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Episodic preservation of pteropods in the eastern Arabian Sea: Monsoonal change, oxygen minimum zone intensity and aragonite compensation depth

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The preservational record of pteropod shells (aragonite) for the last 30 kyr has been studied in a core (SK17) recovered from the eastern Arabian Sea margin at off Goa coast (depth 840m, lat. 15°15'N, long. 72°44'E). The chronostratigraphy of the core established on the basis of high resolution stable isotope record of a planktic foraminifera (*Globigerinoides ruber*) and several AMS radiocarbon ages demonstrates millennial scale variation in $\delta^{18}O$ defining Younger Dryas and Heinrich like Events. Records of absolute abundance of pteropods (1g/dry wt >125 μm), abundance ratio of pteropod and planktic foraminifera, aragonite (wt %), organic carbon (OC) (wt %) and $CaCO_3$ (wt %) show major changes during these isotopic events. Aragonite maxima and higher number of well-preserved pteropod shells, are noticed during cold stadial periods. The study indicates a negative correlation between aragonite and OC % (productivity index). On the other hand, total $CaCO_3$ content (calcite and aragonite) is positively correlated with the aragonite. The variation patterns of pteropod shells and aragonite content in the sediment core are suggested to be controlled by the preservational conditions associated with the fluctuation in Aragonite Compensation Depth (ACD) and Oxygen Minimum Zone (OMZ) intensity. It is suggested that the high biological productivity during intensified summer monsoons in late Holocene and inter-stadial periods might have resulted in severe oxygen depletion (strong OMZ) leading to shallowing of the ACD. A weak summer monsoon and low productivity condition prevailing during cold stadial periods would have resulted in a weak OMZ and deepening of the ACD.

[**Key words:** Pteropods, OMZ, aragonite compensation depth, Arabian Sea, monsoonal change, preservational records, foraminifera, chronostratigraphy, planktic foraminifera, sediment core, gravity core]

Introduction

Pteropods are prime contributors to aragonite flux in the oceans. Aragonite is a metastable polymorph of $CaCO_3$ and more soluble in water than calcite[1, 2]. Therefore, Aragonite Compensation Depth (ACD) lies well above the Calcite Compensation Depth (CCD) [ACD is shallower than CCD by about 3 km on average[3]]. Aragonite preservation/dissolution record is found to be one of the important proxies for deciphering past variations in carbonate chemistry of subsurface and intermediate water masses associated with changes in climatic condition and circulation pattern[4]. The preservation of aragonite occurs where *in situ* CO_3^{2-} concentration exceeds the saturation concentration. In recent years, there is a growing interest among the paleoceanographers in evaluation of aragonite production, accumulation and dissolution, in world oceans. The ACD is recognised by the gradual disappearance of pteropod shells in sea bottom sediments with increasing water depth[5-7]. The extent of preservation of pteropod shells and corresponding aragonite spikes is linked with the position of ACD, which is controlled by the physico-chemical properties of subsurface waters. Hence, the study of temporal changes in pteropod (aragonite) preservation is of great importance in understanding past variations in water column properties in response to the climatic shifts. A few high-resolution studies on marine sediment cores (e.g. The Atlantic[4, 8-9]; the Arabian Sea[10-12]) indicate millennial scale variation in aragonite record, equivalent to well known D/O (Dansgaard-Oeschger) cycles and Heinrich events. Reports of aragonite preservation spikes in the Arabian Sea came mainly from the sediment cores of Pakistan and Somali margins. However, little is known about aragonite preservation/dissolution record from the eastern Arabian Sea, Indian margin. The present paper examines the preservational record of the pteropods shells and the associated aragonite spikes in a core from the eastern Arabian Sea, and correlates them with the cycles of the climatic shifts during the last 30 kyr in a stable isotope stratigraphic framework.

Arabian Sea is characterised by strong seasonal variability of monsoonal upwelling. The monsoonal upwelling produces high primary productivity resulting in strong mid-water Oxygen Minimum Zone (OMZ) between 150-1200 m[13]. The seawater in the OMZ is undersaturated with respect to aragonite due to high consumption of oxygen lowering the Ph and carbonate saturation because of CO_2 addition and the oxidation of ammonia to nitrate[14]. The ACD in northern Arabian Sea is much shallower at about 500 m within the more pronounced OMZ. Variations in OMZ are suggested to be linked with the intensity of summer monsoon and related productivity and thermocline ventilation[13]. The fluctuation in OMZ intensity directly results into variation in the ACD and aragonite preservation. Therefore, pteropod/aragonite preservation spikes in sediment cores of the Arabian Sea can be valuable imprints of the changes in the intensity of climatically controlled OMZ and Aragonite Compensation Depth. For the quantitative reconstruction of aragonite dissolution/preservation in the past, several criteria can be adopted such as (i) abundance of pteropod shells, (ii) aragonite content in sediments. The degree of aragonite dissolution can also be studied by analyzing preservational state of most solution susceptible pteropod such as *Limacina inflata*.

Materials and Methods

A 4.7 m long gravity core recovered from the upper continental slope off Goa, (at about 840 m depth; lat. 15°15'N; long. 72°44'E) (Fig. 1) was studied for the down-core variation patterns of pteropod abundance, preservational modes of pteropod shells and aragonite , calcite contents in sediments. The core location lies in middle of the present oxygen minimum zone resulting in dyoxic or anoxic facies at the sea floor. The sediment core is characterised by alternation of intermittently dark coloured laminated and light coloured homogenous facies[15]. The laminated intervals are organic carbon rich and carbonate poor, whereas homogenous bioturbated intervals contain less C_{org} and more $CaCO_3$. Samples at 2 – 4 cm intervals were used in this study. About 15 g of dry sediments of each sample was washed through 63 µm screen and dried. Dry residue larger than 63 µm was sieved through a 125 µm screen. Census counts of pteropods were made on >125 µm fractions. Large samples were split into suitable aliquots of approximately 250 – 300 pteropod specimens. Those samples containing a low number of pteropod shells were used completely for counting. The absolute abundance was estimated for 1 g dry sediment.

The mode of preservation of pteropods was studied based on the shell transparency of one of the most delicate species, namely, *Limacina inflata* following Singh *et al.*[16] Shells of *L. inflata* were grouped into two categories: (1) transparent – indicating highest state of preservation; and (2) opaque white – reflecting corrosion/dissolution. Various geochemical analyses were carried out on bulk sediments. The carbonate content was calculated based on total carbon (TC) and total organic carbon (TOC) contents measured by the LECO carbon combustion method. The equation $CaCO_3$ % = 8.53 (TC – TOC %) was used. The calcite and aragonite percentages were estimated by X-ray diffraction analysis. Semi-quantitative analysis was made by determining aragonite and calcite peak heights and subsequently by comparing with the respective calibration curves.

The age model for the core is based on the oxygen isotope stratigraphy and several AMS radiocarbon ages[15]. The isotope record suggests that the top 1.2 m portion of the core represents the Holocene. The Younger Dryas event is clearly evident by a broad maximum in $\delta^{18}O$ value preceding distinct lighter value representing Bølling – Allerød climatic intervals. The termination IA is well defined in the isotope record. Chronological record of pteropod spikes as well as corresponding aragonite maxima

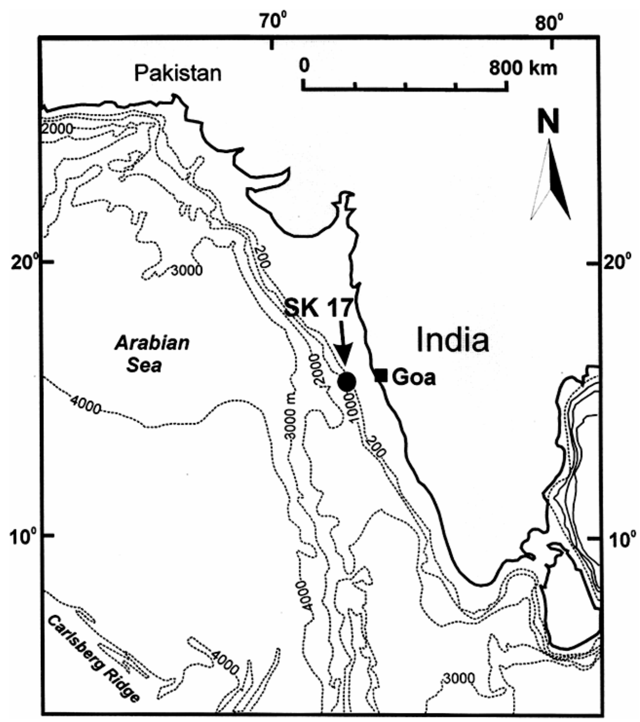

Fig. 1—Map of the Arabian Sea showing core locations of SK17

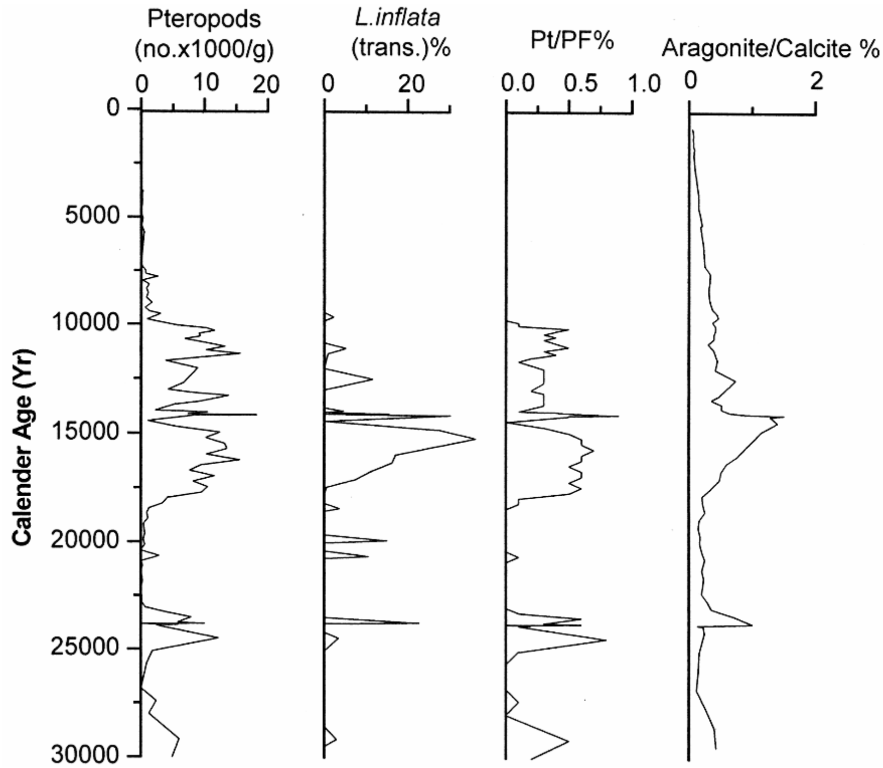

Fig. 2—Absolute abundance of pteropods (per g of dry sediment >125μm), percentage of *Limacina inflata* (solution susceptible pteropod species) transparent shells, ratio of relative abundances of pteropods to planktic foraminifera (Pt/PF%) and ratio of aragonite/calcite wt. percentages.

indicates that these events are equivalent to Heinrich Events of North Atlantic[15].

Results

The pteropod assemblages of the investigated core are characterized by low diversity and composed of both epipelagic and mesopelagic forms. The species include: *Limacina inflata* (d'Orbigny), *L. trochiformis* (d'Orbigny), *Creseis chierchiae* (Boas), *C. acicula* (Rang), *C.virgula* (Rang) [forma *virgula* (Rang) and forma *conica* Escholtz], *Clio convexa* (Boas), *Cavolinia longirostris* (de Blainville) and *Diacria quadridentata* (de Blainville), *Diacria trispinosa* (de Blainville), *Clio pyramidata* Linnaeus, *Cavolinia* sp., *Limacina bulimoides* (d'Orbigny) and *Styliola subula* (Quoy and Gaimard). *Limacina inflata*, a mesopelagic taxon dominates the pteropod population. The numerical abundance of pteropod shells varies significantly down-core (Fig. 2). In the core top and the late Holocene sediments (last 7 ka), pteropods are either absent or rarely present. The maximum abundance of pteropods are recorded between 10 and 12 ka B.P., 15 and 17 ka B.P., 23 and 25 ka B. P. and around 29 ka B. P. (Fig. 2). It is intriguing that majority of shells during these intervals are transparent in appearance indicating best preservation of aragonitic shells. Further, it is observed that pteropod abundance spikes are coincident in general with the aragonite maxima (Fig. 3). The aragonite content of the bulk sediments ranges from 10% to the maximum up to 50%.

$CaCO_3$ contents in the upper part of the core representing Holocene are about 40% (Fig. 3). The carbonate content decreases to ~27% during Younger Dryas interval. The down core total carbonate profile reflects three intervals of carbonate maxima between 14 and 16 ka B. P. (>60%), 23 and 24 ka B. P. (55-65%) and 27 and 30 ka B. P. (>50%) [Fig. 3]. The down core variation in organic carbon (OC) content in the core varies between 5.5 and 1.3% (Fig. 3). The laminated intervals (distinctly/indistinctly) are characterized by higher organic carbon[15]. The variation pattern of OC shows its negative correlation with aragonite and total carbonate records. The intervals with OC maxima correspond to minima in aragonite.

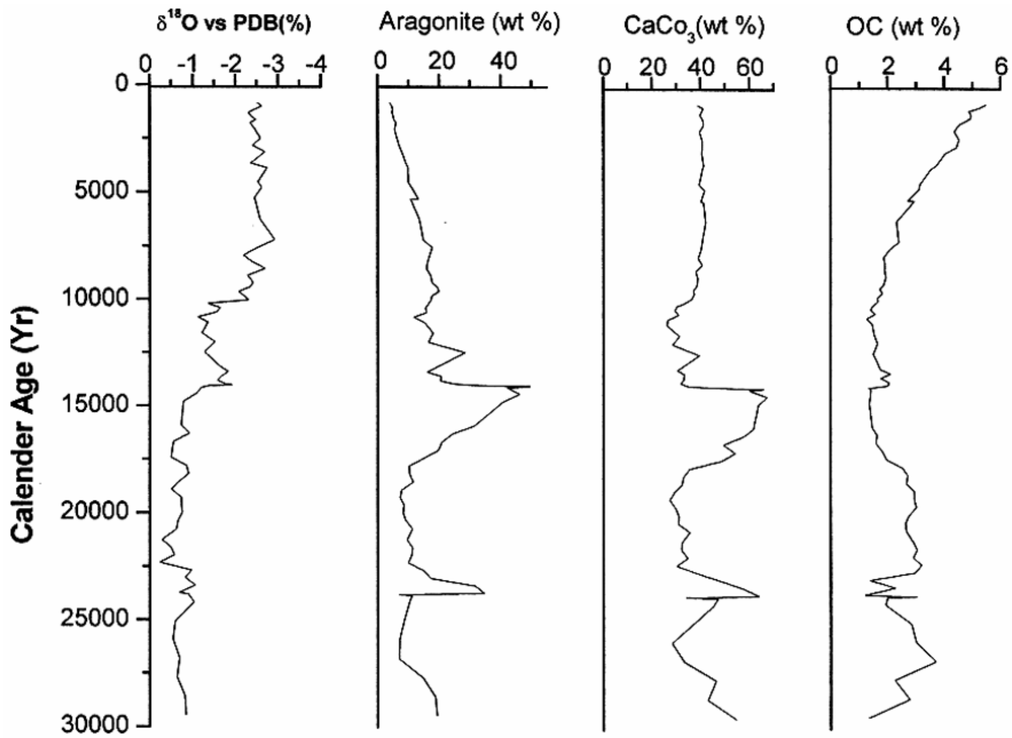

Fig. 3—Records of $\delta^{18}O$ (*Globigerinoides ruber* >125 µm), Aragonite (wt %), $CaCO_3$ (wt %) and organic carbon of bulk sediment.

Discussion

Present study clearly indicates that the significant portion of the total carbonate in core sediments is formed by aragonite and the main contributors of aragonite are pteropod shells. Down core variations in $CaCO_3$ content could be either related to degree of carbonate production or dissolution/preservation. An increased amount of total carbonate and aragonite is recorded during stadial periods (Younger Dryas and Heinrich like Events) between 10 and 12 ka B. P., 15 and 17 ka B. P., 23 and 25 ka B. P. and around 29 ka B. P.

A significant increase in OC is recorded in the late Holocene, between 13 and 14 ka B. P. (Bølling - Allerød) and during the last glacial maximum between 18 and 23 ka B. P. On the other hand, prominent minima in OC are noticed at 15 – 18 ka B. P., 23 – 24 ka B. P. and 29 – 30 ka B. P. (Heinrich-like events) representing bioturbated layers. Following previous workers[17-19], the organic carbon content in the core sediments is considered as of almost marine origin. The OC maxima in sedimentary records of Oman and Pakistan margins have been suggested to be linked with enhanced surface water productivity during intensified SW monsoon in the late Holocene. According to Calvert *et al.*[17], the increased OC content in pre-Holocene sediments of the Indo-Pakistan margin was resulted from high productivity and enhanced preservation in anoxic conditions. Ganeshram *et al*.[19] have documented a positive correlation between variation pattern of OC content and $\delta^{15}N$ in the last glacial-Holocene sedimentary records of the western Indian margins indicating strong coupling between productivity and denitrification in the Arabian Sea. Hence, it is suggested that the fluctuations in C_{org} content in the examined core are mainly associated with variation in surface water primary productivity/and enhanced preservation. The intervals with OC minimum (low productivity period) in core SK17 correspond to maximum in aragonite and total carbonate. This suggests that variation in CaCO3 content might be related to changes in preservational conditions. It seems unlikely that variability in carbonate content is caused by differences in sea surface productivity[20]. As the examined core site lies below the present ACD and well above the CCD, aragonite preservation/dissolution appears to be a prime cause for variation in total carbonate content. The pteropod and aragonite peaks corresponding to the $CaCO_3$

maxima further support this view. The well-preserved transparent shells of *Limacina inflata* (one of the most solution-susceptible species) dominating the aragonite spikes, suggest that the aragonite maxima, are the results of enhanced preservation (Figs 2, 3). The amount of carbonate (calcite and aragonite) content in sediments can also be influenced by (i) input of calcareous material from shallow areas through turbidites or/and (ii) dilution by terrigenous material. The pteropod rich layers in a deep eastern Arabian Sea core (3820 m depth) have been suggested to be formed by turbidity currents[21]. In the present core, there is no evidence of allochthonous origin of these pteropods-rich sedimentary layers having high contents of total $CaCO_3$ and aragonite. Furthermore, the isotope record also does not show any anomalous shifts during these intervals. To overcome the influence of dilution, if any, a ratio of aragonite (wt %) to calcite (wt %) is also considered (Fig. 2). The aragonite and pteropod abundance curves parallel the aragonite/calcite ratio curve. Aragonitic pteropods are more susceptible to dissolution than the calcitic planktic foraminifera. Thus, the ratio of relative abundance of pteropods to planktic foraminifera (Pt/PF) can be used as an indicator of the state of pteropod preservation. Figure 2 clearly reveals that the pteropod abundance spikes correspond to the maxima of Pt/PF ratio and *L. inflata* transparent shells.

Preservation of aragonite depends on the saturation state of the overlying bottom water with respect to aragonite at the sediment-water interface. Variation in aragonite lysocline may occur due to changes in *in situ* CO_3^{2-} concentration. Evidently, the oxygen concentration in intermediate waters or in other words the strength of Oxygen Minimum Zone controls the depth of aragonite compensation and consequently the preservation of aragonite in bottom sediments. Von Rad and Schulz[10] considered surface ocean productivity and bottom water oxygenation as major factors causing variation in lithofacies (dark coloured laminated and light coloured bioturbated) in the late Quaternary sediments recovered from well-developed OMZ in the northeastern Arabian Sea. The primary productivity and oxygenation of intermediate waters in the Arabian Sea are directly linked with the strength of monsoons. The organic carbon-rich laminated sediments in the northern Arabian Sea margin are deposited under suboxic-anoxic conditions during high productivity periods. On the other hand, the homogenous, bioturbated, OC-poor and carbonate-rich sediments accumulate under depositional conditions of increased oxygen level of water column and reduced productivity. Both the pteropod and aragonite spikes in the examined core are associated with homogenous bioturbated sequences characterized by low organic carbon.

The intensification of summer monsoons during the late Holocene and interstadial periods (Bølling-Allerød, between 13 and 14 ka B.P.) resulted in high biological productivity and severe oxygen depletion in intermediate waters. The high consumption of O_2 and the consequent increase in CO_2 during high productivity period lowered Ph and aragonite saturation of intermediate waters within the intensified OMZ and led to shallowing of ACD. A shallow ACD in strong OMZ at the core site might have resulted into strong dissolution of aragonite and poor preservation of pteropod shells. In contrast, aragonite-rich layers/pteropod spikes (coinciding with Heinrich-like Events) in the examined core showing intervals of better preserved pteropod shells/aragonite suggest weakening of OMZ and deepening of ACD.

During the stadial periods (Younger Dryas and Heinrich Events), the strength of summer monsoon and associated upwelling and productivity in the Arabian Sea was weakened[11, 22]. The low surface water productivity and increased oxygen concentrations during stadials would have resulted in a weak oxygen minimum zone. Von Rad and Schulz[10], Reichart *et al.*[11] and Von Rad *et al.*[23] suggested that intensification of winter monsoon winds during cold periods resulted deep mixing of oxygen-rich waters and thus lowered the ACD in the northeastern and northern Arabian Sea. A considerable lowering of ACD during cold periods corresponding to Heinrich Events of the North Atlantic would have led to better preservation of pteropod shells and enhanced aragonite contents. Similar records of pteropod-rich aragonitic layers coinciding with Heinrich events have been documented from the bioturbated intervals in the sediment cores of the Pakistan margin[10, 22, 23]. These records indicate that the pteropod spikes are basin-wide phenomena in the Arabian Sea. The study suggests that the sub-Milankovitch variability in monsoons corresponding to the climatic D/O cycles and Heinrich events seem to have profound influence on the Oxygen Minimum Zone intensity and Aragonite Compensation Depth in the Arabian Sea.

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