



DIFFERENTIAL DISSOLUTION OF BIOGENIC CARBONATES: IMPLICATION OF SECRETION AT HIGHER pH

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ABSTRACT

A selective preferential dissolution of a few initial chambers of several specimens of calcareous planktic foraminifera *Globigerinoides ruber* has been noted in the surface sediments collected from the eastern Arabian Sea and northern Bay of Bengal. Based on a recent finding stating the capability of foraminifera to modulate the vacuolar seawater pH for easy secretion of calcite, it is postulated that these initial two-three chambers were formed at relatively higher pH conditions, inside the cyst during asexual reproduction. The secretion of chambers at relatively higher pH results in increased incorporation of magnesium into the calcareous test. This increased Mg carbonate probably renders the initial chambers more prone to dissolution. The findings have an implication for the application of *G. ruber* for paleoclimatic/paleoceanographic studies.

Keywords: *Globigerinoides ruber*, breakage, dissolution, pH, foraminifera, Indian Ocean

INTRODUCTION

Foraminifera are preferentially marine microorganisms, whose fossil counterparts have often been used for palaeoclimatic studies (Gupta *et al.*, 2005; Naidu and Malmgren, 2005; Nigam, 2005; Murray, 2006; Khare *et al.*, 2007). The major population of foraminifera has a hard calcium carbonate exoskeleton or test, while other forms have the test of sediment particles collected from nearby environment. Breakage and dissolution of calcareous foraminiferal tests is very common and has often been used to infer changes in terrigenous input and seawater chemistry during the past (Johnson *et al.*, 1977; Coulbourn *et al.*, 1980; Cullen and Prell, 1984; Caron *et al.*, 1990; Pfuhl and Shackleton, 2004; Saraswat *et al.*, 2007a). The dissolution susceptibility of the foraminiferal species, however, vary spatially and temporally. The water column dwelling species of foraminifera have been ranked into dissolution susceptible and resistant, based on differential dissolution of these species in experiments and in natural settings (Berger, 1971; Honzo and Erez, 1978). The pattern of dissolution of the tests also varies from species to species and has been attributed to the robustness and morphology of the tests (Malmgren, 1983). The dissolution of the tests is not uniform; a few portions of the tests get selectively dissolved. The reason for selective dissolution of parts of the tests is still not clear. Here, we have studied the dissolution of the tests of surface dwelling planktic foraminifera *Globigerinoides ruber* in surface, sediments collected from the Arabian Sea and the Bay of Bengal. *G. ruber* is a surface-dwelling species and its isotopic and elemental analysis has been widely used to infer past climatic changes from the northern Indian Ocean (Saraswat *et al.*, 2005; 2007b; Anand *et al.*, 2008). *G. ruber* is a dissolution susceptible species (Cullen and Prell, 1984). The dissolution of *G. ruber* is discussed in view of the recent advances in the understanding of secretion of foraminiferal tests.

MATERIALS AND METHODOLOGY

The surface sediments collected during two *Sagar Kanya* cruises, namely SK-187 and SK-237 were used (Fig. 1). A small aliquot of sediment sample was collected in watch glasses and dried overnight. The dried sediment sample was weighed and

then soaked in water for twenty four hours. The following day, overlying water was decanted carefully, without disturbing the sediments. The water was added again if the decanted overlying water was not clear. The process was repeated till the overlying water became clear. Once the overlying water was clear, the sediments were sieved over a 63 μm sieve. The sand fraction ($> 63 \mu\text{m}$) was collected in 25 ml beakers and dried. The dried sand fraction was weighed and transferred to plastic vials. A small aliquot of sand fraction was taken after coning and quartering. This sand fraction was weighed and spread into a picking tray. A minimum of fifty specimens of *G. ruber* were picked from each sample and mounted into micropalaeontological slides.

RESULTS AND DISCUSSION

The spines were missing in the majority of the specimens. In general, the tests of the specimens collected from the Arabian Sea were relatively more dissolved as compared to the specimens retrieved from Bay of Bengal sediments. While the tests collected from the Bay of Bengal had a pale yellow hue, those from the Arabian Sea were mostly opaque and white. Beside this, a peculiar pattern of breakage in *Globigerinoides ruber* was noted. The initial whorl of chambers was missing in a number of specimens of *G. ruber*. The last (later formed) few (three to five in number) chambers however, were fully intact.

It is a known fact that a few of the initial chambers of the foraminiferal offspring are formed within the mother test, whereas the rest of the chambers are secreted by the juveniles, once they come out of the mother test. Temporal changes in the number of broken tests and the state of dissolution of foraminiferal tests are often attributed to the shift in foraminiferal lysocline which refers to a change in carbonate ion concentration of the seawater (Berger, 1970; Igarashi, 2001). If foraminiferal test had a uniform composition throughout, all the chambers should have been equally dissolved. Therefore, this preferential dissolution of initial chambers probably reflects secretion under different seawater chemistry inside and outside the foraminiferal test. Such a difference in the chemistry of microenvironment of the foraminifera and the bulk seawater has been reported by Zeebe *et al.* (1991).

The change in carbonate ion inventory of seawater is

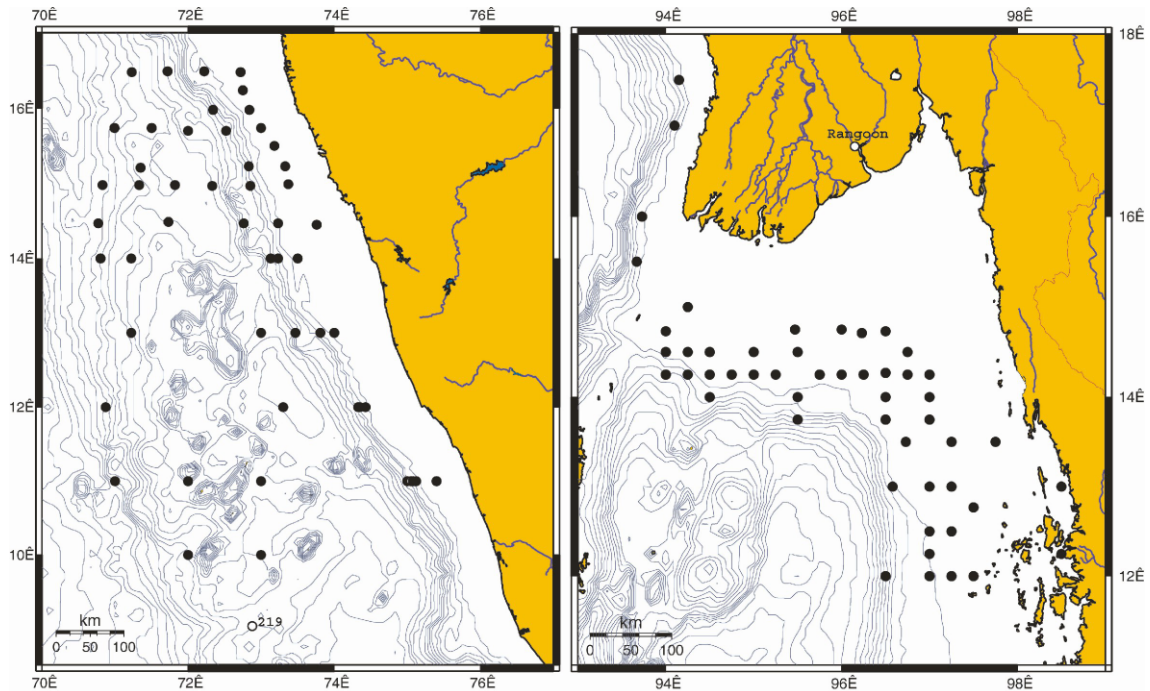


Fig. 1. The location of surface sediment samples used to study the selective dissolution of planktic foraminifera *Globigerinoides ruber*.

closely associated with the change in its temperature (Goyet *et al.*, 1993). The change in seawater temperature is one of the causes for variation in seawater pH (Hunter, 1998). But a larger change in the seawater pH occurs due to a change in atmospheric carbon-di-oxide concentration (Haugan and Drange, 1996), which has been cited as one of the main reasons for the change in seawater pH during recent times and is often attributed to anthropogenic activities (Caldeira and Wickett, 2003). This increased CO_2 lead seawater pH change has affected a large number of marine fauna (Zondervan *et al.*, 2001; Orr *et al.*, 2005). Based on the projected CO_2 levels, it is further postulated that it will be increasingly difficult for the calcareous and aragonitic organisms to survive in a sea of low pH (Feely *et al.*, 2004). Though, the normal seawater conditions are not conducive for secretion of CaCO_3 due to excess magnesium (Stanley, 2006), a few of the groups has mastered this process. Recently, it was found that foraminifera have the capability of increasing the pH by upto 1 unit, at the time of precipitation of calcite (Nooijer *et al.*, 2009). However experiments have shown that the calcites precipitated at higher pH tend to have relatively more amount of magnesium (Zeebe & Sanyal, 2002). Increased amount of Mg renders the calcite unstable as the calcite containing more amount of Mg tends to dissolve first than the one having lesser magnesium (Chave, 1964).

A possible reason for increased magnesium content of the initial chambers can be secretion at higher temperature. The replacement of calcium by magnesium during precipitation of calcite is an endothermic process and is thus exponentially proportional to seawater temperature (Burton and Walter, 1991; Lopez *et al.*, 2009). But, it seems highly unlikely that the foraminifera can modulate and increase the vacuolar temperature to an extent to affect the magnesium content significantly. However, completely ruling out the possibility of secretion of initial chambers at higher seawater temperature is beyond the scope of this paper. It requires point measurement

of both Mg/Ca ratio and oxygen isotopic composition of the initial and final chambers, which can help determine contribution from increased seawater pH and temperature.

The other possible mechanism leading to high Mg content in initial few chambers can be the formation of these chambers of the offsprings at a relatively higher pH than rest of the chambers secreted by babies outside the mother test. The chambers formed at higher seawater pH will have more magnesium and thus increased tendency to break/dissolve than the chambers formed at lower pH which will be relatively more resistant to dissolution due to less magnesium content (Chave, 1964). The secretion of initial chambers at relatively higher pH, seems feasible due to the peculiar way in which foraminifers reproduce. It appears relatively easy for the foraminiferal specimens undergoing reproduction to modulate the vacuolar seawater pH as they tend to form a cyst at the time of reproduction, enwrapping the complete tests (Heinz *et al.*, 2005). The cyst isolates the foraminifera from the ambient seawater. The physico-chemical conditions inside the cysts are different from that of the seawater outside (Heinz *et al.*, 2005). The difference in physico-chemical conditions inside the cyst mainly arises due to the various vital processes of the living cell, especially respiration. The development of offsprings takes place inside this cyst. These initial several chambers of the juveniles are secreted inside the cyst before the juveniles are released out of this cyst (Kimoto and Tsuchiya, 2006). Recently, Nooijer *et al.* (2009) have demonstrated the capability of foraminifera to modulate the vacuolar seawater pH. Increasing the pH at the site of calcification has the added advantage of increasing the availability of carbonate ions which results in a many fold increase in calcite saturation state and thus a more enhanced calcite precipitation than the bicarbonate ions (Lopez *et al.*, 2009). It also helps in dissipation of respired CO_2 into high pH vacuolar seawater thus further increasing the availability of carbonate ions (Nooijer *et al.*,

2009). A few of the planktic foraminiferal species also tend to secrete additional calcite termed as gametogenic calcite, before undergoing reproduction, which results in thickening of the test wall (Caron *et al.*, 1990). The process of formation of initial chambers inside the test is different from the secretion of the chambers by the offsprings outside the tests wherein the new chambers are formed without the cyst formation. Probably, it is difficult for the foraminifera to modulate the vacuolar pH in open conditions than inside the cyst. A further argument for addition of low magnesium, dissolution resistant calcite towards the later phase of foraminifera is the increase in the weight of the individuals of several species during its ontogeny, which indicates calcification in relatively cooler waters at deeper depths (Erez and Honzo, 1981; Schiebel *et al.*, 2005).

CONCLUSIONS

In the surface sediment collected from the Arabian Sea and the Bay of Bengal, a few of the chambers of the initial whorl of the planktic foraminiferal species *Globigerinoides ruber* were found to be dissolved. The preferential dissolution of the chambers of the initial whorl is attributed to its secretion at higher pH, while the juveniles were inside the mother test at the time of reproduction. The secretion at higher pH might have led to increased incorporation of Mg carbonate in the tests rendering this portion of the tests more susceptible to dissolution. These findings have an implication on the application of isotopic and elemental composition of foraminifera for palaeoclimatic studies, wherein whole test is dissolved to find out stable carbon and oxygen isotopic composition and elemental ratio.

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