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New oceanic proxies for paleoclimate

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Abstract

Environmental variables such as temperature and salinity cannot be directly measured for the past. Such variables do, however, influence the chemistry and biology of the marine sedimentary record in a measurable way. Reconstructing the past environment is therefore possible by ‘proxy’. Such proxy reconstruction uses chemical and biological observations to assess two aspects of Earth’s climate system – the physics of ocean–atmosphere circulation, and the chemistry of the carbon cycle. Early proxies made use of faunal assemblages, stable isotope fractionation of oxygen and carbon, and the degree of saturation of biogenically produced organic molecules. These well-established tools have been complemented by many new proxies. For reconstruction of the physical environment, these include proxies for ocean temperature (Mg/Ca, Sr/Ca, $\delta^{44}\text{Ca}$) and ocean circulation (Cd/Ca, radiogenic isotopes, ^{14}C , sortable silt). For reconstruction of the carbon cycle, they include proxies for ocean productivity ($^{231}\text{Pa}/^{230}\text{Th}$, U concentration); nutrient utilization (Cd/Ca, $\delta^{15}\text{N}$, $\delta^{30}\text{Si}$); alkalinity (Ba/Ca); pH ($\delta^{11}\text{B}$); carbonate ion concentration (foraminiferal weight, Zn/Ca); and atmospheric CO_2 ($\delta^{11}\text{B}$, $\delta^{13}\text{C}$). These proxies provide a better understanding of past climate, and allow climate–model sensitivity to be tested, thereby improving our ability to predict future climate change. Proxy research still faces challenges, however, as some environmental variables cannot be reconstructed and as the underlying chemistry and biology of most proxies is not well understood. Few proxies have been applied to pre-Pleistocene times – another challenge for future research. Only by solving such challenges will proxies provide a full understanding of the range of possible climate variability on Earth and of the mechanisms causing this variability. © 2002 Published by Elsevier Science B.V.

Keywords: paleo-oceanography; paleocirculation; sea-surface temperature; paleoclimatology; carbon cycle; climate

1. Introduction

Concern for the future in a warming world has led to a significant expansion of interest, beyond the daily and weekly pattern of the weather we

experience, to the long-term climate of the planet now and into the future [1]. Climate science is able to call upon a wealth of observational data in order to understand today’s climate, and plausible computer models can be built which mimic this climate and allow predictions of the future. These models require understanding of many Earth systems, particularly in two major areas – the physics of ocean–atmosphere circulation and the chemistry of the carbon cycle. Both are complex systems with multiple feedbacks. Models

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which mimic them must get all these feedbacks correct if they are to be as sensitive to changing conditions as is the real world. Such sensitivity is best assessed by looking at changes in climate during the geological past, but here there is a problem. We cannot observe the key physical and chemical variables – temperature, ocean salinity, etc – in a world which no longer exists. Instead, we must turn to proxies – things that can be measured in the sediment and ice records of the past, and that have responded systematically to changes in important but unmeasurable variables, such as temperature. Such proxies rely on either biology (which species were extant in the past?) or on geochemistry (how does the chemistry of the sediment respond to changing conditions?). The challenge for the biologists and geochemists who use proxies is to produce data about the past environment similar to the observational data used to understand present climate. In addressing this challenge, we gain a fuller history of the past climate of our planet and, through appropriate modeling, a better idea of its future.

2. A brief history of climate proxies

Since the birth of geology as a science, qualitative information about the past environment has been gleaned from the nature of preserved rocks and fossils. It was not until the middle of the twentieth century, however, that attempts to develop these observations into quantitative tools were seriously undertaken. Oxygen isotopes [2] were found to reflect changes in both temperature and ice volume and were summarized for the last 800 thousand yr (ka) in the SPECMAP record [3]. High-resolution $\delta^{18}\text{O}$ records now stretch back through the Cenozoic [4].

As early stable isotope measurements were being made, the species assemblage of marine microfossils was also developed as a paleoceanographic tool, leading eventually to the CLIMAP project [5]. This major collaborative effort conducted a global survey of the oceans to assess changes in temperatures and ice-cover during the last glacial–interglacial cycle. CLIMAP remains

the standard against which other proxies are judged and was a key step in developing quantitative understanding of Earth's past environment.

Stable isotopes [4] and species assemblages [6] have continued to be major paleoclimate tools but, in the years following CLIMAP, they have been complemented by many new proxies in oceanic, terrestrial and ice records. This review focuses on recently developed ocean-sediment proxies. Established tools, such as $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ and species assemblage have been summarized recently [7] and will not be discussed here. Similarly, this review stops short of discussing the past climates about which proxies have taught us [4,8].

3. Reconstructing the physical environment

3.1. Ocean temperature

Sea surface temperature (SST) is the most important variable for the Earth's climate system. It is the lower boundary which drives circulation in the atmosphere, generating winds and weather. It influences evaporation, controlling the water cycle and precipitation patterns. And it is the dominant variable controlling seawater density which drives deep-ocean circulation. Fortunately, it is also the variable which we are best able to reconstruct with respect to the past. Since the 1980s, ratios of biogenically produced unsaturated alkenones have been developed as a temperature proxy and have produced broadly consistent results with $\delta^{18}\text{O}$ and species assemblage approaches [9]. The use and limitations of this U_k^{37} paleothermometer have been fully summarized [9,10]. In addition to these established proxies, new paleothermometers applicable to marine carbonates have been developed. These proxies have enabled a re-evaluation of CLIMAP paleotemperatures and have led to a fierce debate about tropical SST during the last glacial. CLIMAP's species assemblage approach suggested SST similar to today, but early work with new proxies (coralline Sr/Ca) indicated up to 5°C of cooling. Application of further proxies (alkenones and Mg/Ca) have led to a developing consensus of glacial tropics cooler by $3 \pm 1^\circ\text{C}$ [9]. This 1°C precision is an indication of the uncer-

tainty on SST that can realistically be achieved with existing techniques.

3.1.1. Foraminiferal Mg/Ca

The development of Mg/Ca in foraminifera as a proxy for temperature is a perfect example of the development of a new paleoclimate tool. Such a development leads from the empirical or theoretical expectation of a relationship between a climate variable and a proxy, via testing in the laboratory and with modern sediments, to understanding of the use and limits of the proxy, and finally to application of the proxy to the past. In this case, Mg/Ca in marine carbonates varies

with latitude suggesting a temperature dependence. Early attempts to quantify this proxy were disappointing and indicated the presence of more than one control on foraminiferal Mg/Ca. The proxy only became useful when careful laboratory experiments isolated and quantified the temperature dependence [11,12] (Fig. 1). Core-top studies demonstrated that this relationship held in the real ocean [13] and the earlier problems were identified as due to partial dissolution of foraminifera at the sea floor [14]. Mg/Ca has since been successfully used to provide information about ocean temperatures during the Pleistocene [15,16] and on longer timescales suggesting,

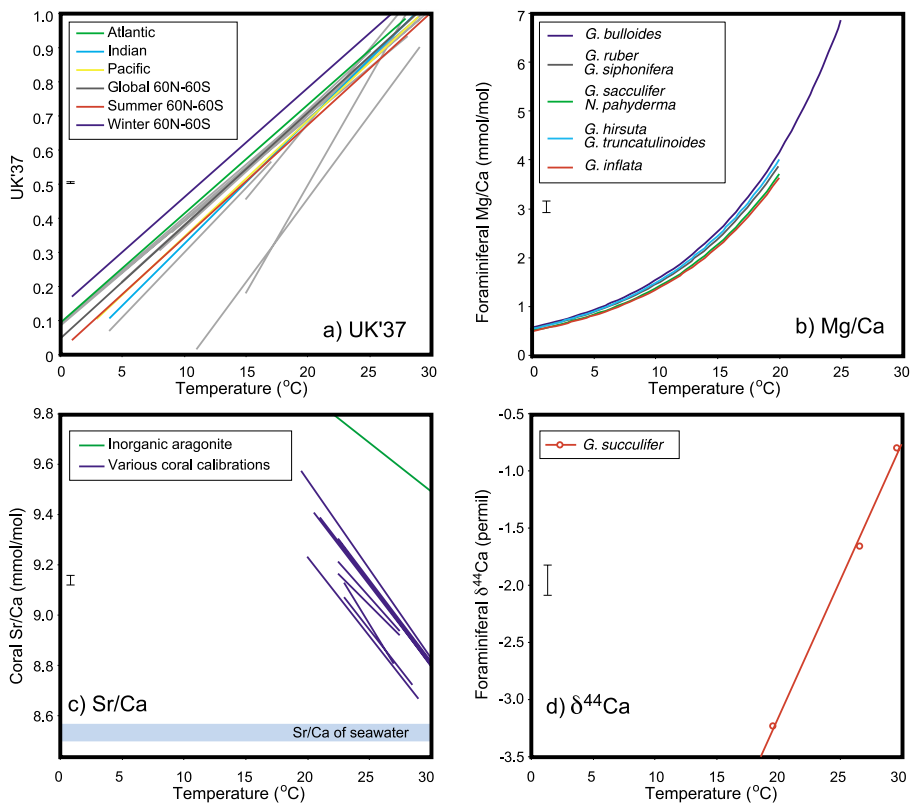


Fig. 1. Temperature sensitivity of ocean temperature proxies and their calibrated ranges. Typical 2σ measurement error is shown on the left hand axis for each proxy, but should not be taken as an indication of achievable temperature precision as calibration uncertainties generally outweigh analytical error. (a) UK'37 after Muller [10]. Gray lines are previous reconstructions summarized in that paper; colored lines represent whole ocean or global compilations; summer and winter calibrations use the same UK'37 data, but plotted against seasonal temperature. (b) Calibration curves for Mg/Ca in various species of planktonic foraminifera based on core-top measurements [13]. The curve for *G. bulloides* agrees with a laboratory culture study [11] which extended to warmer temperatures. (c) A compilation of calibrations of Sr/Ca in corals [20]. (d) The first calibration of $\delta^{44}\text{Ca}$ in foraminifera [21].

for instance, that the marine $\delta^{18}\text{O}$ change at ≈ 33 Ma is a change in ice volume rather than temperature [17]. The applicability of Mg/Ca on these longer timescales is limited, however, by lack of knowledge about past seawater composition. Seawater Mg/Ca cannot have changed significantly during the Pleistocene because of the long residence time of both elements but it may have changed on the million-yr timescale.

3.1.2. Coralline Sr/Ca

The trace element composition of coral skeletons also reflects changes in their growth environment [18]. Concentrations of several elements are known to vary with SST including Mg, U, and particularly, Sr. Despite initial concerns about changing seawater Sr/Ca and growth-rate effects, and lingering questions over the role of symbionts [19], this proxy is now reasonably mature with many completed studies, particularly of El Niño variability [20]. The major advantage of coralline Sr/Ca is that it offers subannual resolution so that both seasonal and interannual variability can be assessed. The big disadvantage is that surface-dwelling corals are limited to the tropical oceans.

3.1.3. Foraminiferal Ca isotopes

Foraminiferal $\delta^{44}\text{Ca}$ is a new and largely untested tool which may provide paleotemperatures [21] (Fig. 1). $\delta^{44}\text{Ca}$ might be more robust to diagenesis than Mg/Ca as Ca is a major element of calcite. Much work still needs to be done, however, to assess the temperature dependence of $\delta^{44}\text{Ca}$ and the $\delta^{44}\text{Ca}$ history of seawater [22].

3.2. Salinity

Salinity is the second variable, with temperature, that controls seawater density and deep-ocean circulation. Unfortunately no independent geochemical proxy for salinity has been discovered. Only two approaches allow assessment of paleosalinity. One is to use an independent temperature proxy, such as those above, to correct $\delta^{18}\text{O}$ for temperature so that residual $\delta^{18}\text{O}$ variations reflect changing salinities [23]. The other is to use a foraminiferal assemblage approach. Nei-

ther of these provide salinity assessments better than $\%_o$ 1 psu. Recent pore-water measurements have allowed deep-ocean salinity at the last glacial to be assessed at much better precision for a single site [24]. But extending paleosalinity measurements to other times and to the surface ocean, presents a major future challenge.

3.3. Ocean circulation

Tracers of past ocean circulation can be divided into two, i.e. those that record information about water mass distribution, and those that provide information about rates of flow. In the former category, the traditional proxies have been those that mimic nutrients – $\delta^{13}\text{C}$ and Cd/Ca [8,25]. Recent developments have seen radiogenic isotopes developed as water mass tracers, and new tools to reconstruct past flow rates.

3.3.1. Radiogenic isotope tracers of circulation

Isotope ratios of Nd, Pb and Hf exhibit spatial variability in the oceans due to variability in their continental sources and the short residence time of these elements. This gives them the potential to differentiate water masses which have indistinguishable nutrient signals. One problem with the use of radiogenic tracers is that of finding suitable substrates to record past seawater composition. Early work used manganese crusts [26] – an approach that, while successful, is limited to a resolution of $\approx 10^5$ yr. Other possible substrates are foraminifera [27] and Mn-rich material leached from deep-sea sediment [28]. Both show promise for reconstruction of past Nd-isotope compositions, but there are concerns about diagenetic increases in foraminiferal Nd concentrations and about mobility of tracers in Mn coatings.

A second problem with the use of radiogenic isotope tracers is that they are controlled not only by ocean circulation, but also by changes in the sources of Nd, Pb and Hf to the oceans. Assumptions about uniformity of source, or of circulation, have generally had to be made. This problem might be solved by using more than one of the isotope systems (as their differing residence times lead to a different length scale of advection) or by 3-D modeling [29].

3.3.2. The rate of deepwater flow

The rate of deepwater flow has traditionally been assessed using the radioactive decrease in ^{14}C which occurs when a water mass is removed from atmospheric exchange at the ocean surface [30]. Comparison of the ^{14}C age of planktonic with benthonic foraminifera from one depth in a sediment core provides an estimate of the ‘age’ of the deepwater and therefore of the rate of deepwater formation. This approach has been limited by bioturbation in marine sediments but has been rejuvenated by the success of paired U/Th and ^{14}C ages on deep-sea corals which make higher resolution studies possible [31,32].

Two insoluble products of uranium decay, i.e. ^{231}Pa and ^{230}Th , can also provide information about past flow rates (Fig. 2). As U has a constant concentration in seawater, these nuclides are formed uniformly at a known rate. ^{230}Th is very insoluble and is removed quickly to the sea floor [33]. ^{231}Pa is not so insoluble and can be advected away by circulation before it is removed to the sediment. For instance, low values of $^{231}\text{Pa}/^{230}\text{Th}$ under most of the Atlantic and high values in the Southern Ocean reflect advection of ^{231}Pa south-

ward in North Atlantic Deep Water (NADW) and its removal in the south. The Atlantic $^{231}\text{Pa}/^{230}\text{Th}$ distribution is similar for glacial sediments suggesting little change in the rate of deepwater flow [34]. Such an approach has been called into question by the realization that ^{231}Pa and ^{230}Th removal from seawater is very dependent on the composition of particles [35] making the Southern Ocean opal belt an effective remover of ^{231}Pa regardless of circulation rates. This is not a problem for the North Atlantic, however, and modeling of $^{231}\text{Pa}/^{230}\text{Th}$ data suggests that the flux of NADW could not have been more than 30% lower in the Last Glacial Maximum (LGM) than it is today [36].

Another approach to assessing flow rate is the average grain size in the fine fraction of sea-floor sediments. This technique relies on an observed relationship between bottom current speeds and the average grain size within the 10–63 μm portion of sediment [37]. It has been most recently applied to changes in deepwater flow into the Pacific [38].

3.4. Atmospheric circulation

Observational reconstruction of past atmospheric circulation is significantly more difficult than ocean circulation. In general, models of past atmospheric circulation remain untested against data [39]. One promising approach is the use of mineral dust in the atmosphere to trace circulation [39,40]. Dust source regions are fingerprinted mineralogically, chemically, and isotopically [40], allowing the provenance of dust found in ocean sediments or ice cores to be assessed [41].

4. Reconstructing the carbon cycle

The principal goal underlying carbon cycle research is to understand the controls on atmospheric CO_2 concentration (pCO_2^{at}). The oceans contain 50 times more carbon than the atmosphere [1] and, on timescales of 10^6 yr and shorter, must control pCO_2^{at} . Understanding the ocean carbon cycle is therefore crucial, but is made difficult by the fact that CO_2 does not simply dissolve in seawater but reacts with water so that the

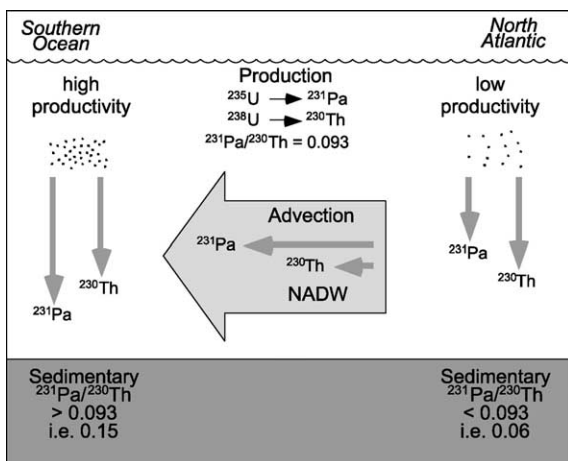


Fig. 2. Schematic of ^{231}Pa – ^{230}Th fractionation in the oceans. Both nuclides are formed from decay of U throughout the water column. The length of gray arrows represents the size of the fluxes illustrating that ^{230}Th is rapidly scavenged everywhere, while ^{231}Pa can be advected from areas of low to high productivity. Sedimentary $^{231}\text{Pa}/^{230}\text{Th}$ is therefore a function of both the productivity, and the advection of ^{231}Pa by ocean circulation.

total dissolved inorganic carbon (DIC) consists of four species, i.e. dissolved CO_2 ($[\text{CO}_2]_{\text{aq}}$), carbonic acid, bicarbonate ion, and carbonate ion. The relative concentrations of these species are controlled by the concentration of DIC relative to the acid-titrating capacity of seawater, its ‘alkalinity’. Only $[\text{CO}_2]_{\text{aq}}$ can interact with the atmosphere to set pCO_2^{at} , but assessment of other variables in the carbon cycle is necessary if the amplitude and mechanisms of past $[\text{CO}_2]_{\text{aq}}$ variations are to be understood. A full description of the carbon cycle lies outside the scope of this review but can be found elsewhere [42,43]. Proxies developed in the last few years offer potential to significantly improve our understanding of the past carbon cycle making this an exciting time for such research.

4.1. Productivity

Biological productivity in the surface ocean transports carbon to depth, removing it from the atmosphere. Past productivity cannot be assessed by simply looking at the accumulation rate of biogenic sediments because most biogenic materials partially dissolve in the water or at the sediment surface. Biogenic barite does not dissolve so readily, however, so sedimentary fluxes of this mineral have been used to assess past productivity. This approach has been complemented by two new chemical proxies.

The difference in solubility of Th, Pa, and Be provides a paleoproductivity proxy (Fig. 2). Pa and Be are more soluble than Th and can be advected by ocean currents to be removed in areas of high particle flux, leading to a positive correlation between Pa/Th (or Be/Th) and productivity [44]. The use of these proxies is complicated by the importance of ocean circulation in advecting the nuclides (see above and Fig. 2) but they have nevertheless provided past productivity estimates in agreement with those derived from other proxies [45].

Another productivity proxy is sedimentary U concentration [44,46]. U is in its soluble 6+ oxidation state in seawater, but is insoluble when reduced to its 4+ state. High fluxes of organic material to sea-floor sediment causes it to become

reducing and therefore to concentrate U from the overlying water. Whether sediments become reducing is also dependent on the supply of oxygen from the overlying water so this effect must again be deconvolved, either by the use of other proxies [45] or by collecting records from geographically distributed sites [46].

4.2. Nutrient utilization

Waters upwelling from the deep-ocean bring high concentrations of nutrients and DIC to the surface. Over most of the oceans these nutrients are quickly utilized and returned to depth as biogenic particles, thereby reabsorbing the DIC brought to the surface. In some areas, however, nutrients are not fully utilized so that some of the upwelling DIC is liberated to the atmosphere as CO_2 . Changes in Southern Ocean nutrient utilization may have played an important role in modulating pCO_2^{at} during glacial cycles [43]. There are three major biolimiting nutrients – phosphate, nitrate, and silicate. Utilization proxies exist for each of these, and new proxies are being developed to assess the utilization of key trace elements such as Fe.

Phosphate is incorporated in the organic portion of biogenic material and is not well preserved in the sediment. Cd, however, has a very similar oceanic behavior to phosphate (Fig. 3) and substitutes readily into calcite (see appendix section 1). Cd/Ca in benthonic foraminifera has been used extensively to reconstruct the phosphate content of deepwaters and learn about the pattern of past deepwater flow [25]. In planktonic foraminifera, Cd/Ca allows reconstruction of surface ocean phosphate utilization. Measured Cd/Ca requires correction for the temperature dependence of Cd/Ca incorporation into foraminifera [47] and for a slight preference during productivity for Cd over phosphate [48]. But these problems can be negotiated and Cd/Ca has been used to assess phosphate utilization during glacial cycles in the Southern Ocean [48].

Organic material preferentially incorporates the light isotope of nitrogen. As nitrate is used in the surface ocean the remaining nitrate becomes isotopically heavier (see Appendix, Section 2). $\delta^{15}\text{N}$

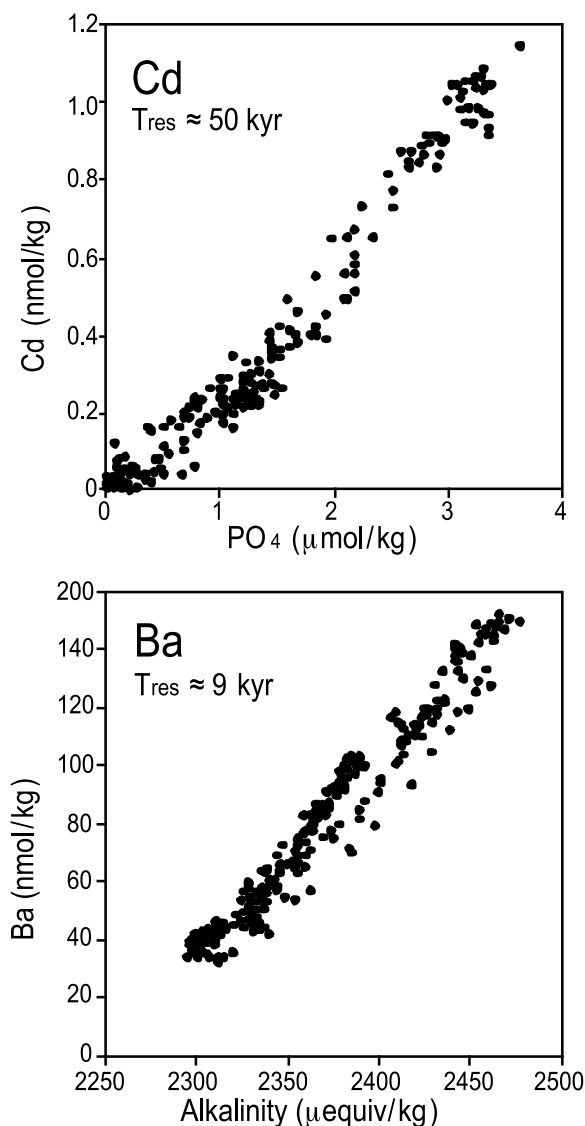


Fig. 3. Phosphate and alkalinity are important ocean variables which are not directly recorded in ocean sediments. Seawater Cd and Ba show a strong empirical relationship to these properties, however, and readily replace Ca in the calcite structure to provide measurable proxies. Also shown are ocean residence times for Cd and Ba which indicate the time-scale on which the seawater concentration might change and complicate the use of the proxy.

in marine organic matter therefore reflects the degree of nitrate utilization in the surface ocean [49] – the higher it is, the more completely nitrate is being used. Similarly, biogenic opal preferentially incorporates the light isotope of Si so that $\delta^{30}\text{Si}$

can be used to assess silicate utilization [50]. And the recent ability to measure transition metal isotope ratios indicates that biological productivity also prefers the light isotopes of important trace metals such as Zn [51], Fe [52,53], and Mo [54].

4.3. Alkalinity and weathering fluxes

There are two important aspects to ocean alkalinity – its average ocean value, and its distribution. Together, these influence the speciation of carbon in the surface ocean and therefore the amount of CO₂ that can be drawn from the atmosphere into the oceans. Foraminiferal Ba/Ca has been used to reconstruct past alkalinity distributions [55] but, as Ba has only a 9-kyr residence time, it is also possible that such measurements reflect whole ocean changes. No unambiguous proxy presently exists to assess past whole ocean alkalinity. Even the past flux of alkalinity to the oceans from continental weathering is poorly constrained. Oceanic $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{187}\text{Os}/^{186}\text{Os}$ have been used to assess its Pleistocene [56,57] and longer-term variability [58,59]. Both these proxies rely on the high ratios found in continental rocks increasing the oceanic value during times of high continental weathering. But they are both ambiguous as the ocean value is also controlled by the precise isotope ratio of weathered material, and by the flux of hydrothermal material to the oceans. As continental weathering plays an important part in the carbon cycle, not just for its role in supplying alkalinity to the ocean, but also in providing nutrients and in the draw-down of CO₂ during silicate weathering, the lack of a reliable weathering proxy is a serious omission from our toolbox.

4.4. pH

The reconstruction of past seawater pH is possible because B occurs as two species in seawater whose relative concentration is dependent on pH. $\text{B}(\text{OH})_4^-$ is $\approx 20\%$ isotopically lighter than $\text{B}(\text{OH})_3$ and so has a $\delta^{11}\text{B}$ that varies from the average seawater value when all B is $\text{B}(\text{OH})_4^-$, to 20% lighter than average seawater when nearly all B is in the other form. Only $\text{B}(\text{OH})_4^-$ is incor-

porated into marine carbonate so the $\delta^{11}\text{B}$ of carbonates changes with B speciation, and therefore with pH. This proxy has been tested in the laboratory by inorganic and by culturing experiments [60] and has been used to assess pH during glacial cycles [61] and on longer timescales [62]. Despite the long residence time of B (14 Ma), seawater $\delta^{11}\text{B}$ may vary with time [63]. But reconstruction of surface and deep-ocean $\delta^{11}\text{B}$, coupled with the curvature of the $\delta^{11}\text{B}$ –pH relationship, suggest that changes in ocean $\delta^{11}\text{B}$ have not been large, otherwise unrealistic surface to deep pH contrasts would be implied [62].

4.5. Carbonate ion concentration

Carbonate ion concentration ($[\text{CO}_3^{2-}]$) in the deep-ocean has traditionally been assessed by reconstructing the water depth at which all calcite has dissolved from the sediment. A more quantitative proxy for $[\text{CO}_3^{2-}]$ is the mass of individual foraminifera of a particular size [64]. Foraminifera dissolution begins well above the depth at which they completely dissolve and the degree of this partial dissolution is dependent on the saturation state of the water, i.e. its $[\text{CO}_3^{2-}]$. The use of foraminiferal mass has been used to reconstruct $[\text{CO}_3^{2-}]$ changes during glacial cycles [65]. It is also possible that foraminiferal Zn/Ca may be a proxy for $[\text{CO}_3^{2-}]$ [66] but this tool has not yet been applied to paleorecords.

4.6. Atmospheric CO_2 concentrations

Extending knowledge of pCO_2^{at} beyond the oldest direct measurements possible in ice cores has been a long-standing desire of proxy research. Significant recent advances have been made using two oceanic proxies. The first is a refinement of a long-standing proxy – carbon isotopes in marine organic material. Measuring $\delta^{13}\text{C}$ on molecules distinct to a single group of organisms, rather than on total marine organic material, circumvents many of the previous problems with this proxy. This approach has indicated that pCO_2^{at} remained at levels quite similar to today from 15 to 5 Ma [67].

This result is in good agreement with a longer

record of pCO_2^{at} reconstructed using the pH of the oceans [62]. pH does not uniquely constrain pCO_2^{at} but can be used to calculate it if assumptions about past ocean alkalinity and DIC are made. Even if such assumptions are wrong in detail, the general sense of pCO_2^{at} changes will be correct, i.e. lower pH = higher pCO_2^{at} . In addition to supporting the $\delta^{13}\text{C}$ reconstructions of pCO_2^{at} for 15–5 Ma, this approach has indicated pCO_2^{at} up to ten times present level at ≈ 60 Ma. This result should be tested against $\delta^{13}\text{C}$ reconstructions before the ability of both proxies to reconstruct high pCO_2^{at} can be fully trusted.

5. Future challenges

Major challenges still limit our ability to use proxies to fully understand the past environment. An obvious example is that there are environmental variables for which we have no precise proxy (e.g. salinity, alkalinity, continental weathering, atmospheric circulation).

Even for existing proxies, more work is required to ground truth and better understand them. It is tempting, when handed a new tool, to apply it to many paleoclimate questions but such application must be accompanied by thorough testing of the proxy. All proxies respond to more than one variable, some of which can be overlooked. An example has been the recent discovery of changes in foraminiferal $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ with changes in $[\text{CO}_3^{2-}]$ [68]. This result forces a reinterpretation of many existing stable isotope records and demonstrates the need to fully understand the controls on a proxy before overusing it. Most efforts to achieve such understanding have relied on empirical studies. Another challenge for the future is to support these empirical observations with chemical and biological understanding of the processes that control the proxy. What biological mechanism is it, for example, that causes changes in foraminiferal Mg/Ca with temperature to be larger than those observed for inorganic calcite? Such understanding, as well as being a worthwhile scientific goal in its own right, will teach us about the limits in applicability of proxies.

A major challenge for proxy research is to generate sufficient data to thoroughly test climate models. Observations of modern climate form a dense spatial and temporal grid. Ideally, proxy data should aim to deliver similar data densities. Clearly, this is unrealistic, but the density of reliable proxy information needs to be increased to better reconstruct climate in both space and time. To ensure the usefulness of such data, scientists developing and applying proxies must work ever more closely with physical modelers to ensure a focus on critical regions within the climate system.

The future will also see application of new proxies to the pre-Pleistocene. Some, like $\delta^{11}\text{B}$, have already joined $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the study of climate history throughout the Cenozoic. But most new proxies have only been applied to the Pleistocene. High-resolution records of pre-Pleistocene climate events (e.g. [69]) demonstrate that they can be investigated at similar resolution to that common for the Pleistocene. Two challenges in extending proxies to longer timescales are, however, that diagenesis becomes a bigger problem [70] and that seawater chemistry is not well known. It does not matter how well we know the controls on incorporation of Mg into foraminifera, for instance, if the seawater Mg concentration was dramatically different in the past. Fluid inclusion analysis seems to offer a means to address this problem [71] and will be important if many geochemical proxies are to be used to construct long records.

Despite the challenges that lie ahead, the good news for paleoclimate proxy research is clear. The last two decades has seen major advances beyond the work of SPECMAP and CLIMAP. These advances have provided a wealth of new proxies, and a wealth of new climate knowledge. Such proxies are the key to the past, and the past the key to the future.

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Appendix

1. The biology

Proxy information is recorded in many sediment materials including opal, manganese crusts, detrital particles and organic matter. It is biogenically produced carbonates, however, that have provided the majority of such information.

Corals form an aragonite skeleton which contains annual density bands allowing subannual environment reconstruction. Surface-dwelling hermatypic corals that contain symbiotic zooanthellae grow rapidly and have been most useful, particularly those, such as *Porites*, that form as massive ‘head’ corals and may contain several hundred years of growth. The growth and geochemistry of such corals has been well summarized [18], as has their use for paleoclimate reconstruction [20]. Unlike these hermatypic corals, solitary corals are not restricted to tropical surface waters and have been the focus of recent interest [31]. Their annual banding is finer, less distinct, and morphologically more complicated [72], posing analytical challenges for their use as high-resolution recorders of the past environment.

Foraminifera are protozoans which form carbonate shells tens to hundreds of microns in diameter. Both surface-dwelling (planktonic) and sea-floor dwelling (benthonic) forms exist, allowing reconstruction of surface and deep paleoceanography. Planktonic species can be spinose and symbiont bearing, or non-spinose and devoid of symbionts. Both types capture the chemistry and conditions at the depth where they grow in their shells, or ‘calcify’. Few species calcify entirely while in the uppermost mixed layer of the water column. As temperature, salinity and nutrients all vary greatly with depth this leads to complications in the interpretation of proxy records. The presence of symbionts in spinose species leads to the formation of a micro-environment around the foraminifera and chemical proxies such as $\delta^{18}\text{O}$ are slightly offset from equilibrium. There are a large number of benthonic species. Those used for paleoreconstructions must be reasonably common and epifaunal (rather than living within the sedi-

ment where pore-water chemistry may differ from bottom-water chemistry). Commonly used species which fit these criteria include *Cibicides wuellerstorfi* and *Uvigerina* sp. A limitation in the use of both planktonic and benthonic foraminifera is that bioturbation in the sediment limits the achievable time resolution to about 1000 yr in typical marine sediments and about 100 yr in rapidly accumulating drift deposits.

2. The chemistry

Most proxies rely on the geochemistry of marine sediments. These geochemical proxies can be divided into four classes:

1. Organic molecules

These are long-chain molecules generated by particular marine organisms, also known as biomarkers. The most commonly used is the degree of unsaturation in an alkenone molecule (U_k^{37}) to assess SST [9], but other proxies exist.

2. Stable isotope ratios

Isotope fractionation of O and C have been the mainstays of proxy work [7] but isotope fractionation of many other elements is also useful. The degree of fractionation is normally ex-

pressed in parts per thousand (‰) relative to a standard:

$$\delta^nZ = 1000 \times (R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}}$$

where R is the ratio of two isotopes of element Z, with n the numerator. n is normally the heavier of the two isotopes so that positive δ^nZ represents a sample isotopically heavier than the standard. A common feature of stable isotope fractionation in nature is that of Rayleigh fractionation in which a chemical constituent is removed from the system as it forms. If the constituent removed is isotopically light, then the material remaining in the system must become isotopically heavy. An example is the incorporation of isotopically light material into organic matter and subsequent removal from the surface ocean. This means that the heavier the organic material found in marine sediment, the more completely has that element been removed from the surface ocean system (Fig. 4).

3. Radiogenic isotopes

Isotopes formed from radioactive decay have a wide use. Those that are stable (e.g. ^{87}Sr , ^{187}Os , ^{143}Nd) can be used to assess the flux of material from continent to ocean. Those that are insoluble and are rapidly removed to the

Commonly used planktonic foraminifera

Non-spinose

<i>Globorotalia menardii</i>	Large tropical thermocline or subthermocline species.
<i>Globorotalia truncatulinoides</i>	Cool subtropical species with a large depth range.
<i>Globorotalia inflata</i>	Subtropical to subpolar species growing below the thermocline.
<i>Neogloboquadrina dutertrei</i>	Tropical thermocline dweller.
<i>Neogloboquadrina pachyderma</i>	Lives over a wide depth range. The sinistral form favors polar waters and the dextral one subpolar–subtropical waters.
<i>Pulleniatina obliquiloculata</i>	Tropical surface and thermocline dweller.
Spinose:	
<i>Globigerina bulloides</i>	Subpolar, surface layer and upper thermocline. Unusual for a spinose form in lacking symbionts.
<i>Globigerina quinqueloba</i>	Subpolar, surface layer and upper thermocline.
<i>Globigerinoides sacculifer</i>	Commonly used due to its wide latitude range from tropical to subtropical. Calcifies in the surface mixed layer.
<i>Globigerinoides ruber</i>	Calcifies entirely in the surface mixed layer making it ideal for surface reconstruction. Found in tropical and subtropical waters.
<i>Orbulina universa</i>	Found over a wide latitude range. Commonly used for culturing experiments as it grows much of its calcite in a final encasing stage. As this forms at some depth it is not a good species for sea surface reconstruction.

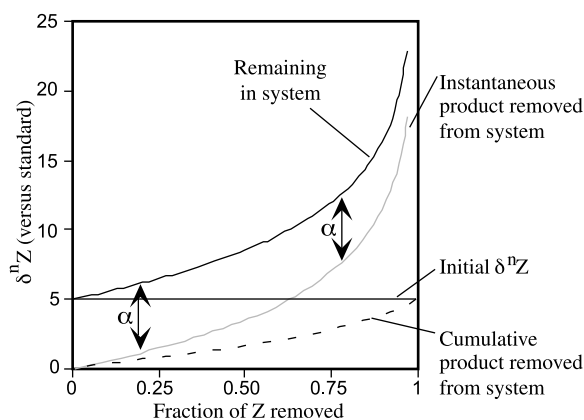


Fig. 4. The effect of Rayleigh fractionation on the isotope ratio of surface ocean nutrients and organic material [73]. α is the isotope fractionation factor between the dissolved species and the organic material. As organic product is removed to the sediment, the surface ocean becomes isotopically heavier.

sediment by ‘scavenging’ onto particles show spatial variability which allows their use to assess ocean circulation and productivity (e.g. ^{143}Nd , ^{231}Pa , ^{10}Be).

4. Trace metal ratios

Trace metal concentrations in carbonates are normally expressed as a ratio to Ca (e.g. Cd/Ca). Z/Ca measurements can be used to assess the chemistry of the water in which the carbonate grew, or may be fractionated by environmental factors in a similar manner to stable isotopes. A major challenge for trace metal techniques is to adequately clean samples prior to analysis as surface coatings, added after formation of the carbonate, often contain significant quantities of the trace metal of interest. This challenge was solved by the pioneering work of Boyle [25]. Trace metals are generally not incorporated into carbonate at the Z/Ca found in seawater. This reflects the imperfect fit of the trace metal into the structure of the carbonate, and the processes of biological calcification. Attempts to understand this incorporation have been made [74], but are still in their infancy. Incorporation is normally assessed empirically and is expressed as a distribution coefficient, D (where $D = (\text{Z/Ca})_{\text{carbonate}} / (\text{Z/Ca})_{\text{seawater}}$). D can vary with environmental factors such as temperature or carbonate ion

concentration. Such variation is useful as it enables these environmental factors to be assessed in the past. But it can also be a complication when attempting to reconstruct past seawater chemistry.

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