

Does Sea-Water pH Influence Carbon and Oxygen Isotopic Composition of Modern Planktic Foraminiferal Species *Globigerina Bulloides* in South West Indian Ocean?

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Abstract: Present study aims to understand the possible influence of changing sea-water pH on the isotopic composition ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) of modern planktic foraminiferal shell in twenty three surface sediment samples (including grab and core tops of piston and gravity cores), collected along a north-south trending transect in the western Indian Ocean. The results, though initial indicate that the isotopic values ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) in general increase as the sea-water becomes less alkaline. It suggests that the sea-water pH also appears to influence isotopic values of planktic foraminiferal species *G. bulloides*, besides other factors influencing isotopic values in planktic foraminiferal shell.

Keywords: Planktic foraminifera, globigerina ballordes, carbon isotopes, oxygen isotopes, pH.

1. INTRODUCTION

The development of climate / environment sensitive tools 'the stable isotopic composition of foraminiferal shell', since the pioneer work of Emiliani (1955) added new dimension to the field of paleoceanography. While Oxygen isotopes ($\delta^{18}\text{O}$ values) of planktic foraminiferal species are temperature dependent and are used extensively to understand growth and decay of polar ice caps as well as local changes in temperature, salinity, sea level changes, etc. [1-5], Carbon isotopes ($\delta^{13}\text{C}$ values) of planktic foraminiferal species mainly reflect the isotopic composition of dissolved CO_2 in sea water from which foraminiferal shells are calcified [6], and are useful proxies for assessing paleoproductivity, global carbon cycle possibly related to upwelling and / or orbitally driven climate variability [7-11]. Besides temperature and salinity isotopic composition of foraminiferal shell has also been shown to vary under changing carbonate ion concentration of the sea-water as well as pH [12]. Based on a number of experiments Spero *et al.* [13] demonstrated that planktic foraminiferal $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ are influenced by sea-water carbonate chemistry. The carbonate chemistry of sea-water is largely controlled by the twin constraints of atmospheric pCO_2 and ocean carbonate ion concentration [14]. Independently a number of studies have been undertaken to study the spatial and temporal isotopic variations in the foraminiferal shells [15-17]. Similarly, boron isotopic composition of the selected foraminiferal species has emerged out as a potential tool to assess the variations in the

past sea water pH [18]. Paleo pH proxies were subsequently used to estimate paleo atmospheric pCO_2 . Nevertheless, studies dealing with the effects of changing sea-water pH on the isotopic composition of foraminiferal shells in modern marine environment are limited. Here we attempt to understand the possible influence of changing sea-water pH on the isotopic composition ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) of modern planktic foraminiferal shell in a set of samples collected along a north-south trending transect in the western Indian Ocean (Figure 1).

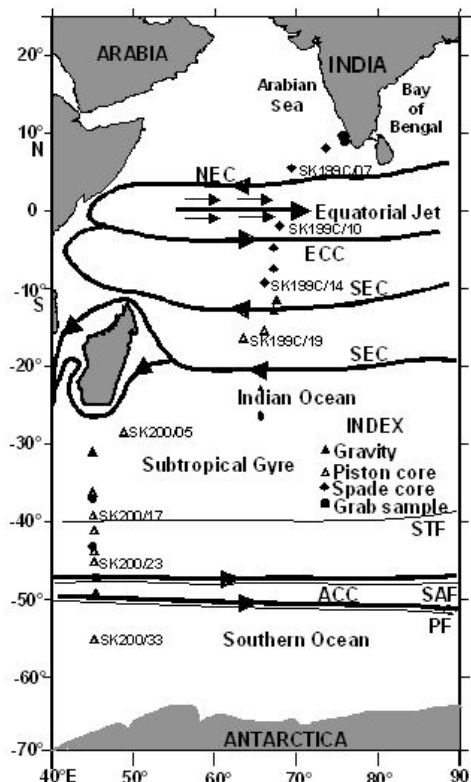


Figure 1: Location of sampling station across N-S transect in the Indian Ocean sector of Southern Ocean.

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2. MATERIALS AND METHODS

The present study is based on isotopic ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values) composition of *Globigerina bulloides* (a non symbiotic planktic species) that is typically associated with temperate to sub-polar water masses but is also characteristics in lower latitudes upwelling areas [19].

All twenty three surface sediment samples (including grab and core tops of piston and gravity cores), were processed following standard procedures [20]. 10-12 specimens of *G. bulloides* were picked from each sample to measure the isotopic composition ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) at the Alfred Wegner Institute for Polar and Marine Research, Germany, with a Finnigan MAT 251 Isotope Ratio Gas Mass Spectrometer coupled to an automatic carbonate preparation device (Kiel I) and calibrated via NBS 19 to the PDB scale. The notation versus VPDB δ values are given in (Vienna Pee Dee Belemnite). Precision of oxygen measurements based on repeated analyses of a laboratory standard over a one-year-period was better than 0.09% for oxygen and 0.06% for carbon.

Though we have long N-S transect for stable isotopic evaluation in the planktic foraminiferal species, we have selected the transect for obtaining pH values only in the geographical region falling south of 25°S latitude (Figure 2) on the assumption that the Southern

Ocean (SO) has often been projected as the potential sink for the excess carbon, owing to its high nutrient availability and low chlorophyll content. In order to test the role of SO in changing CO_2 concentration over glacial-interglacial periods, suitable proxies have to be developed or evaluated in the modern marine environment of this particular region.

The pH was measured in-situ at different depths (0, 10, 25, 50, 100, 200, 500, 750, 1000, 1500, 2000, 3000m / max) with the help of Niskin water samplers, attached to the CTD probe. The pH was determined immediately after the collection of seawater with the help of Digital pH meter (ELICO model: LI 127), provided with automatic temperature compensation (ATC) probe. The pH meter was calibrated with multi-point known pH standards. The values determined were repeatable with the error of 0.01 pH unit scale. The pH averaged (average of the pH values recorded at various water depths upto 500 meters) for the top 500 m of the water column was used for the present study, because of occurrence of live planktic foraminifera up to this depth, during different stages of their life-cycle [21].

3. RESULTS AND DISCUSSION

The pH varies between 7.9 and 9.1 (Figure 2) with anomalously high pH value at few locations in the present study area, as compared to the reported range

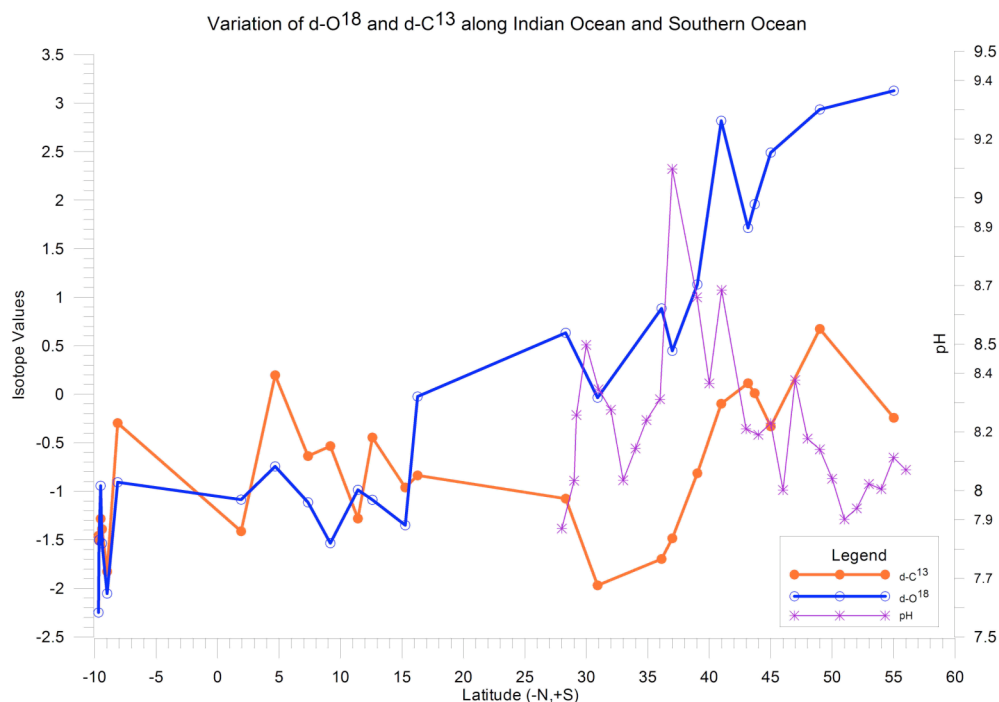


Figure 2: Latitudinal distribution of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of planktic foraminiferal species *G. bulloides* and pH values (South of 25°S latitude) along N-S transect in the Indian Ocean sector of Southern Ocean.

of seawater pH from different parts of the world oceans. At this point we are not able to understand the cause of such aberrations in pH values. However, the objective of the present manuscript is to understand the possible influence of relative changes in the seawater pH on the stable isotopic composition ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values) of planktic foraminiferal species in the modern marine environment of the southwestern Indian ocean. Apparently an increased pH is reported between 35°S and 40°S latitudes and an inverse relationship is exhibited between the stable isotopic variations ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values) and sea-water pH with high values of both isotopes at the stations with comparatively less alkaline pH (Figure 2).

The pH of sea-water mainly indicates marine carbonate chemistry which in turn can be used to infer changing atmospheric pCO_2 [22-23]. An understanding of past changes in atmosphere pCO_2 is useful to understand the role of greenhouse gases in regulating the global temperature [23]. The isotopic equilibrium of surface sea water with atmospheric CO_2 raises $\delta^{13}\text{C}$ in cold surface waters and increases $\delta^{13}\text{C}$ in warm surface water [24-28]. Our results are in agreement with this explanation with higher values of both isotopes ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values) in colder regions with decreasing pH south of 40°S latitude compared to relatively warmer regions north of 40°S latitudes (Figure 2).

The apparent inverse relationship between isotopic variations of planktic species *G. bulloides* and sea-water pH indicates that the sea-water with comparatively lower alkaline pH is conducive for higher values of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in their calcareous shell along the north-south transect in the study area, though the change in pH might affect $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of different planktic species to varying extent.

Our inferences are in conformity with the results of earlier laboratory experiments conducted on living planktic (both symbiotic and asymbiotic species) foraminiferal shells which showed that a shift in pH has a significant impact on foraminiferal shell's $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ concentrations and the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of planktic foraminiferal calcite decrease with increasing sea-water pH and / or carbonate concentration [12] independent of symbiotic activities and temperature [11].

Venn *et al.* [29] designed a laboratory experiment to demonstrate the relationship between temperature and solubility of carbon dioxide in water. The results showed an inverse relationship between temperature

and CO_2 saturation. Accordingly, the decreasing sea-water pH combined with decreasing temperature towards higher latitudes will lead to increased solubility of carbon dioxide and thus under-saturation of sea-water. The under saturated sea-water in turn affect the isotopic values ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) of planktic species *G. bulloides* leading to an increased value in this region. It has long been demonstrated that the carbon and oxygen isotopic composition of planktic foraminiferal shell is directly influenced by the carbonate equilibrium state of sea-water [13]. The effect may be species dependent and based on a combination of kinetics and metabolic fractionation process [12-13, 30]. However, because pH and carbonate ion vary together in sea-water, it is rather difficult to single out controlling variable [30].

The pH / carbonate isotope effect has important implications for the interpretation of stable isotope data in the fossil record [12]. Therefore, the present study indicates the potential applications to many paleoceanographic problems. Because the pCO_2 of the sea surface and the atmosphere must be in approximate equilibrium, the glacial drop in atmospheric CO_2 must have been accompanied by an increase in sea-surface water carbonate ion concentration. Such an increase is expected to influence the isotopic composition of planktic foraminifera [30]. However, since carbonate chemistry controls the temporal geochemical variability in the fossil record, such aspect has to be ascertained before hand.

CONCLUSIONS

Based on the present study, it may be inferred that isotopic values ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) in general increase as the sea-water becomes less alkaline. Though the possibility of other factors influencing isotopic values in planktic foraminiferal shell may not be ruled out completely, the sea-water pH also appears to influence isotopic values of planktic foraminiferal species *G. bulloides*. Such an impact on stable isotopic composition of calcareous shells of planktic foraminifera looks significant from the view point of recent rise in CO_2 emitted by the burning gas, oil and the fossil fuels being absorbed by the oceans making them increasingly acidified. Impacts to marine organisms will likely to be more severe in higher latitude sea as colder water can absorb more CO_2 and the sea-water in these regions mixes downwards into the deep ocean carrying carbon-di-oxide to deep waters. The results of present study underline the need

for the development of quantitative determination of stable isotopic variations in response to the pH changes in modern marine environment prior to their application in assessing pCO₂ in the past. However, many such transects from different marine regimes of the world ocean need to be considered for such investigations to further augment the present inferences.

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