater concentrations. *Geochim. Cosmochim. Acta* **60**(19), 3701–3715.
- Hastings D. W., Russell A. D., and Emerson S. R. (1998) Foraminiferal magnesium in *Globeriginoidea sacculiferas* a paleotemperature proxy. *Paleoceanography* **13**(2), 161–169.
- Hays J. D., Imbrie J., and Shackleton N. J. (1976) Variations in the earth's orbit: pacemaker of the Ice ages. *Science* **194**, 1121–1132.
- Hecht A. D., Eslinger E. V., and Garmon L. B. (1975) Experimental studies on the dissolution of planktonic foraminifera. In *Dissolution of Deep-sea Carbonates* (eds. W. V. Sitter, A. W. H. Bé and W. H. Berger). Cushman Foundation for Foraminiferal Research, pp. 59–69.
- Hendy E. J., Gagan M. K., Alibert C. A., McCulloch M. T., Lough J. M., and Isdale P. J. (2002) Abrupt decrease in tropical Pacific Sea surface salinity at end of little Ice age. *Science* **295**(5559), 1511–1514.
- Hughen K. A., Schrag D. P., Jacobsen S. B., and Hantoro W. (1999) El Niño during the last interglacial period recorded by a fossil coral from Indonesia. *Geophys. Res. Lett.* **26**(20), 3129–3132.
- Imbrie J. and Kipp N. G. (1971) A new micropaleontological method quantitative paleoclimatology: application to a late pleistocene Caribbean core. In *The Late Cenozoic Ice Ages* (ed. K. Turekian). Yale University Press, New Haven and London, pp. 71–181.
- Imbrie J., Boyle E. A., Clemens S. C., Duffy A., Howard W. R., Kukla G., Kutzbach J., Martinson D. G., McIntyre A., Mix A. C., Molfino B., Morley J. J., Peterson L. C., Pisias N. G., Prell W. L., Raymo M. E., Shackleton N. J., and Toggweiler J. R. (1992) On the structure and origin of major glaciation cycles: 1. Linear responses to Milankovitch forcing. *Paleoceanography* **7**(6), 701–738.
- Izuka S. K. (1988) Relationships of magnesium and other minor elements in tests of *Cassidulina Subglobosa* and *C. Oriangulata* to physical oceanic properties. *J. Foraminiferal. Res.* **18**(2), 151–157.
- Juillet-Leclerc A. D. and Labeyrie L. D. (1986) Temperature dependence of the oxygen isotopic fractionation between diatom silica and water. *Earth Planet. Sci. Lett.* **84**, 69–74.
- Katz A. (1973) The interaction of magnesium with calcite during crystal growth at 25–90 °C and one atmosphere. *Geochim. Cosmochim. Acta* **37**, 1563–1586.
- Kim S.-T. and O'Neil J. R. (1997) Equilibrium and nonequilibrium oxygen isotope effects in synthetic calcites. *Geochim. Cosmochim. Acta* **61**(16), 3461–3475.
- Kinsman D. J. J. and Holland H. D. (1969) The co-precipitation of cations with CaCO_3 : IV. The co-precipitation of Sr^{2+} with aragonite between 16° and 96 °C. *Geochim. Cosmochim. Acta* **33**, 1–17.
- Koutavas A., Lynch-Stieglitz J., Marchitto T. M. J., and Sachs J. P. (2002) Deglacial and Holocene climate record from the Galapagos islands: El Niño linked to Ice age climate. *Science* **297**(5579), 226–230.
- Koziol A. M. and Newton R. C. (1995) Experimental determination of the reactions magnesite + quartz = enstatite + CO_2 and magnesite = periclase + CO_2 and the enthalpies of formation of enstatite and magnesite. *Am. Mineral.* **80**, 1252–1260.
- Labeyrie L. D. and Juillet A. (1982) Oxygen isotopic exchangeability of diatom valve silica: interpretation and consequences for paleoclimatic studies. *Geochim. Cosmochim. Acta* **46**, 967–975.
- Lea D. W. (2002) The glacial tropical Pacific: not just a west side story. *Science* **297**, 202–203.
- Lea D. W., Shen G. T., and Boyle E. A. (1989) Coralline barium records temporal variability in equatorial Pacific upwelling. *Nature* **340**, 373–376.
- Lea D. W., Mashiotto T. A., and Spero H. J. (1999) Controls on magnesium and strontium uptake in planktonic foraminifera

- determined by live culturing. *Geochim. Cosmochim. Acta* **63**(16), 2369–2379.
- Lea D. W., Pak D. K., and Spero H. J. (2000) Climate impact of late quaternary equatorial Pacific sea surface temperature variations. *Science* **289**(5486), 1719–1724.
- Lea D. W., Martin P. A., Pak D. K., and Spero H. J. (2002) Reconstructing a 350 ky history of sea level using planktonic Mg/Ca and oxygen isotopic records from a Cocos ridge core. *Quat. Sci. Rev.* **21**(1–3), 283–293.
- Lear C. H., Elderfield H., and Wilson P. A. (2000) Cenozoic deep-sea temperatures and global ice volumes from Mg/Ca in benthic foraminiferal calcite. *Science* **287**, 269–272.
- Linsley B. K., Wellington G. M., and Schrag D. P. (2000) Decadal sea surface temperature variability in the subtropical South Pacific from 1726 to 1997 AD. *Science* **290**, 1145–1148.
- Lohmann G. P. (1995) A model for variation in the chemistry of planktonic foraminifera due to secondary calcification and selective dissolution. *Paleoceanography* **10**(3), 445–457.
- Lorens R. B., Williams D. F., and Bender M. L. (1977) The early nonstructural chemical diagenesis of foraminiferal calcite. *J. Sed. Petrol.* **47**(4), 1602–1609.
- Lyle M. W., Prahl F. G., and Sparrow M. A. (1992) Upwelling and productivity changes inferred from a temperature record in the central equatorial Pacific. *Nature* **355**, 812–815.
- Mann M. E., Bradley R. S., and Hughes M. K. (1998) Global-scale temperature patterns and climate forcing over the past six centuries. *Nature* **392**(23), 779–787.
- Mantua N. J., Hare S. R., Zhang Y., Wallace J. M., and Francis R. C. (1997) A Pacific interdecadal climate oscillation with impacts on salmon production. *Bull. Am. Meteorol. Soc.* **78**(6), 1069–1079.
- Martin P. A., Lea D. W., Mashiota T. A., Papenfuss T., and Sarnthein M. (1999) Variation of foraminiferal Sr/Ca over quaternary glacial-interglacial cycles: evidence for changes in mean ocean Sr/Ca? *Geochim. Geophys. Geosys.* **1** Paper Number 1999GC000006.
- Martin P. A., Lea D. W., Rosenthal Y., Shackleton N. J., Sarnthein M., and Papenfuss T. (2002) Quaternary deep sea temperature histories derived from benthic foraminiferal Mg/Ca. *Earth Planet. Sci. Lett.* **198**, 193–209.
- Mashiota T. A., Lea D. W., and Spero H. J. (1999) Glacial-interglacial changes in Subantarctic sea surface temperature and $\delta^{18}\text{O}$ -water using foraminiferal Mg. *Earth Planet. Sci. Lett.* **170**(4), 417–432.
- McConnaughey T. (1989a) ^{13}C and ^{18}O isotopic disequilibrium in biological carbonates: I. Patterns. *Geochim. Cosmochim. Acta* **53**(1), 151–162.
- McConnaughey T. A. (1989b) ^{13}C and ^{18}O isotopic disequilibrium in biological carbonates: II. *In vitro* simulation of kinetic isotopic effects. *Geochim. Cosmochim. Acta* **53**, 163–171.
- McCorkle D. C., Martin P. A., Lea D. W., and Klinkhammer G. P. (1995) Evidence of a dissolution effect on benthic shell chemistry: $\delta^{13}\text{C}$, Cd/Ca, Ba/Ca, and Sr/Ca from the Ontong Java Plateau. *Paleoceanography* **10**(4), 699–714.
- McCulloch M. T., Gagan M. K., Mortimer G. E., Chivas A. R., and Isdale P. J. (1994) A high-resolution Sr/Ca and $\delta^{18}\text{O}$ coral record from the Great Barrier Reef, Australia, and the 1982–1983 El Niño. *Geochim. Cosmochim. Acta* **58**(12), 2747–2754.
- McCulloch M., Mortimer G., Esat T., Xianhua L., Pillans B., and Chappell J. (1996) High resolution windows into early Holocene climate: Sr/Ca coral records from the Huon Peninsula. *Earth Planet. Sci. Lett.* **138**, 169–178.
- McCulloch M. T., Tudhope A. W., Esat T. M., Mortimer G. E., Chappell J., Pillans B., Chivas A. R., and Omura A. (1999) Coral record of equatorial sea-surface temperatures during the penultimate deglaciation at Huon Peninsula. *Science* **283**, 202–204.
- McGregor H. V. and Gagan M. K. (2003) Diagenesis and geochemistry of Porites corals from Papua New Guinea: implications for paleoclimate reconstruction. *Geochim. Cosmochim. Acta* (in review).
- Min G., Edwards R., Taylor F., Gallup C., and Beck J. (1995) Annual cycles of U/Ca in coral skeletons and U/Ca thermometry. *Geochim. Cosmochim. Acta* **59**(10), 2025–2042.
- Mitsuguchi T., Matsumoto E., Abe O., Uchida T., and Isdale P. J. (1996) Mg/Ca thermometry in coral skeletons. *Science* **274**, 961–963.
- Mix A. C. (1992) The marine oxygen isotope record: constraints on timing and extent of ice-growth events (120–65 ka). In *The Last Interglacial Transition in North America* Geological Society of America Special Paper (eds. P. U. Clark and P. D. Lea). GSA, Boulder, Co. vol. 270, pp. 19–30.
- Mix A. C., Morey A. E., Pisias N. G., and Hostetler S. W. (1999) Foraminiferal faunal estimates of paleotemperature: circumventing the no-analog problem yields cool ice age tropics. *Paleoceanography* **14**(3), 350–359.
- Mucci A. (1987) Influence of temperature on the composition of magnesium calcite overgrowths precipitated from seawater. *Geochim. Cosmochim. Acta* **51**, 1977–1984.
- Müller P. J., Kirst G., Ruhland G., von Storch I., and Rosell-Melé A. (1998) Calibration of the alkenone paleotemperature index UK'37 based on core-tops from the eastern South Atlantic and the global ocean (60°N–60°S). *Geochim. Cosmochim. Acta* **62**(10), 1757–1772.
- Müller A., Gagan M. K., and McCulloch M. T. (2001) Early marine diagenesis in corals and geochemical consequences for paleoceanographic reconstructions. *Geophys. Res. Lett.* **28**(23), 4471–4474.
- Nägler T. F., Eisenhauer A., Müller A., Hemleben C., and Kramers J. (2000) The $\delta^{44}\text{Ca}$ -temperature calibration on fossil and cultured *Globigerinoides sacculifer*: new tool for reconstruction of past sea surface temperatures. *Geochim. Geophys. Geosys.* **1** (Paper number: 2000GC000091).
- Nürnberg D. (1995) Magnesium in tests of *Neogloboquadrina pachyderma* sinistral from high Northern and Southern latitudes. *J. Foraminiferal. Res.* **25**(4), 350–368.
- Nürnberg D., Bijma J., and Hemleben C. (1996a) Assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperatures. *Geochim. Cosmochim. Acta* **60**(5), 803–814.
- Nürnberg D., Bijma J., and Hemleben C. (1996b) Erratum: assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperatures. *Geochim. Cosmochim. Acta* **60**(13), 2483–2484.
- Nürnberg D., Müller A., and Schneider R. R. (2000) Paleo-sea surface temperature calculations in the equatorial east Atlantic from Mg/Ca ratios in planktic foraminifera: a comparison to sea surface temperature estimates from UK'37, oxygen isotopes, and foraminiferal transfer function. *Paleoceanography* **15**(1), 124–134.
- O'Neil J. R., Clayton R. N., and Mayeda T. K. (1969) Oxygen isotope fractionation in divalent metal carbonates. *J. Chem. Phys.* **51**(12), 5547–5558.
- Oomori T., Kaneshima H., and Maezato Y. (1987) Distribution coefficient of Mg^{2+} ions between calcite and solution at 10–50 °C. *Mar. Chem.* **20**, 327–336.
- Oppo D. W., Linsley B. K., Rosenthal Y., Dannenmann S., and Beaufort L. (2003) Orbital and suborbital climate variability in the Sulu Sea, western tropical Pacific. *Geochim. Geophys. Geosys.* **4**(1), 1003, doi: 10.1029/2001GC000260.
- Pearson P. N., Ditchfield P. W., Singano J., Harcourt-Brown K. G., Nicholas C. J., Olsson R. K., Shackleton N. J., and Hall M. A. (2001) Warm tropical sea surface temperatures in the late Cretaceous and Eocene epochs. *Nature* **413**, 481–487.
- Pelejero C. and Calvo E. (2003) The upper end of the U_{37}^{K} temperature calibration revisited. *Geochim. Geophys. Geosys.* **4**, 1014, doi:10.1029/2002GC000431.
- Pelejero C., Grimalt J. O., Heilig S., Kienast M., and Wang L. (1999) High resolution U_{37}^{K} temperature reconstructions in

- the South China Sea over the past 220 kyr. *Paleoceanography* **14**(2), 224–231.
- Pierrehumbert R. (1999) Huascarán delta O-18 as an indicator of tropical climate during the last glacial maximum. *Geophys. Res. Lett.* **26**(9), 1345–1348.
- Rathburn A. E. and Deckker P. D. (1997) Magnesium and strontium compositions of recent benthic foraminifera from the Coral Sea, Australia and Prydz Bay, Antarctica. *Mar. Micropaleontol.* **32**, 231–248.
- Rickaby R. E. M. and Elderfield H. (1999) Planktonic foraminiferal Cd/Ca: paleonutrients or paleotemperature? *Paleoceanography* **14**(3), 293–303.
- Rodbell D. T., Seltzer G. O., Anderson D. M., Abbot M. B., Enfield D. B., and Newman J. H. (1999) An ~15,000-year record of El Niño-driven alluviation in southwestern Ecuador. *Science* **283**, 516–520.
- Rosenthal Y. and Boyle E. A. (1993) Factors controlling the fluoride content of planktonic foraminifera: an evaluation of its paleoceanographic utility. *Geochim. Cosmochim. Acta* **57**(2), 335–346.
- Rosenthal Y. and Lohmann G. P. (2002) Accurate estimation of sea surface temperatures using dissolution corrected calibrations for Mg/Ca paleothermometry. *Paleoceanography* **17**, 1044. doi:10.1029/2001PA000749.
- Rosenthal Y., Boyle E. A., and Slowey N. (1997) Temperature control on the incorporation of Mg, Sr, F and Cd into benthic foraminiferal shells from Little Bahama Bank: prospects for thermocline paleoceanography. *Geochim. Cosmochim. Acta* **61**(17), 3633–3643.
- Rosenthal Y., Lohmann G. P., Lohmann K. C., and Sherrell R. M. (2000) Incorporation and preservation of Mg in *Globigerinoides sacculifer* implications for reconstructing the temperature and $^{18}\text{O}/^{16}\text{O}$ of seawater. *Paleoceanography* **15**(1), 135–145.
- Rosenthal Y., Dannenmann S., Oppo D. W., and Linsley B. K. (2003) The amplitude and phasing of climate change during the last deglaciation in the Sulu Sea, western equatorial Pacific. *Geophys. Res. Lett.* **30**(8), 1428. doi:10.1029/2002GL016612.
- Rostek F., Ruhland G., Bassinot F. C., Müller P. J., Labeyrie L. D., Lancelot Y., and Bard E. (1993) Reconstructing sea surface temperature and salinity using $\delta^{18}\text{O}$ and alkenone records. *Nature* **364**, 319–321.
- Russell A. D., Emerson S., Nelson B. K., Erez J., and Lea D. W. (1994) Uranium in foraminiferal calcite as a recorder of seawater uranium concentrations. *Geochim. Cosmochim. Acta* **58**(2), 671–681.
- Russell W. A., Papanastassiou D. A., and Tombrello T. A. (1978) Ca isotope fractionation on the Earth and other solar system materials. *Geochim. Cosmochim. Acta* **42**, 1075–1090.
- Sanyal A., Hemming N. G., Broecker W. S., Lea D. W., Spero H. J., and Hanson G. N. (1996) Oceanic pH control on the boron isotopic composition of foraminifera: evidence from culture experiments. *Paleoceanography* **11**(5), 513–517.
- Savin S. M. and Douglas R. G. (1973) Stable isotope and magnesium geochemistry of recent planktonic foraminifera from the south Pacific. *Geol. Soc. Am. Bull.* **84**, 2327–2342.
- Schmidt G. A., Hoffmann G., and Thresher D. (2001) Isotopic tracers in coupled models: a new paleo-tool. *PAGES News* **9**(1), 10–11.
- Schrag D. P. (1999a) Effects of diagenesis on the isotopic record of late paleogene tropical sea surface temperatures. *Chem. Geol.* **161**(1–3), 215–224.
- Schrag D. P. (1999b) Rapid analysis of high-precision Sr/Ca ratios in corals and other marine carbonates. *Paleoceanography* **14**(2), 97–102.
- Schrag D. P. and Linsley B. K. (2002) Paleoclimate: corals, chemistry, and climate. *Science* **296**(5566), 277–278.
- Schrag D. P., Depaolo D. J., and Richter F. M. (1995) Reconstructing past sea surface temperatures—correcting for diagenesis of bulk marine carbonate. *Geochim. Cosmochim. Acta* **59**(11), 2265–2278.
- Schrag D. P., Hampt G., and Murray D. W. (1996) Pore fluid constraints on the temperature and oxygen isotopic composition of the glacial ocean. *Science* **272**, 1930–1932.
- Shackleton N. (1967) Oxygen isotope analyses and Pleistocene temperatures re-assessed. *Nature* **215**, 15–17.
- Shackleton N. J. (1974) Attainment of isotopic equilibrium between ocean water and the benthonic foraminifera genus *Uvigerina*: isotopic changes in the ocean during the last glacial. *Cent. Nat. Rech. Sci. Colloq. Int.* **219**, 203–209.
- Shackleton N. J. (1987) Oxygen isotopes, ice volume and sea level. *Quat. Sci. Rev.* **6**, 183–190.
- Shackleton N. J. and Opdyke N. D. (1973) Oxygen isotope and paleomagnetic stratigraphy of Equatorial Pacific core V28-238: oxygen isotope temperatures and ice volumes on a 10^5 and 10^6 year scale. *Quat. Res.* **3**, 39–55.
- Shemesh A., Charles C. D., and Fairbanks R. G. (1992) Oxygen isotopes in biogenic silica-global changes in ocean temperature and isotopic composition. *Science* **256**(5062), 1434–1436.
- Shemesh A., Burckle L. H., and Hays J. D. (1994) Meltwater input to the southern ocean during the last glacial maximum. *Science* **266**(5190), 1542–1544.
- Shemesh A., Burckle L. H., and Hays J. D. (1995) Late pleistocene oxygen isotope records of biogenic silica from the Atlantic sector of the southern ocean. *Paleoceanography* **10**(2), 179–196.
- Shen C.-C., Hastings D. W., Lee T., Chiu C.-H., Lee M.-Y., Wei K.-Y., and Edwards R. L. (2001) High precision glacial-interglacial benthic foraminiferal Sr/Ca records from the eastern Equatorial Atlantic Ocean and Caribbean Sea. *Earth Planet. Sci. Lett.* **190**(3–4), 197–209.
- Shen G. T. (1996) Rapid changes in the tropical ocean and the use of corals as monitoring systems. In *Geoindicators: Assessing Rapid Environmental Changes in Earth Systems* (eds. A. Berger and W. Iams). A. A. Balkema, Rotterdam, pp. 155–169.
- Shen G. T. and Dunbar R. B. (1995) Environmental controls on uranium in reef corals. *Geochim. Cosmochim. Acta* **59**(10), 2009–2024.
- Shen G. T., Cole J. C., Lea D. W., Linn L. J., McConnaughey T. A., and Fairbanks R. G. (1992) Surface ocean variability at Galapagos from 1936 to 1982: calibration of geochemical tracers in corals. *Paleoceanography* **7**(5), 563–588.
- Sinclair D. J., Kinsley L. P. J., and McCulloch M. T. (1998) High resolution analysis of trace elements in corals by laser ablation ICP-MS. *Geochim. Cosmochim. Acta* **62**(11), 1889–1901.
- Smith J. E., Risk M. J., Schwarcz H. P., and McConnaughey T. A. (1997) Rapid climate change in the North Atlantic during the Younger Dryas recorded by deep-sea corals. *Nature* **386**, 818–820.
- Smith S. V., Buddemeier R. W., Redalje R. C., and Houck J. E. (1979) Strontium-calcium thermometry in coral skeletons. *Science* **204**, 404–407.
- Spero H. J. and Lea D. W. (1993) Intraspecific stable isotope variability in the planktonic foraminifera *Globigerinoides sacculifer*: results from laboratory experiments. *Mar. Micropaleontol.* **22**, 221–234.
- Spero H. J. and Lea D. W. (1996) Experimental determination of stable isotopic variability in *Globigerina bulloides*: implications for paleoceanographic reconstructions. *Mar. Micropaleontol.* **28**, 231–246.
- Spero H. J., Bijma J., Lea D. W., and Bemis B. (1997) Effect of seawater carbonate chemistry on planktonic foraminiferal carbon and oxygen isotope values. *Nature* **390**, 497–500.
- Stoll H. M. and Schrag D. P. (1998) Effects of quaternary sea level cycles on strontium in seawater. *Geochim. Cosmochim. Acta* **62**(7), 1107–1118.
- Stoll H. M., Schrag D. P., and Clemens S. C. (1999) Are seawater Sr/Ca variations preserved in quaternary foraminifera. *Geochim. Cosmochim. Acta* **63**(21), 3535–3547.

- Stott L., Poulsen C., Lund S., and Thunell R. (2002) Super ENSO and global climate oscillations at millennial timescales. *Science* **279**(5579), 222–226.
- Sturchio N. C. (1999) A conversation with Harmon Craig. *The Geochemical News* **98**, p 12–20.
- Toyofuku T., Kitazato H., Kawahata H., Tsuchiya M., and Nohara M. (2000) Evaluation of Mg/Ca thermometry in foraminifera: comparison of experimental results and measurements in nature. *Paleoceanography* **15**(4), 456–464.
- Trend-Staid M. and Prell W. L. (2002) Sea surface temperature at the last glacial maximum: a reconstruction using the modern analog technique. *Paleoceanography* **17**(4) 10.1029/2000PA000506.
- Tudhope A. W., Chilcott C. P., McCulloch M. T., Cook E. R., Chappell J., Ellam R. M., Lea D. W., Lough J. M., and Shimmield G. B. (2001) Variability in the El Niño southern oscillation through a glacial-interglacial cycle. *Science* **291**(5508), 1511–1517.
- Urban F., Cole J., and Overpeck J. (2000) Influence of mean climate change on climate variability from a 155-year Tropical Pacific coral record. *Nature* **407**(6807), 989–993.
- Urey H. C. (1947) The thermodynamic properties of isotopic substances. *J. Chem. Soc.*, 562–581.
- Visser K., Thunell R., and Stott L. (2003) Magnitude and timing of temperature change in the Indo-Pacific warm pool during deglaciation. *Nature* **421**, 152–155.
- Weber J. N. (1973) Incorporation of strontium into reef coral skeletal carbonates. *Geochim. Cosmochim. Acta* **37**, 2173–2190.
- Weber J. N. and Woodhead P. M. J. (1972) Temperature dependence of oxygen-18 concentration in reef coral carbonates. *J. Geophys. Res.* **77**, 463–473.
- Wu G. and Berger W. H. (1989) Planktonic foraminifera: differential dissolution and the quaternary stable isotope record in the west equatorial Pacific. *Paleoceanography* **4**(2), 181–198.
- Zachos J., Pagani M., Sloan L., Thomas E., and Billups K. (2001) Trends, rhythms, and aberrations in global climate 65 Ma to present. *Science* **292**(5517), 686–693.
- Zhou G.-T. and Zheng Y.-F. (2003) An experimental study of oxygen isotope fractionation between inorganically precipitated aragonite and water at low temperatures. *Geochim. Cosmochim. Acta* **67**(3), 387–399.
- Zhu P. and Macdougall J. D. (1998) Ca isotopes in the marine environment and the oceanic Ca cycle. *Geochim. Cosmochim. Acta* **62**(10), 1691–1698.

Title: Treatise On Geochemistry (TOG)

Article/Number: MRW06114

Queries and/or remarks

- Q1** Unless the figs. are redrawn or modified from the sources you mentioned, permission to reproduce from is required.
- Q2** Please confirm that the cross-ref to 'Chapter 6.15' is ok.
- Q3** Please check the insertion of 'Chapter 6.15'.
- Q4** 7.3 not defined

ELSEVIER: UNCORRECTED PROOF