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Preface

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

1. 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.

2. 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 Project Members, 1976, 1981). However, CLIMAP reconstructed seawater temperature had ±1.6 °C error. Subsequently, the alkenone unsaturation ratio ($U^{k'}{}_{37}$) (Brassell et al., 1986) of the sedimentary organic matter of marine origin as well as tetraether index of tetraethers consisting of 86 carbon atoms (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

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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 °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 $^{44}Ca/^{40}Ca$ 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}Ca from the β decay of ^{40}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}C—^{18}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 $^{13}C^{18}O^{16}O$ enrichment in CO_2 released after dissolving carbonate in phosphoric acid, relative to its expected concentration in a random distribution of isotopes among all CO_2 isotopologues (Ghosh et al., 2006). A common calibration has been proposed for diverse biogenic carbonates as the ^{13}C—^{18}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.

3. 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 $\delta^{18}O$ 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 δD) of lipid biomarkers was suggested as a paleosalinity proxy, provided the source water isotopic composition is known from independent proxies like $\delta^{18}O$ of biogenic carbonates. Water gets enriched in deuterium as the salinity of source water increases, resulting in higher δD values. The δD 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 δD-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 $\delta^{18}O$ and temperature on the same set of sediments, will help in assessing the applicability of these proxies.

4. 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 $B(OH)_3$ (boric acid) and $B(OH)_4^-$ (borate ion) (Hershey et al., 1986). Of these, only the isotopically lighter tetrahedral $B(OH)_4^-$ enters in marine carbonates with insignificant boron isotopic fractionation between seawater and carbonate, during its incorporation (Hemming and Hanson, 1992). Since the availability of $B(OH)_4^-$ 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 $\delta^{11}B$ (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 (δ^7Li) 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 δ^7Li can also be used to understand past carbon cycling.

5. 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.