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Planktonic foraminifera and their proxies for the reconstruction of surface-ocean climate parameters

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Resum

Els foraminífers planctònics són organismes que permeten avaluar el paper que té la superfície dels oceans en el procés de canvi climàtic, a causa del seu hàbitat superficial, l'estructura calcària de la seva closca i la seva preservació al registre sedimentari oceànic. De fet, l'existència abundant de sediments carbonatats rics en les closques calcítiques dels foraminífers fan d'aquests una eina útil per a una gran varietat d'estudis paleoceanogràfics a escales de temps que varien entre dècades i mil·lennis. En aquest article es revisen els mètodes *proxy* més importants emprats per a reconstruir variables climàtiques relacionades amb la superfície oceànica mitjançant foraminífers, que comprenen tant els mètodes geoquímics (isotòpics i elementals) com els basats en associacions. La temperatura gaudeix d'un èmfasi especial, perquè és el paràmetre climàtic més important de la superfície de l'oceà, tot i que també es tracten propietats relacionades de caràcter físic, químic i biològic —com són la salinitat, la productivitat, l'ús de nutrients, la meteorització, la circulació—, i propietats del sistema carbonat —com l'alcalinitat, el pH i el [CO_3^{2-}]. S'avalua cada *proxy* de manera sistemàtica i s'especifica, per a cada mètode, la seva base científica, alguns exemples breus i una projecció futura de la seva evolució.

Paraules clau: foraminífers planctònics, superficie oceànica, geoquímica marina, *proxys* climàtiques

Abstract

Planktonic foraminifera are useful organisms to assess the surface ocean's role in climate change, due to their upper water column habitat, calcium carbonate mineral structure, and preservation in the deep-sea sedimentary record. Carbonate sediments rich in the calcitic shells of foraminifera are abundant in both space and time, which allows their use in an array of paleoceanographic studies over time scales ranging from decadal to glacial-interglacial, as well as beyond and between. Here we review the most important "proxy" methods to reconstruct surface-ocean climatic variables using planktonic foraminifera. These methods include assemblage-based and geochemical-based (both isotopic and elemental) approaches. The natural emphasis is on temperature, the most important climatic parameter of the surface ocean, although related physical, chemical, and biological properties are addressed as well, such as salinity, productivity, nutrient utilization, weathering, circulation, and oceanic C-system properties including alkalinity, pH, and [CO_3^{2-}]. In our systematic evaluation of each foraminiferal proxy, we provide the basis for each method, brief examples, and a glimpse into the future, when current research needs will hopefully be met.

Keywords: planktonic foraminifera, surface ocean, marine geochemistry, climate proxies

Introduction to foraminifera

Foraminifera are single-celled, amoeba-like, protists with exoskeletal shells (tests). The shells are commonly divided into chambers, which are added sequentially during growth. On the basis of the morphology of these shells, 15 extant foraminiferal orders can be recognized [1]. In seven orders, the shell is made of secreted calcite; in others, the species secrete aragonite or opaline silica, or make their shells with organic matter or foreign particles.

Foraminifera constitute the most diverse group of shelled microorganisms in modern oceans [1]. The majority of modern foraminifera are benthic; while there are only about 40–50 planktonic species (Fig. 1). They are abundant and diverse in modern oceans, where they occur throughout planktonic and benthic marine habitats [2]. Planktonic foraminifera live mostly in the photic zone but descend to deeper water, as much as several hundred meters, and are found in diverse oceanic regimes, including tropical waters as well as subtropical and polar water masses.

The mineralized shells of foraminifera preserve a record of the ocean's chemical and physical properties that can be uti-

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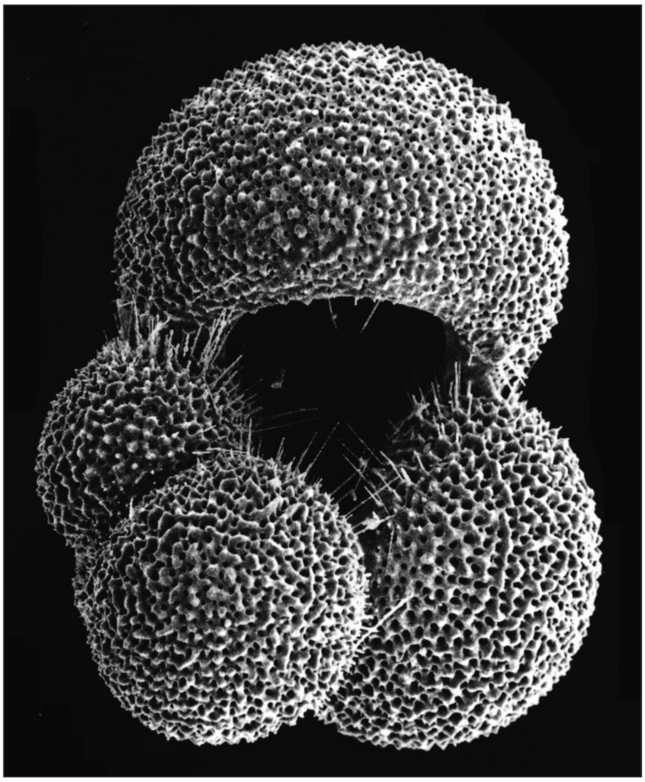

Figure 1. Scanning electron microscope image of planktonic foraminifera *G. bulloides*, umbilical side. (Courtesy of Frank Peeters).

lized for evolutionary, paleobiological, and geochemical analyses of global environmental change. They are the most widely used fossil organisms for biostratigraphy, age dating, and correlation of sediments. A major impetus for foraminiferal research has resulted from isotope and trace-element analysis of foraminiferal test calcite to infer physical, chemical, and biological properties of the oceans [3].

Planktonic foraminiferal surface-ocean habitat and links to climate

Earth's climate system can be divided into five main components [4, 5]: the lithosphere, the hydrosphere, the cryosphere (glaciers, sea ice, and ice sheets), the atmosphere, and the biosphere. Each of these climate components interacts with the others, over a variety of time scales ranging from millions of years to seconds. The oceans comprise the vast majority of the hydrosphere, which also includes lakes, rivers, and groundwater; they cover some 71% of the globe and are the world's largest reservoir of heat derived from solar insolation. Therefore, the portion in direct contact with the Sun's energy, the surface ocean, is clearly of particular importance.

As the upper ~3.2 m of the ocean contains as much heat as the entire atmosphere [6], it is this layer that is particularly relevant in any study of Earth's climate. The upper ocean regulates ocean-atmosphere heat exchange, the formation of pressure gradients and wind fields, as well as the formation and circulation of water masses that comprise the oceanic thermohaline circulation. As a consequence, the surface ocean is involved in both deep and shallow circulation, both of which are crucial for heat transport around the globe. Furthermore, it can be argued that the surface ocean, and particularly its temperature, modulates global climate.

The temperature of the surface ocean is therefore the most critical aspect in terms of climate, although several other factors play a key role and there are important interactions and feedbacks among them. For example, the upper ocean is a critical player in the marine, and therefore global, carbon (C) cycle, and temperature influences various parts of these systems, such as precipitation or preservation of calcium carbonate ($CaCO_3$) and regulation of the physical state of the surface ocean (stratification), which in turn affects nutrient cycling and biological "pumping" of C from the surface to the deep. The principal goal underlying carbon-cycle research is to understand atmospheric CO_2 [7]. In this respect, the surface ocean is paramount as it is the interface between the marine reservoir "that contains 50 times more C than the atmosphere" [8], and the atmosphere itself. Here we have provided just a few examples of how surface-ocean temperature is linked to climate not only directly but also indirectly, through important interactions and feedback mechanisms.

What follows is a brief review of the main ways that planktonic foraminifera have been essential in studies of the past and present surface oceans and their role in the Earth's climate evolution. While we naturally emphasize temperature as the surface-ocean variable of particular importance, subsequent examples also illustrate how these organisms can be used to reconstruct other variables related to temperature, such as nutrient concentrations, biological productivity, and carbonate-system parameters such as alkalinity, pH, and $[CO_3^{2-}]$.

The use of planktonic foraminifera in the reconstruction of oceanic properties

Temperature

Assemblage-based methods

Transfer functions. A transfer function (TF) is a statistical micropaleontological method [9] that uses microfossil assemblage data to reconstruct an environmental parameter of interest. Planktonic foraminifera are just one of the many microfossil assemblage groups that can be used for this purpose, and temperature is the main oceanic parameter sought from the TF application, although others, such as productivity [10], are possible and will be discussed further below. Here we focus on the particular role of planktonic foraminiferal TFs toward temperature reconstructions.

The TF method first uses factor analyses to establish a small number of factors, or assemblages, based on the relative proportions of different foraminiferal species over an environmental gradient. As an example [9], six major Atlantic Ocean assemblages have been defined: polar, subpolar, subtropical, equatorial, gyre, and ocean margin. Once the factors are defined, which is usually done with modern surface sediment "core-top" sample materials, multiple regression analysis is used to formulate equations that relate the factors to the climate parameter of interest, usually temperature. The same equations are then used to calculate paleotemperatures from downcore assemblages, usually at distinct times of climatic interest.

The classic example of a TF application was the Climate Long-range Investigation, Mapping, and Prediction (CLIMAP) project [11], which pioneered a first global reconstruction of ice-age climate during the last glacial maximum (LGM). The results provided an important benchmark for understanding the sensitivity of environmental systems to change [12]. Planktonic foraminifera were especially useful in the Atlantic and Indian Oceans due to their prevalence [13, 14], while other faunal and floral microfossil assemblage groups were incorporated as well (see [12] for a brief summary).

The TF method requires that whatever properties actually control species distributions are linearly related to temperature. If this chain of relationships varies through time, then estimates based on TFs may be biased [12]. The TF technique suffers from another drawback, in the form of data gaps or unreliable data in cases in which the ancient faunal composition differs significantly from modern faunas, and no modern analog fit can be made [13, 15].

The Modern Analog Technique. Recognition of other possible problems and biases in statistical TFs, such as foraminiferal preservation [16, 17], prompted the development of alternate assemblage-based statistical approaches. The modern analog technique (MAT) technique attempts to match a geological sample from the past with a set of modern samples containing a similar faunal or floral assemblage [18, 19]. The MAT approach incorporates statistical measures known as *coefficients of dissimilarity* that are used to compare two assemblages on the basis of the relative proportions of key taxa. Environmental estimates are then based on an average, or weighted average, of a number of best modern analog samples (Fig. 2). The basic assumption of MAT is similar to that of the TF statistical approach, in which modern spatial variability (in core-top samples) serves as a proxy for past temporal variability in a downcore record of planktonic foraminiferal species assemblage change.

A variety of schemes have been explored to obtain an average of environmental properties (e.g., temperature) in an array of best-analog samples [12], including a simple arithmetic average [19], weighting by geographic distance [21], or gridding and smoothing the core-top data along property gradients [22]. In some cases, species percentage data are modified with a log transform in order to minimize problems associated with species dominance [23-25].

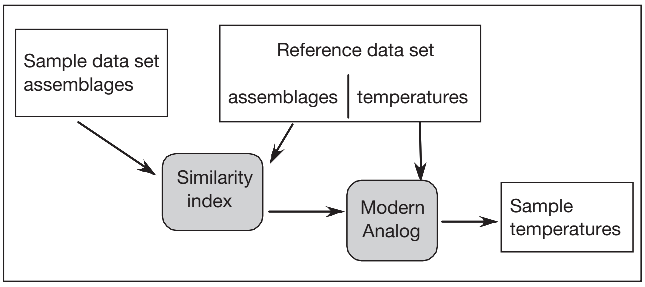

Figure 2. The modern analog technique (MAT) for temperature determination from planktonic foraminiferal assemblages. The similarity of a sample assemblage to all reference assemblages is checked, and the temperatures corresponding to the most similar reference assemblages (the modern analogs) are weighted according to the similarity index and averaged. (Modified from [20]).

As an example, the MAT technique, and specifically the approach described by Pflaumann et al. [21], has been employed recently to estimate sea surface temperatures from western Atlantic Quaternary sediments [25]. Although a certain degree of method confidence was attained due to the fact that temperatures from uppermost samples agreed with modern observations, a cluster analysis was carried out to assist in understanding the variability that occurs in foraminiferal assemblages. It was shown that fairly similar samples may have unexpectedly different estimated temperatures due to small differences in key species and, conversely, quite different assemblages can result in similar temperature estimates [25].

Uncertainties remain with both types (TF and MAT) of planktonic foraminiferal assemblage-based methods involving statistical estimations of temperature. We therefore turn our attention to other modes of surface-ocean climate reconstructions using these important organisms.

Geochemical methods

Oxygen isotopic composition ($\delta^{18}O$). Measurement of the $\delta^{18}O$ of carbonates has the longest and most distinguished history of all foraminiferal approaches to temperature determination. This proxy system has been summarized in recent review papers [26, 27], most extensively in the late 1990s [28]. Urey [29] first theorized that the effect of temperature on the partitioning of oxygen isotopes between water and carbonate might provide a useful geological tool [26]. Major advances then came from those who followed in Urey's footsteps, and before long a $\delta^{18}O$ "paleotemperature equation" was achieved based on calcite precipitated by mollusks in either controlled experiments or field-collected samples [30]. Analysis of this calcite yielded a paleotemperature equation with a sensitivity of approximately –0.2‰ in $\delta^{18}O$ per ºC (Fig. 3). Following the discovery that planktonic foraminiferal $\delta^{18}O$ varied cyclically in eight Caribbean sediment cores [31], other laboratory groups soon established the capability to apply $\delta^{18}O$ variations to the study of ocean temperature history [26].

The $\delta^{18}O$ of planktonic foraminiferal shells depends on the temperature of calcification [27]. The other most important factor is the $\delta^{18}O$ of the seawater itself, which varies in time and space and can substantially affect temperature determination. Foraminiferal $\delta^{18}O$ composition is defined as the deviation of the ratio $^{18}O/^{16}O$ measured in the shell carbonate from the same ratio in a standard, in tenths of a percent (permil, ‰). The fractionation between O isotopes is a logarithmic function of temperature with a slope, over the oceanic temperature range of –2ºC to 30ºC, between –0.20 and –0.27‰ per ºC [26], in agreement with thermodynamic predictions [32-35]. Since the $\delta^{18}O$ proxy is based on a thermodynamic principle, it is expected to be robust and relatively unaffected by secondary kinetic factors [26], although there are indications of a seawater $[CO_3^{2-}]$

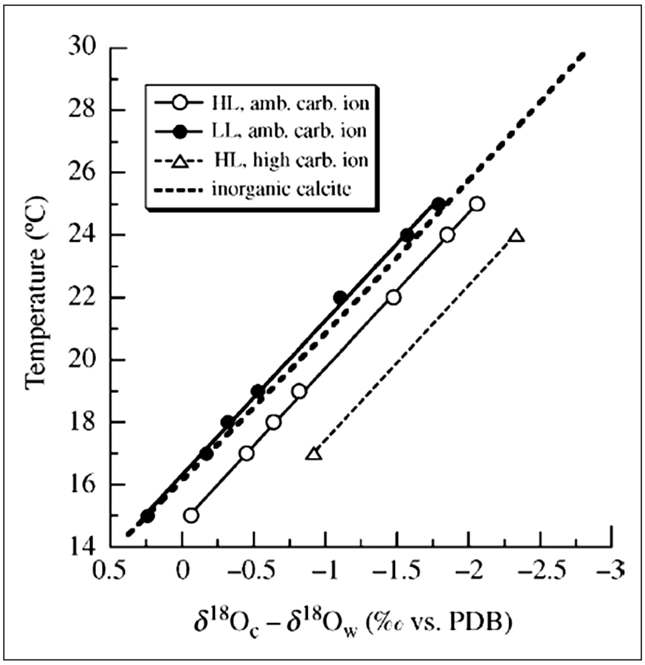

Figure 3. Comparison of $\delta^{18}O$ paleotemperature equations for laboratory-cultured *Orbulina universa* [28], a symbiont-bearing planktonic foraminifera, against values for inorganic calcite precipitation [32]. C and W subscripts refer to calcite and water $\delta^{18}O$ compositions, respectively, both according to the PDB scale ([28] and references therein); subtraction of the water term from the calcite term allows direct comparison with temperature (T), and explicit comparison of the various T-sensitivities. These data demonstrate that the low-light (LL) $\delta^{18}O$ equation at ambient carbonate ion concentration [CO_3^{2-}] is essentially indistinguishable from the inorganic calcite equation. For high-light (HL) conditions, in which symbiont photosynthetic activity is maximized, $\delta^{18}O$ shifts to more negative values; for high [CO_3^{2-}] conditions, $\delta^{18}O$ shifts to even more negative values. Overall, these trends demonstrate the range of biological influences on foraminiferal $\delta^{18}O$, even though T-sensitivity (i.e. the slope) is quite constant. (Modified from [26], with permission from Elsevier).

influence [36], an effect of light on symbiotic algae [28, 37], and variations related to shell ontogeny (growth) [38] and addition of gametogenic calcite at deeper depths of the water column [39]. Another more fundamental problem in foraminiferal $\delta^{18}O$ is that the assumption of $\delta^{18}O$ "equilibrium" is often unmet when in-situ water column studies put this important proxy system to the test (see [40] for a review of this issue).

Despite these points, the biggest problem with using planktonic foraminiferal $\delta^{18}O$ for either absolute or relative temperature reconstructions is that $\delta^{18}O$ reflects both temperature and the $\delta^{18}O$ of the seawater from which the shell precipitated, as mentioned above. The seawater $\delta^{18}O$ composition in turn reflects the mean $\delta^{18}O$ composition [41], determined by the amount of continental ice (varying on glacial-interglacial time scales, for example), and the evaporation-precipitation (rainfall) balance (E-P) for that part of the surface ocean in which the carbonate shell was primarily precipitated. This second factor is often described as a "salinity effect" since $\delta^{18}O$ tends to track with salinity, as both respond to E-P. The $\delta^{18}O$–salinity relationship does vary considerably in the ocean. however, due to the varying $\delta^{18}O$ composition of freshwater [42].

Despite the obvious caveats and uncertainties, this method still stands as the most widely used temperature proxy system, due to the remarkable consistency among various types of carbonates in terms of T sensitivity (Fig. 3).

Ca isotopic composition ($\delta^{44}Ca$). Initial work has demonstrated promise for this relatively new technique, although subsequent efforts, especially from culture studies, have shown difficulty in resolving T sensitivity with respect to analytical errors ([26] and references therein). Further complications arise from seawater compositional histories [43]. While this approach is still in its infancy with respect to other methods for T determination from planktonic foraminifera, it shows potential (see [7, 26] for detailed reviews).

Mg/Ca. The ratio of magnesium to calcium (Mg/Ca) is nearly constant throughout the ocean, and the residence time for both elements is longer than a million years. Thus, it is not expected to vary on glacial-interglacial timescales.

The Mg/Ca ratio in planktonic foraminifera is a temperature proxy that has been the focus of intense research efforts during the last decade. Since the initial work of Nürnberg and others [44-46], this proxy has been subjected to calibration, validation, and subsequent application to diverse paleoclimatic issues.

Mg/Ca has been calibrated with respect to temperature by means of culture, core-top, and water column studies, and it tends to fit with equations of the form:

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

where *b* is the pre-exponential constant, *m* the exponential constant, and *T* the temperature. The exponential constant determines the magnitude of temperature change calculated from variations in Mg/Ca, while the pre-exponential constant determines the absolute temperature (Fig. 4).

Culture-based calibrations [45, 48-51] present the advantage that environmental factors (e.g., temperature, salinity, nutrients, light, pH) affecting Mg uptake can be constrained during the experiment, becoming independent variables. However, potential caveats of this strategy are: (i) only a limited number of species can be studied, (ii) foraminiferal reproduction cannot be achieved in the laboratory, and (iii) laboratory conditions may not realistically reproduce the natural environment sufficiently to ensure natural chamber growth [52].

Calibration of the proxy by means of core-top materials [53-55] integrates all the processes that take place from the initial foraminiferal chamber formation to residence at the sea floor (e.g., addition of gametogenic calcite and crust, dissolution) [54]. Thus, their importance stems from the similar characteristics of the material used for calibration and subsequent applications in the sedimentary record. Nevertheless, there are also disadvantages and limitations, such as the possibility of post-depositional alteration (dissolution) of the samples or the impossibility of distinguishing and quantifying the variables influencing trace-element uptake.

The "third way" [47] to calibrate the Mg/Ca proxy is the use of foraminifera collected either by sediment traps [47, 56, 57] or by plankton-tows [58-60]. Sediment traps present the advan-

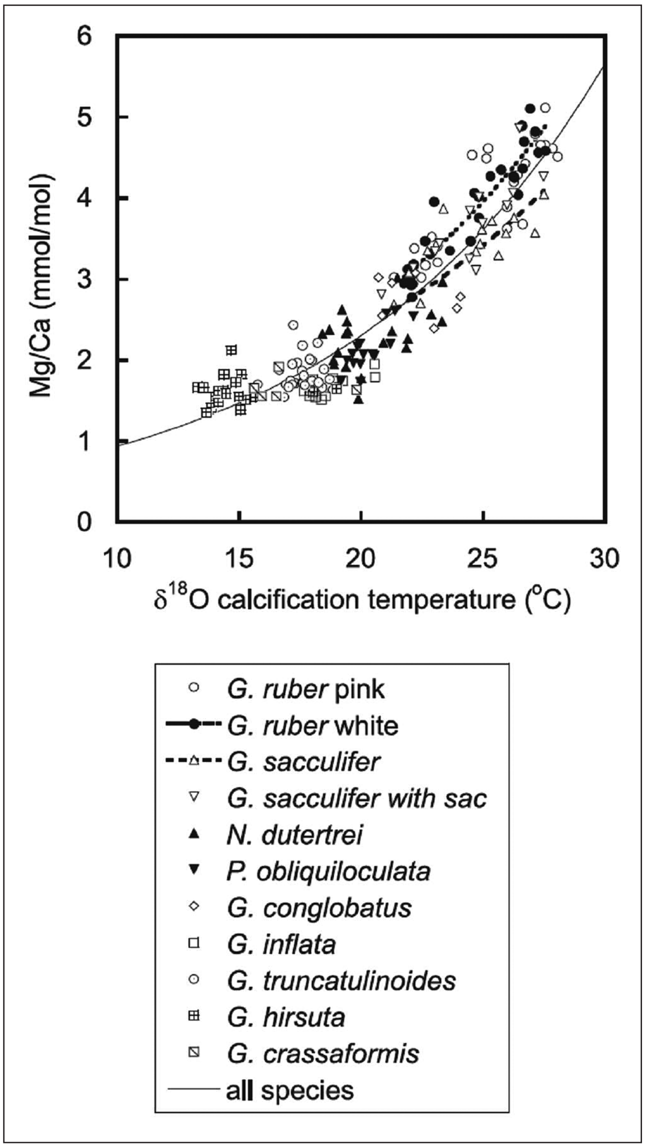

Figure 4. Mg/Ca vs. $\delta^{18}O$ calcification temperature for a group of species collected from a sediment trap deployed in the Sargasso Sea [47]. (Reproduced by permission of the American Geophysical Union).

tage that the timing/rate/etc. of foraminiferal production is known, so direct comparison between the geochemical signal and the *in-situ* and simultaneous instrumental record is possible. Furthermore, trap material is also valuable because it most closely represents the material entering the sedimentary record without reaching the ocean floor [52].

Depth-discrete tows from the water column afford two main advantages: (i) it is not necessary to assume oxygen isotopic equilibrium to arrive at calcification temperatures, and (ii) there is a variety of *in-situ* environmental variables, temperature among others, against which Mg/Ca can be compared. However, it is a "snapshot" of the ocean's surface, and isotopic data ($\delta^{18}O$) are necessary to confirm the depth habitat of the collected species.

Other metal ratios (Sr/Ca). Strontium is a conservative element in seawater with a residence time of about 5 million years (My). In initial studies, systematic attempts to isolate the factors controlling foraminiferal Sr, using core-top, sediment trap, sediment, and cultured samples, failed to yield unambiguous relationships [61, 62]. However, these studies revealed that Sr/Ca is much more uniform than Mg/Ca in planktonic foraminifera (ranging from about 1–2 mmol mol^{-1} vs. 1–10 mmol mol^{-1}) [63]. Further work tried to determine whether records of foraminiferal Sr/Ca reflect past changes in seawater Sr/Ca [64-68]. A culture study of the planktonic species *Globigerina bulloides* and *Orbulina universa* reported an increase of ~1% in Sr/Ca per ºC temperature increase [48, 69].

More recently, Elderfield et al. [64] examined the relationship of various foraminiferal species to calcification temperature in a suite of North Atlantic sediment core-top samples. The authors found a positively correlated weak temperature dependence for species belonging to the globorotaliid genus, although a dissolution effect was also described [70]. In the most recent study [70], globorotaliid species from core-tops and plankton tows were reported to change with temperature (2–3% change per ºC)–being independent of dissolution processes–although only along a restricted temperature range (5–15ºC). However, comparison of sedimentary foraminiferal Sr/Ca across glacial-interglacial transitions suggested a [CO_3^{2-}] influence that may override any temperature dependence on these time scales.

Salinity: $\delta^{18}O$ combined with independent T estimators

As a consequence of the combined influences on foraminiferal $\delta^{18}O$, salinity (S) is generally estimated with the combined use of independent temperature estimators and $\delta^{18}O$, so as to ascribe the remainder to S exclusively [71]. After temperature, salinity is probably the most important surface-ocean variable in terms of climatic importance, since the two together control seawater density, convective overturning, and therefore also deep-ocean thermohaline (a term derived from both T and S influences) circulation. Unfortunately, no independent geochemical proxy for salinity has yet been developed; instead, there are two approaches (both in conjunction with $\delta^{18}O$) for the reconstruction of this important surface-ocean parameter: those that are also derived from foraminifera and those that are not.

Other foraminiferal methods, such as the Mg/Ca ratio (see above), offer less ambiguity than T estimators from another phase (such as alkenone measurements derived from the organic fraction of bulk sediments [72]), in that having the same "carrier organism" for two purposes removes considerable doubt about chronology, differing depth habitats, etc. While the focus of this review is planktonic foraminifera, it should be noted that recent pore-water measurements have allowed deep-ocean salinity at the last glacial to be assessed geochemically at high precision for a single site [73].

Planktonic foraminiferal assemblage data and the use of TFs or the MAT can be employed to independently estimate T so that it can be accounted for in $\delta^{18}O$, with the remainder ascribed to salinity. This approach, which was invoked to reconstruct the salinity of the North Atlantic for the LGM, showed significant differences with modern patterns and the presence of a sharp gradient associated with the polar front [74].

More recent attempts [20] have been made with direct estimates of salinity, but they have proven to be difficult. There is little evidence that organisms from the pelagic realm are themselves sensitive to salinity changes within the common oceanic range [27]; consequently, much of the correlation observed may be due to the correlation of salinity to other factors, such as temperature. Even when temperatures can be determined independently (i.e., not from assemblages) with some confidence [75], there is still a large uncertainty in salinity calculations due to the different δ^{18}O-salinity relationships in the modern ocean, which therefore suggests also a lack of constancy for the past, even at the same location. If we assume an error of at least 1°C in the temperature estimate, then the error for the estimated salinity is at least 1.2‰, which is in the range of modern open-ocean salinity fluctuations. At present, reconstructed salinity patterns must be considered mainly as qualitative information [27]. It stands to reason that one of the greatest potential breakthroughs for future paleoceanographic research will come from independent S estimations made from foraminiferal geochemical methods, rather than those that depend on assemblages.

Productivity: Microfossil assemblages

Within each group of planktonic organisms (including foraminifera), some species occur preferentially in high-productivity regions while others avoid these or simply cannot compete in “bloom” situations. The relative abundances of key species can therefore provide clues to the intensity of production at the time of sedimentation [27]. A number of foraminiferal species have been identified as indicators of high productivity [76, 77]. In low latitudes, these include *Globigerina bulloides*, *Neogloboquadrina dutertrei*, and *Globorotalia tumida*. In temperate latitudes, *Turborotalita quinqueloba* is a good candidate, while left-coiling *Neogloboquadrina pachyderma* indicates cold upwelling water, particularly at higher latitudes. Thus, simply recording the changes in abundance of such species relative to the more ubiquitous tropical (or temperate) species should provide useful clues to productivity variations [27].

Productivity can be treated, like temperature is, as another parameter to be calibrated with respect to modern foraminiferal assemblage data (similar to the TF and MAT approaches described above). A prerequisite is a sufficiently large calibration set that includes the range of variation to be encountered in down-core assemblage changes. This approach was employed [10, 78] with a previous calibration set [11] and a productivity map [79] in order to assess glacial productivity changes in the Atlantic Ocean. As expected from previous results [80], strong increases were indicated in those regions that today have high productivity, suggesting increased nutrient content in subsurface waters, increased mixing, or both.

In certain regions, foraminiferal assemblage-based estimates differ considerably from those of other approaches, indicating that one or more of the approaches (or all) may have produced incorrect results. Such discrepancies, although directly disconcerting for paleoceanographic purposes, can and should be viewed with opportunity as they provide new insights to the limits of the proxies themselves, ultimately leading to improvements in their accuracy and to utility in their combined application.

Nutrient availability/utilization: Carbon isotopic composition (δ^{13}C) and Cd/Ca

The classical marker for the fertility of surface-ocean waters is the carbon (C) isotope ratio (^{13}C/^{12}C) of carbonate-secreting organisms (foraminifera), expressed as δ^{13}C in ‰ PDB units. Within the water, δ^{13}C is controlled by competing processes of CO_2 exchange with the air, removal of C in solids by export production, and re-supply of dissolved C (and macro-nutrients such as phosphate ([PO_4^{3-}]) by subsurface waters. The net result of these processes is that surface waters are generally enriched in ^{13}C relative to subsurface waters and that a representative depth-profile of δ^{13}C mirrors that of [PO_4^{3-}] (Fig. 5). Photosynthesis preferentially uses ^{12}C in the formation of organic matter, and ^{13}C tends to be left behind. The process of primary production is ultimately limited by the supply of nutrients that also get incorporated into organic matter, and hence δ^{13}C and [PO_4^{3-}] are very tightly coupled. The nutrients supplied to the photic zone, however, arrive “tagged” with excess ^{12}C, which along with the organic matter is rained down from the surface into deeper depths. The absolute value of δ^{13}C in surface waters, and therefore also in the planktonic foraminiferal shells that record them, is difficult to interpret because it contains mixed signals. What is needed to understand the fertility of the surface-ocean water column as a whole is the maximum seasonal range or the gradient from surface to subsurface, an approach taken in a plethora of studies and effectively summarized recently [27].

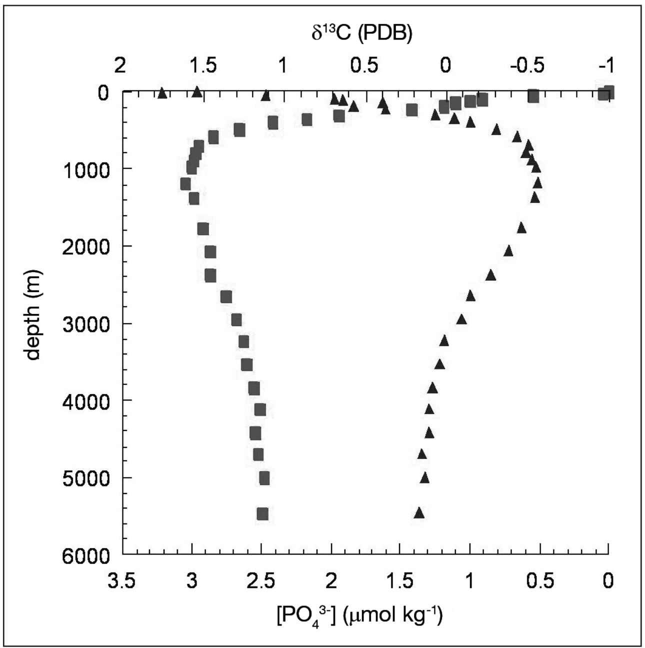

Figure 5. Comparison of aqueous δ^{13}C (triangles) and [PO_4^{3-}] (squares) plotted together with depth for a NW Pacific Ocean station. Data are from station 6039 (approximately 165°E, 40°N), occupied during the 1992 WOCE Section P13 data acquisition. Full cruise data and analytical protocols are detailed elsewhere [81].

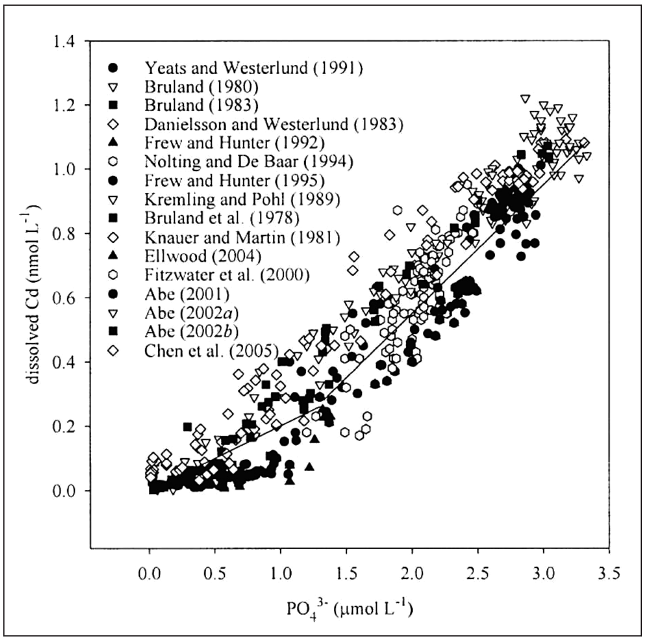

Figure 6. Selected dissolved Cd vs. [PO_4^{3-}], as compiled from the global database. Lines present two distinct relationships, for [PO_4^{3-}] < 1.3 mmol l^{-1}, and for [PO_4^{3-}] > 1.3 mmol l^{-1}, as defined in [82]. (Modified from [87]).

Cadmium (Cd) has a very similar oceanic behavior to [PO_4^{3-}] (Fig. 6) and substitutes readily into foraminiferal calcite. Cd/Ca ratios in benthic foraminifera have been extensively used to reconstruct [PO_4^{3-}] of deep waters and hence learn about the pattern of past thermohaline circulation [82, 83]. In the surface ocean, Cd/Ca in planktonic foraminifera allows reconstruction of [PO_4^{3-}] utilization, although a temperature dependence of this tracer [84] and a slight preference during productivity for Cd over [PO_4^{3-}] [85] have been reported. Recently, however, it was demonstrated that T and [PO_4^{3-}] influences on planktonic Cd/Ca are difficult to isolate from one another and that further work, probably from culture studies, will be required to separate these effects clearly and quantitatively [58, 86].

Alkalinity: Ba/Ca

The distribution of barium (Ba) in the global ocean has a general linear relationship with alkalinity and silica, since it is depleted in surface waters and regenerated at depth [88-90]. Surface Ba depletion is caused by the precipitation of barite ($BaSO_4$) [91], which predominantly dissolves on the seafloor, thus enriching deep waters [69, 88]. The major sources of Ba to the ocean are rivers [92] and mid-ocean ridge hydrothermal effluents [93, 94]. One potential problem with using Ba/Ca as a proxy for alkalinity is that the abundance of Ba (being of very low concentration) is likely to vary substantially between glacial and interglacial periods [27].

The main paleoceanographic application of Ba has focused on benthic foraminifera, in order to reconstruct circulation changes and alkalinity shifts [95-99]. However, there have also been studies on planktonic foraminifera. Initial results showed that Ba incorporation into foraminiferal tests occurs in direct proportion to seawater concentration and does not vary with temperature or salinity [100-102]. Partition coefficients were found to be lower than for benthic species–probably due to differences in calcification rates–and variation was also found between spinose and non-spinose species [69]. However, little work has been done on the sedimentary record, since initial downcore Ba studies from planktonic foraminifera did not reveal climatically significant shifts [97, 100].

More recently, Hall and Chan [89] revisited the application of planktonic Ba/Ca, in this case as a meltwater proxy. They reported that a combination of Ba/Ca and $\delta^{18}O$ can be used to trace continental meltwater discharge. Changes in Ba/Ca in the planktonic foraminifera *N. pachyderma* (sin.) were found to correlate with the retreat of the Laurentide ice sheet and the evolution of the Mackenzie River drainage basin during the last 13,000 years.

pH: boron isotopic composition ($\delta^{11}B$)

Boron isotopic composition ($\delta^{11}B$) in foraminiferal calcite has been used to study past changes in the ocean/atmosphere carbon system by means of reconstructing the ancient oceanic pH. The basis of this proxy is the consideration that B incorporation is an equilibrium process between bulk solution and foraminiferal carbonate. The presence of the different B species in seawater (boric acid [$B(OH)_3$] and borate [$B(OH)^{4-}$]) is controlled by pH [103]. At higher pH, the borate species, which is the only one incorporated by foraminifera during calcification [104-106], is more abundant and $\delta^{11}B$-enriched. Consequently, the B concentration and isotopic composition of foraminifera provides information about the pH of the seawater where these organisms were formed.

During the last decade, the $\delta^{11}B$ proxy has been used to reconstruct changes in oceanic pH during both recent and older geologic time periods [106-113]. More recently, uncertainties in current assumptions regarding B systematics have been reported [114], highlighting the need for further work and questioning the reliability of long-term interpretations (for a more extensive review see Pelejero and Calvo [115] in this volume).

Carbonate system: U/Ca and Li/Ca

Proxies of carbonate system parameters allow reconstruction of changes in the distribution of carbon species in the surface and deep ocean, thus providing the constraints necessary to evaluate the different mechanisms proposed to account for atmospheric CO_2 fluctuations.

Uranium (U) exists in seawater almost exclusively as a group of highly stable carbonate complexes, formed between uranyl ion (UO_2^{2+}) and carbonate ion (CO_3^{2-}) [50, 116]. Thus, the carbonate ion concentration ([CO_3^{2-}]) influences the aqueous geochemistry of U, because the formation of these complexes increases the solubility of U-containing minerals and decreases the extent of adsorption onto surfaces, thereby increasing the mobility of U in the aqueous environment.

Initial culture experiments reported that U incorporation into foraminiferal calcite occurred in proportion to seawater U con-

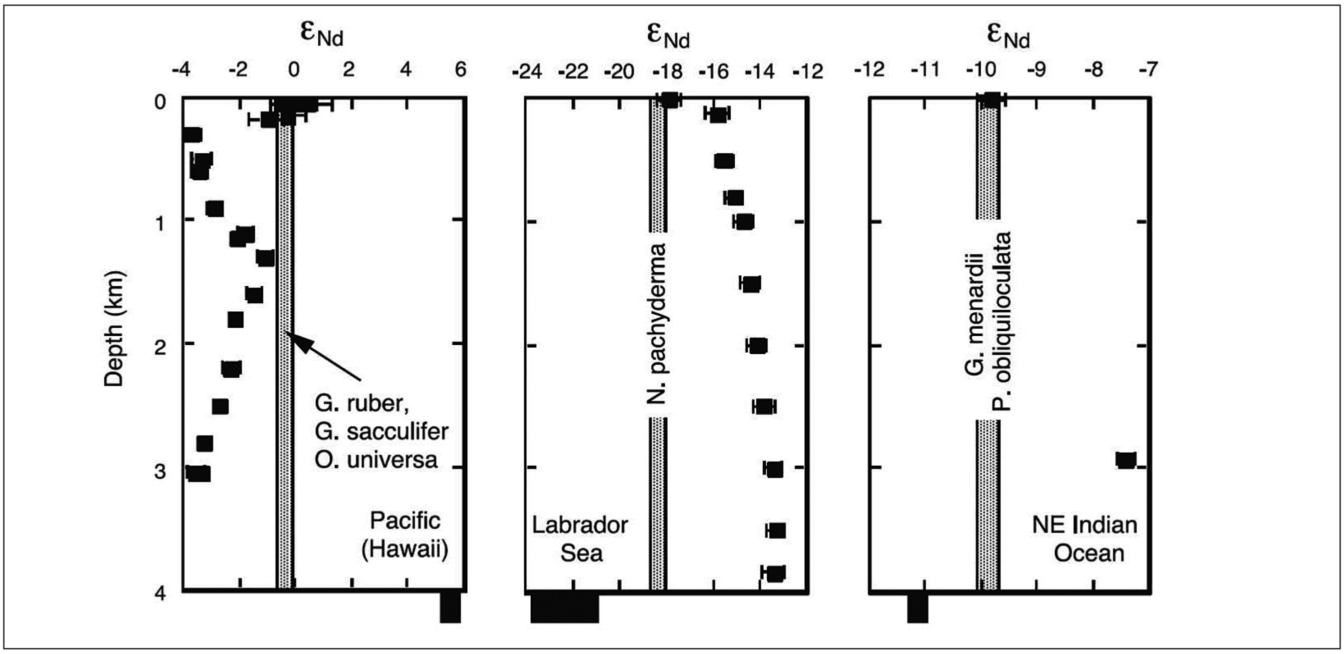

Figure 7. Depth profiles of water column ε_{Nd} for a Pacific site near Hawaii, the Labrador Sea, and the eastern Indian Ocean, compared to data for Holocene sedimentary planktonic foraminifera (stippled bands extending the length of the profile) and bulk sediment (solid rectangles at the base of the depth profile) [121] (reproduced by permission of American Geophysical Union). For each site, the data for planktonic foraminifera are identical to those for surface seawater and very different from those for bottom water or bulk sediment.

centration and showed that partial dissolution had the potential to lower U/Ca in foraminifera tests [117]. In subsequent studies, U/Ca ratios of glacial planktonic foraminifera (*G. ruber* and *G. sacculifer*) from the Caribbean and the eastern equatorial Atlantic Ocean were reported to be approximately 35% lower than Holocene values [118]. Since this change was too large to be explained by changes in the U concentration of seawater, Russell and others [118] hypothesized that the observed change in U/Ca ratio of planktonic foraminifera was controlled by changes in [CO_3^{2-}] or temperature.

In order to address this question, the most recent study dealing with U/Ca ratios [50] investigated the effects of changes in [CO_3^{2-}] and temperature on the U/Ca in the calcite shells of planktonic foraminifera (*O. universa* and *G. bulloides*) grown in controlled laboratory cultures. The results demonstrated that the U/Ca ratio of both species decreased exponentially with increasing seawater [CO_3^{2-}], while no relationship with temperature could be established. The application of the derived relationship to the sedimentary record for a glacial-interglacial cycle yielded results consistent with studies based on the more-established boron-isotope technique. Results suggested that down-core records of foraminiferal U/Ca may provide information about changes in the ocean's carbonate concentration (in settings where the addition of U by diagenetic processes is not a factor).

Regarding the Li/Ca proxy, early work by Delaney and others [62] indicated that Li/Ca in foraminiferal calcite is directly related to the Li/Ca ratios of the seawater in which these organisms grow [119], while there was no clear relationship to temperature. Further studies [120] used the Li content of foraminifera to infer changes in past hydrothermal input (assuming that seawater Li/Ca controls foraminifera composition).

The latest study on this ratio [119] showed how Li/Ca could be used as a carbonate-system proxy, since Li content in foraminiferal calcite is hypothesized to depend on calcification rate and, consequently, on [CO_3^{2-}] of ambient sea water. Nevertheless, future work is necessary to isolate the influences of the different environmental variables.

Continental weathering and oceanic circulation: Nd isotopic composition (ε_{Nd})

The isotopic composition of dissolved neodymium in the world's oceans is heterogeneous, on a basin scale, on much smaller geographic scales within basins and with depth at a single geographic location [121]. There are differences between ocean basins, with the highest values found in the Pacific Ocean (ε_{Nd}= 0 to –4) and the lowest in the North Atlantic (ε_{Nd} ~-14), approximately reflecting the ages of the surrounding continents as well as the effects of ocean mixing. The evolution of this variability through time can be used to infer past changes in both continental weathering processes and oceanic circulation.

The isotopic composition of the different water masses can be traced through the ocean, since it remains constant even if the total concentration of Nd is changed [122]. The variations in ε_{Nd} values can be caused by the mixing of water masses or the addition of a different isotopic component.

The study of the Nd isotopic composition of sedimentary planktonic foraminifera is a relatively new high-resolution approach that allows investigation of the surface-ocean ε_{Nd} signal. It complements analysis of the sediment Fe-Mn oxyhydroxide fraction–which only records bottom or deep-water features–as well as studies of ferromanganese (Fe-Mn) crusts and fish teeth, which are more appropriate for longer-term/lower-resolution studies.

Articles published to date [121, 123-125], have shown that core-top sedimentary planktonic foraminifera indeed record the surface-water ε_{Nd} composition (Fig. 7) and that down-core Quaternary foraminifera follow a climatic signal, as defined by oxygen-isotope compositions. However, the Nd/Ca ratios were found to be 500 times higher than those in seawater, inconsistent with the typical ratios of other marine carbonates [121]. Plankton-towed foraminiferal Nd/Ca confirmed the upper-ocean signal acquisition [121], although other studies [126] suggest a markedly lower Nd/Ca ratio. Further work is necessary in order to address this issue, especially studies on plankton-tow samples collected in areas of contrasted oceanographic features.

Synthesis

From this review it is evident that the use of planktonic foraminifera to reconstruct surface-ocean climate has both an interesting history and a promising future. In our view this field will significantly benefit in the near-term through a number of developments and approaches. One major benefit is the rapid advance of analytical methods and applications that have allowed “more from less” with respect to geochemical measurements and their linkage with oceanographic variables. Furthermore, such technology needs to be increasingly applied to a wider range of foraminiferal sample materials (such as plankton tow) in order to better complement similar work that is traditionally done via sediment core-top materials.

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