

## **Marine paleoclimatic proxies: A shift from qualitative to quantitative estimation of seawater parameters**

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### **Abstract**

Understanding past climate during contrasting boundary conditions can help in assessing imminent climate changes. Marine sediments offer a vast archive of past climate. Various indirect methods called proxies are used to infer principal climate parameters like temperature, salinity, productivity, monsoon intensity, ocean circulation, seawater pH, and others, from the marine sediments. The relationship between a climate parameter and marine paleoclimate proxy may vary from region to region. Additionally, the marine proxies are often affected by more than one climate parameter, thus making it difficult to assess the change in any particular parameter from a single proxy. Diagenetic alteration can also significantly affect the parameter-proxy relationship. A growing emphasis now is on quantifying changes in key climatic parameters in the past. Proxies for quantitative estimation of seawater temperature, runoff, sea-level and pH are now fairly well established. Similar robust quantitative proxies for dissolved oxygen concentration and productivity, are, however, still being developed. Additionally, the uncertainty associated with quantitative estimation of past climate has to be reduced. Therefore, continuous efforts are being made to develop novel paleoclimate proxies and to evaluate existing proxies in different regions of the world oceans.

## **Introduction**

Oceans occupy two-third of the earth and act as the ultimate sink for a large fraction of terrestrial detritus as well as freshwater. The type and volume of terrestrial flux into the ocean depend on climatic conditions. The oceanic state and thus the organisms are also a manifestation of the prevailing climate. The terrestrial flux as well the remains of organisms in the oceans, finally settle down to the ocean bottom. The thick pile of sediments on the ocean floor, a direct result of continuous deposition of this material, acts a vast paleoclimatic archive. The oceanic deposits have helped to unravel earth's past. A continuous effort has been made to develop effective proxies to reconstruct earth's past from marine archives. The proxies were initially developed by studying the relationship between modern ambient physico-chemical conditions and the proxy carriers in the field. In this manner, at times, it was difficult to assign a particular response to ambient parameters. Subsequently, attempts were made to simulate the field conditions in the laboratory and study the response of the proxy carriers to a particular or a combination of parameters (Lea *et al.*, 1999; Saraswat *et al.*, 2015). The laboratory simulations helped both in developing novel and refining existing proxies. The proxy carriers include sediments as well as remains of both terrestrial and marine organisms. The sediment based proxies include grain-size, clay mineralogy, and geochemistry (major, minor and trace element composition, rare earth elemental composition, isotopic ratios). The organic remains based proxies make use of climate-induced changes in the abundance, diversity, and composition of an organism (Bradley, 2014). A majority of the paleoclimatic studies tried to reconstruct past seawater temperature, salinity, dissolved oxygen, productivity, water column stratification, freshwater influx, pH, thermohaline circulation, diagenetic processes and carbon cycling. For long, proxies provided valuable information on qualitative changes in the past climate. General circulation models have since been developed to understand climate dynamics, however, these models require quantitative estimates of key parameters during different boundary conditions in the past. Therefore, increasing emphasis is on developing proxies to reconstruct quantitative changes in the key climatic parameters in the past. Marine proxies, especially those used for quantitative estimation of a few key parameters (temperature, salinity, pH, sea-level, dissolved oxygen, productivity), are discussed in the subsequent section.

### **Temperature proxies**

The seawater temperature, especially at the surface varies with atmospheric temperature. Thus, past records of seawater temperature are useful to understand changes in global temperature. The development of a technique to measure the stable isotopic ratio of biogenic carbonates resulted in a

big shift in past climatic reconstruction (Epstein *et al.*, 1951). The stable isotopic analysis helped in quantitative estimation of key climatic parameters. Initially, the entire change in stable oxygen isotopic ratio of marine biogenic carbonates was attributed to seawater temperature (Emiliani, 1955). However, soon, it was realized that ice volume drives the large part of the change in isotopic composition (Shackleton, 1967). Later, vital effects (Erez, 1978), salinity and carbonate ion concentration (Spero *et al.*, 1997), were also identified to influence the stable oxygen isotopic ratio. Given these complications, the need for an independent temperature proxy was widely felt. This led to the application of artificial neural network to reconstruct past temperature from microfossils (foraminifera, radiolarian, coccolithophores) abundance. The first comprehensive effort to reconstruct past sea-surface temperature variations, especially during the last glacial maximum, was made as a part of the Climate Long-range Investigation, Mapping and Projection (CLIMAP) Project. CLIMAP applied abundance variations of planktic organisms (foraminifera, radiolarian, coccolithophore) to reconstruct past seawater temperatures. The CLIMAP study showed that the August sea surface temperature (SST) was cooler by 1°C to 8°C during the last glacial maximum (CLIMAP, 1976; 1981). However, CLIMAP reconstructed seawater temperature had  $\pm 1.6^\circ\text{C}$  error. Subsequently, the alkenone unsaturation ratio ( $U^{k}_{37}$ ) (Brassel *et al.*, 1986) of the sedimentary organic matter of marine origin as well as tetraether index of tetraethers consisting of 86 carbon atoms ( $\text{TEX}_{86}$ ) (Schouten *et al.*, 2002) were found to vary in tandem with the ambient temperature. The biomarker proxies, however, are affected by a deeper export depth (Hertzberg *et al.*, 2016), seasonality of marine productivity, lateral advection, diagenetic alteration (Hoefs *et al.*, 1998) and change in species composition over long time intervals (Bijma *et al.*, 2001).

Meantime, the empirical relation between magnesium to calcium ratio (Mg/Ca) of foraminifera and strontium to calcium ratio of corals and ambient temperature was demonstrated and used to reconstruct past temperature. Initially, Mg/Ca ratio of foraminifera was reportedly dominantly affected by ambient temperature (Mg incorporation in shells being an endothermic process) and minimally affected by both the pH and salinity (Lea *et al.*, 1999). Later, several studies from high salinity regions as well as laboratory culture studies suggested a pronounced effect of salinity on benthic foraminiferal Mg/Ca ratio (e.g., Dissard *et al.*, 2010). Additionally, the resolution of foraminiferal Mg/Ca temperature depends on sedimentation rate and is usually coarser than a decade. Coral chemistry has been used to reconstruct shorter timescale, sub-decadal to annual resolution, paleotemperature. The corals also incorporate several elements in a trace amount, in their aragonite skeleton. The strontium to calcium ratio of massive hemispherical *Porites* coral is a reliable seawater temperature proxy with a precision of  $0.5^\circ\text{C}$  (Beck *et al.*, 1992). The coral Sr/Ca

paleotemperature estimates are, however, restricted to tropical regions with a temperature above 18°C (Corrège, 2006). Additionally, the growth rate also significantly affects the coral Sr/Ca (de Villiers *et al.*, 1995).

The long residence time of calcium in seawater (Zhu and Macdougall, 1998) and imperceptible diagenetic effects (Nägler *et al.*, 2000), suggested a potential application of  $^{44}\text{Ca}/^{40}\text{Ca}$  ratio to infer past temperatures. The Ca isotopic composition of various compounds has been reported to vary as per both the isotopic fractionation during biological (Skulan *et al.*, 1997) and physical-chemical processes, and the production of  $^{40}\text{Ca}$  from the  $\beta$  decay of  $^{40}\text{K}$ . But, contrasting results and limited fractionation have hampered the application of calcium isotopes as an efficient paleotemperature proxy (Skulan *et al.*, 1997; Nägler *et al.*, 2000; Sime *et al.*, 2005; Griffith *et al.*, 2008).

Recently, the clumped-isotopic ratio of biogenic carbonates was suggested as another seawater temperature proxy (Ghosh *et al.*, 2006). The technique relies on the fact that the concentration of  $^{13}\text{C}-^{18}\text{O}$  bonds in both the inorganic and biogenic carbonate is a function of the ambient temperature. The advantage of this technique lies in the fact that the thermodynamically controlled preferential pairing of two heavy isotopes is independent of their absolute abundance in the carbonate. The temperature is estimated by calculating the  $^{13}\text{C}^{18}\text{O}^{16}\text{O}$  enrichment in  $\text{CO}_2$  released after dissolving carbonate in phosphoric acid, relative to its expected concentration in a random distribution of isotopes among all  $\text{CO}_2$  isotopologues (Ghosh *et al.*, 2006). A common calibration has been proposed for diverse biogenic carbonates as the  $^{13}\text{C}-^{18}\text{O}$  pairing does not depend on its absolute concentration in the source material (Eiler, 2011). However, a few organisms do not follow the common calibration most likely because of the group specific vital effect related to the growth rate (Saenger *et al.*, 2012). Therefore, further work is required to understand the robustness of clumped-isotopic ratio of biogenic carbonates as a paleotemperature proxy.

### **Salinity proxies**

Seawater salinity depends on the evaporation-precipitation budget as well as riverine and glacial melt influx. On glacial-interglacial time scales, ice-volume contribution corrected salinity estimates are good indicator of regional monsoon changes (Saraswat *et al.*, 2012). Quantitative estimates of past salinity have so far been reconstructed from either stable oxygen isotopic ratios or a combination of both the  $\delta^{18}\text{O}$  and an independent temperature record estimated from Mg/Ca or alkenone unsaturation ratio. Salinity estimated by following this method, however, has large associated uncertainty (Rohling, 2007). As an alternative, deuterium to hydrogen ratio (D/H or  $\delta\text{D}$ ) of lipid

biomarkers was suggested as a paleosalinity proxy, provided the source water isotopic composition is known from independent proxies like  $\delta^{18}\text{O}$  of biogenic carbonates. Water gets enriched in deuterium as the salinity of source water increases, resulting in higher  $\delta\text{D}$  values. The  $\delta\text{D}$  value, however, also varies with changes in the isotopic composition of the source water (Sachse and Sachs, 2008). Additionally, differences in the core metabolism of the microorganisms modulate the effect of salinity on the D/H ratio of fatty acids, resulting in a large difference in  $\delta\text{D}$ -salinity relationship between photoautotrophic and heterotrophic microorganisms (Heinzelmann *et al.*, 2015). The salinity from freshwater influx dominated regions can also be estimated from the barium to calcium (Ba/Ca) ratio of foraminifera (Lea and Boyle, 1991; Saraswat *et al.*, 2013). The application of the Ba/Ca ratio for freshwater influx induced variations in salinity arises from the fact that riverine water is rich in Ba. The use of Ba/Ca ratio to reconstruct past salinity is, however, restricted to regions affected by the large freshwater influx. Recently, Wit *et al.* (2013) studied sodium incorporation in benthic foraminifera cultured at a range of salinity. The culture experiment, as well as a later field study (Mezger *et al.*, 2016), suggests that ambient salinity controls foraminiferal Na/Ca ratio and thus can be used to reconstruct past salinity. A comparison of salinity estimated from Na/Ca ratio with that from Ba/Ca and paired  $\delta^{18}\text{O}$  and temperature on the same set of sediments, will help in assessing the applicability of these proxies.

### **pH proxies**

Anthropogenic greenhouse gas emission-induced drop in ocean pH led to increased efforts to reconstruct past ocean pH. Both the elemental and stable isotopic ratio of biogenic carbonates have been used to reconstruct past pH. Boron has two dominant aqueous species in seawater, namely  $\text{B}(\text{OH})_3$  (boric acid) and  $\text{B}(\text{OH})_4^-$  (borate ion) (Hershey *et al.*, 1986). Of these, only the isotopically lighter tetrahedral  $\text{B}(\text{OH})_4^-$  enters in marine carbonates with insignificant boron isotopic fractionation between seawater and carbonate, during its incorporation (Hemming and Hanson, 1992). Since the availability of  $\text{B}(\text{OH})_4^-$  in seawater depends on the pH of seawater (Hemming and Hanson, 1992), the boron isotopic composition of foraminifera indicates the pH of seawater. Spivack *et al.* (1993) showed the potential application of foraminiferal boron isotopes to infer past seawater pH. This possibility was further strengthened by laboratory culture experiments of foraminifera and inorganic precipitation of calcite at different pH values (Sanyal *et al.*, 1996; 2000). However care should be taken in application of boron isotopic ratio to reconstruct past pH, as species-specific vital effects, mainly due to respiration and photosynthesis, strongly modulate  $\delta^{11}\text{B}$  (Hönisch *et al.*, 2003). The boron to calcium ratio of biogenic carbonates also depends on ambient pH and thus can be used to

reconstruct past pH. However, B/Ca ratio has to be corrected for ambient temperature by using an independent proxy, as a strong species-specific dependence on calcification temperature has been determined in planktic foraminifera (Yu *et al.*, 2007). Additionally, subsequent studies clearly suggest that salinity and phosphate ion concentration, as well as seawater boron concentration significantly affect foraminiferal B/Ca ratio (Henehan *et al.*, 2015). Recently, it was demonstrated that on time scales shorter than the residence time, both the lithium isotopic ratio ( $\delta^7\text{Li}$ ) as well as lithium/calcium of benthic foraminifera is insensitive to ambient temperature and pH but varies in tandem with the dissolved inorganic carbon (Vigier *et al.*, 2015). Therefore, both the Li/Ca and  $\delta^7\text{Li}$  can also be used to understand past carbon cycling.

### **Sea-level proxies**

A large fraction of the human population resides in coastal regions. Additionally, some human-inhabited islands are barely above the present mean sea-level and threatened by anthropogenic greenhouse gas induced global warming. Therefore, it is important to understand factors affecting sea-level. Tide-gauge data of sea-level is available for only the last hundred or so years (Unnikrishnan and Shankar, 2007). Corals with annually resolved growth bands, have often been used to reconstruct short-term regional sea-level changes. Paleo sea-level reconstructions from corals rely on their species-specific restricted depth habitat and precise dating of old corals by uranium-thorium chronology. Corals try to maintain the pace with the ambient sea-level and thus preserve the sea-level signatures. Corals are, however, geographically restricted. Additionally, abrupt sea-level changes cannot be precisely reconstructed from corals. The coral reef based sea-level records before the last interglacial are rare, thus limiting their application (Woodroffe and Webster, 2014). The temporal variation in the ice-sheet extent is the major contributor to the glacial-interglacial sea-level changes (Pirazzolli, 1996). The long-term past sea stand has been reconstructed from stable oxygen isotopic ratio of deep dwelling benthic foraminifera. Evaporation results in preferential removal of the lighter oxygen isotope ( $^{16}\text{O}$ ) from seawater. During the glacial period, lighter oxygen isotope rich water gets locked up in ice sheets. The resultant seawater is enriched in the heavier oxygen isotope ( $^{18}\text{O}$ ). The influx of lighter oxygen isotope rich glacial melt water during warm interglacial reduces seawater oxygen isotopic ratios. The relationship between the amount of glacial influx and a subsequent change in oceanic  $\delta^{18}\text{O}$  is precisely estimated and used to quantify glacial-interglacial sea-level variations (Rohling *et al.*, 2014). The uncertainty associated with sea-level reconstructed by using this technique is on the order of a few meters (Rohling *et al.*, 2014). The increase in abundance of planktic foraminifera with depth, as compared to that of benthic, has also been used to develop

paleo-depth models that can be used to reconstruct past sea-level (Nigam and Henriques, 1992). The high sea stand in the past also leaves its signatures on the land. The resultant geomorphological signatures help to reconstruct past high sea stands (Hashimi *et al.*, 1995).

### **Dissolved oxygen proxies**

The dissolved oxygen concentration in seawater is one of the main environmental factors that controls the distribution, abundance and diversity of macro- as well as micro-organisms in the oceans (Levin, 2003; Nigam *et al.*, 2007; Jorissen, 2007; Woulds *et al.*, 2007; Gooday *et al.*, 2010). The qualitative changes in dissolved oxygen concentration in the past has been reconstructed from molybdenum concentration (Emerson and Husted, 1991; Algeo and Tribovillard, 2009), sulfur isotopic ratio (Thode, 1991; Planavsky *et al.*, 2012), organic carbon to sulfur ratio and morphology of benthic foraminifera (Kaiho, 1994; Nigam *et al.*, 2007). Benthic foraminiferal characteristics have often been used to reconstruct intensity and extent of past oxygen minimum zones (OMZ), as they are an important link in organic matter processing in the OMZ. At low oxygen concentration (dissolved oxygen <0.11 ml/L), organic matter uptake is dominated by benthic foraminifera (Woulds *et al.*, 2007). Foraminiferal assemblages have the added advantage to delineate oxic (>1.5 ml/L O<sub>2</sub>) and suboxic (0.3-1.5 ml/L O<sub>2</sub>) facies (Kaiho, 1994). Previous studies suggest an increase in infaunal benthic foraminifera in low oxygen environments (Kaiho, 1994; Bernhard and Sen Gupta, 1999). Distribution of recent benthic foraminifera in surface sediments along the western continental margin of India, also suggests an increase in the relative abundance of angular asymmetrical benthic foraminifera in low oxygen zones (Nigam *et al.*, 2007). Based on the relative abundance of oxic and dysoxic specimens, a benthic foraminifera oxygen index (BFOI) has also been proposed to quantify past dissolved oxygen levels. BFOI, however, varies from ocean to ocean (Kaiho, 1994). The test pore density of selected benthic foraminifera also varies with ambient dissolved oxygen (Glock *et al.*, 2012). Thus an empirical relationship between pore density and ambient dissolved oxygen has been established and proposed as a potential proxy to quantify dissolved oxygen concentration in the past (Kuhnt *et al.*, 2013). The relationship between pore density and ambient dissolved oxygen concentration may, however, vary from species to species and also regionally. Therefore, regional species-specific equations have to be developed for effective application of benthic foraminifera shell pore density to reconstruct past dissolved oxygen concentration.

### **Productivity proxies**

Marine primary productivity removes inorganic carbon from the surface ocean and fuels the biological pump in the ocean – resulting in the transformation of carbon (and nutrients) from

inorganic to organic forms and cycling between reservoirs within the Earth system on geologically long to much shorter timescales. Quantifying changes in these fluxes (and sizes of the reservoirs) are critical to test and validate various scenarios using models for the past and the future with direct implications for climate changes. It is understood that the biological pump is not operating at its full capacity today – several areas of the ocean are high in nutrients but low in chlorophyll indicating low primary production (De La Rocha, 2006). These conditions have varied in the past. It is, therefore, important to reconstruct not only temporal variations in productivity, but also spatial variability and the transport of carbon at various depths. For example, the efficiency of the biological pump in exporting carbon from the surface to depth varies today between ocean regions and likely during the past and can be influenced by climate change in sometimes unexpected ways (e.g., Sarmiento and Gruber, 2006; Lopes *et al.*, 2015). Various approaches to reconstruct productivity in the past include using organic matter, phosphorous, carbonate, opal, barite or Ba accumulation in sediments, microfossil assemblages, carbon isotope records, other geochemical indicators like Al/Ti,  $^{231}\text{Pa}/^{230}\text{Th}$ , and  $^{10}\text{Be}/^{230}\text{Th}$ , nutrient content and organic biomarkers (Paytan, 2008; Li *et al.*, 2011). Each proxy provides valuable information, but one must consider its limitations and careful interpretation especially when attempting quantification of various components of ocean productivity.

### **Future Prospects**

It is evident that increasing emphasis today is on developing proxies to quantify past climatic changes. Such quantitative proxies for temperature are many. Efforts now should be to reduce the uncertainty associated with past temperature reconstructed from various proxies. It will require improved analytical facilities as well as instrumentation. The same holds true for salinity and pH. As robust proxies to quantify past dissolved oxygen concentration as well as productivity are still being developed, additional efforts are needed in this direction. Quantitative estimates of productivity and dissolved oxygen concentration at various depths, during different boundary conditions in the past, will help in a big way to assess future changes in response to anthropogenic activities. This special issue includes contributions wherein efforts are made to evaluate the existing marine paleoclimatic proxies or to develop novel proxies to understand past climatic changes. The contributions include both the qualitative and quantitative reconstruction of past climate.

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