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Malformation in Coccolithophores in low pH waters: evidences from the eastern Arabian Sea

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Abstract:

Oceanic calcifying plankton such as coccolithophores are expected to exhibit sensitivity to climate change stressors such as warming and acidification. Observational studies on coccolithophore communities along with carbonate chemistry provide important perceptions of possible adaptations of these organisms to ocean acidification. However, this phytoplankton group remains one of the least studied in the northern Indian Ocean. In 2017, the biogeochemistry group at the Council for Scientific and Industrial Research- National Institute of Oceanography (CSIR-NIO) initiated a coccolithophore monitoring study in the eastern Arabian Sea (EAS). Here, we document for the first time a detailed spatial and seasonal distribution of coccolithophores and their controlling factors from the EAS, which is a well-known source of CO₂ in the atmosphere. To infer the seasonality, data collected at three transects (Goa, Mangalore, and Kochi) during the Southwest Monsoon (SWM) of 2018 was compared with that of the late SWM of 2017. Apart from this, the abundance of coccolithophores was studied at the Candolim Time Series (CaTS) transect, off Goa during the Northeast Monsoon (NEM). The most abundant coccolithophore species found in the study region was *Gephyrocapsa oceanica*. A high abundance of *G. oceanica* (1800 x10³ cells L⁻¹) was observed at the Mangalore transect during the late SWM despite experiencing low pH and can be linked to nitrogen availability. The high abundance of *G. oceanica* at Mangalore was associated with high dimethylsulphide (DMS). Particulate inorganic carbon (PIC) and scattering coefficient retrieved from satellites also indicated a high abundance of coccolithophores off Mangalore during the late SWM of 2017. Interestingly, *G. oceanica* showed malformation during the late SWM in low-pH waters. Malformation in coccolithophores could have a far-reaching impact on the settling fluxes of organic matter and also on the emissions of climatically important gases such as DMS and CO₂, thus influencing atmospheric chemistry. The satellite data for PIC in the EAS indicates a high abundance of coccolithophore in recent years, especially during the warm El-nino years (2015 and 2018). This warrants the need for a better assessment of the fate of coccolithophores in high-CO₂ and warmer oceans.

Keywords: Calcifying, Phytoplankton, Arabian Sea, Malformation, nutrients, carbonate

1. Introduction

Coccolithophores are one of the key actors of the climate system, as they provide ballast for sinking organic debris besides playing an important role in the marine biogeochemical cycle (Riebesell et al., 2009; Taylor et al., 2017). Coccolithophores are single-celled calcifying algae of the division haptophyta and class Prymnesiophyceae that produce calcite scales, called coccoliths (Balch et al., 2019). They are important contributors to the sulfur cycle (Malin and Steinke, 2004) through the production of Dimethylsulphoniopropionate (DMSP), a precursor of DMS (Vairavamurthy et al., 1985), which is recognized as a biological regulator of climate by contributing to cloud formation (Park et al., 2021). Coccolithophores also account for a major fraction of the global marine calcium carbonate (CaCO_3) production and export to the deep sea (Hernandez et al., 2020).

However, relatively little is known of the global-scale patterns or environmental controls of coccolithophore diversity (O'Brien et al., 2006; Charalampopoulou et al., 2011, 2016; Balch et al., 2014; Poulton et al., 2017; Smith et al., 2017; Cerino et al., 2017). They are potentially threatened by a changing ocean environment in which Ocean Acidification (OA) (Krumhardt et al., 2016) and warming may affect their ability to calcify and compete. Many studies have reported malformation in coccolithophores as a result of factors such as changing seawater carbonate chemistry, nitrogen limitation, phosphate limitation, low salinity, and high urea (Roth and Berger, 1975; Okada and Honjo 1975; Schneidermann, 1977; Kleijne 1990; Giraudeau 1993; Batvik et al., 1997; Yang et al., 2004; Benner, 2008; Rickaby et al., 2010; Ziveri et al. 2014; Gerecht et al., 2015; D'Amario et al., 2020; Faucher et al., 2020; Kottmeier et al., 2022; Langer et al., 2022). Such stressors are expected to affect coccolithophores with concomitant effects on ocean carbon fluxes, DMS fluxes (Matrai et al., 2007), carbonate geochemistry, phytoplankton community structure (Rost and Riebesell, 2004) and could have far-reaching ecological and biogeochemical implications.

OA may result in changes to biodiversity, trophic interactions, and other ecosystem processes (Kleypas et al., 2006; Hoegh-Guldberg et al. 2007; Fabricius et al. 2011; Hall-Spencer et al., 2008). OA is expected to be more detrimental to organisms with calcareous shells, scales, or skeletons (Orr et al., 2005; Hoegh-Guldberg et al., 2007; Fabry et al., 2008; Anthony et al., 2008; Talmag and Gobler, 2010; Bednarsek et al., 2012). Coccolithophores being calcifying marine nanoplankton have potential sensitivity to OA (Riebesell et al., 2000; Iglesias-Rodriguez et al., 2008; Beaufort et al., 2011). The negative effects of OA on coccolithophore calcification reduces CaCO_3 precipitation (Riebesell et al., 2000; Raven and Crawford, 2012) and thus the particle sinking rates (Riebesell et al., 2017). Earlier experimental studies have suggested carbonate as the most important factor controlling coccolithophore calcification (Riebesell et al., 2000; Meyer and Riebesell, 2015) and is expected to be

affected due to OA. However, a region such as the north Atlantic Ocean has been showing an increase in coccolithophore abundance along with an increase in OA and temperature (Rivero et al. 2015; Krumhardt et al., 2016). Recently Krumhardt et al. (2019) suggested that coccolithophore abundance increases in high CO₂ conditions while their calcification decreases, with a tipping point in global calcification at approximately ~600 μ atm of CO₂. Riebesell et al. (2017) suggested that under high CO₂ treatments *Emiliana huxleyi* lost the ability to form blooms. On the contrary, Schlüter et al. (2014) reported high growth rates, PIC, and POC production under combined warming and OA scenarios. Later, Schlüter et al. (2016) through a long-term evolution experiment (2100 generations) on *E. huxleyi* showed that coccolithophores may evolve complex phenotypic plasticity that can affect biogeochemically important traits, such as calcification. Coccolithophores are expected to be more prevalent under future warming scenarios due to their low nutrient requirements (Cermeno et al., 2008). Upwelling systems present an opportunity to see the effects of low pH on coccolithophores, however, their distributions in upwelling systems have received very little attention (Holligan et al., 1983; Houghton, 1988).

The Arabian Sea presents itself as a natural laboratory with climate stressors such as temperature (Roxy et al., 2014; Dinesh Kumar et al., 2016; Sun et al., 2019) and CO₂ (Kanuri et al., 2017) increasing rapidly, while pH has been rapidly decreasing (Piontkovski and Queste, 2016; Shetye et al., 2020). Since calcification in the Arabian Sea is high (Balch et al., 2000) as compared to the Atlantic, Pacific, and Indian Ocean (Maranon et al., 2016), it makes a very interesting case to study the fate of calcifying plankton under the ongoing climatic changes. Although Banse (1994) proposed that coccolithophores might be the most important primary producers in the Arabian Sea, very few studies focused on coccolithophores so far (Kleijne et al. 1989; 1991; 1992; Gupta et al., 1995; Andruleit et al., 2003; Chowdhury et al., 2022). Hardly any studies have reported the effects of OA on this sensitive plankton in the Arabian Sea. In this context, a valuable approach to assessing the relationship between coccolithophores, carbonate chemistry, and other biogeochemical parameters based on insitu observations was needed. In 2017, a long-term coccolithophore monitoring study was initiated by the biogeochemistry group at CSIR-NIO through which we documented the first-ever detailed spatial and seasonal distribution of coccolithophores and their controlling factors in the EAS. This study of coccolithophore abundance and their environmental controls is an important step in understanding how coccolithophores may be affected by OA in this part of the World's Ocean.

2. Methodology

2.1 Sample collection

Three coastal transects (off Goa, Mangalore, and Kochi) between 9°N to 16°N and 72°E to 77°E were sampled onboard *RV Sindhu Sadhana* (SSD) during the late SWM (SSD 041, 4 to 26 September 2017) and peak SWM (SSD 052, 27 June to 5 July 2018). In addition, sampling was also carried out at the CaTS transect located off Goa, central west coast of India (Fig. 1) during the NEM (February 2018) using a mechanized boat. Four stations (G3, G4, G5, and G6) were covered during this sampling. A Sea-Bird CTD SBE911+ with a rosette was used onboard *RV Sindhu Sadhana*, while a portable CTD SBE 19+V2 was used during the CaTS field trip, for measuring temperature and salinity. The temperature and conductivity accuracy was $\pm 0.001^\circ\text{C}$ and $\pm 0.0001 \text{ S m}^{-1}$ respectively. Niskin samplers of 10 L and 5 L capacities were used to collect seawater samples onboard the ship and mechanized boat respectively. Samples for dissolved gases were collected first, followed by inorganic carbon parameters and nutrients. Samples for coccolithophores were collected in 5 L plastic carboys and 2 L was filtered immediately on a polycarbonate membrane filter (Nucleopore, 47mm, 1 micron) using a vacuum pump with minimum pressure ($< 200 \text{ Mb}$). The filter papers were oven dried for 12 h, stored in plastic petri dishes, and kept in zip-lock bags for subsequent analyses at the CSIR-National Institute of Oceanography (NIO) and ESSO-National Centre for Polar and Ocean Research (NCPOR), Goa.

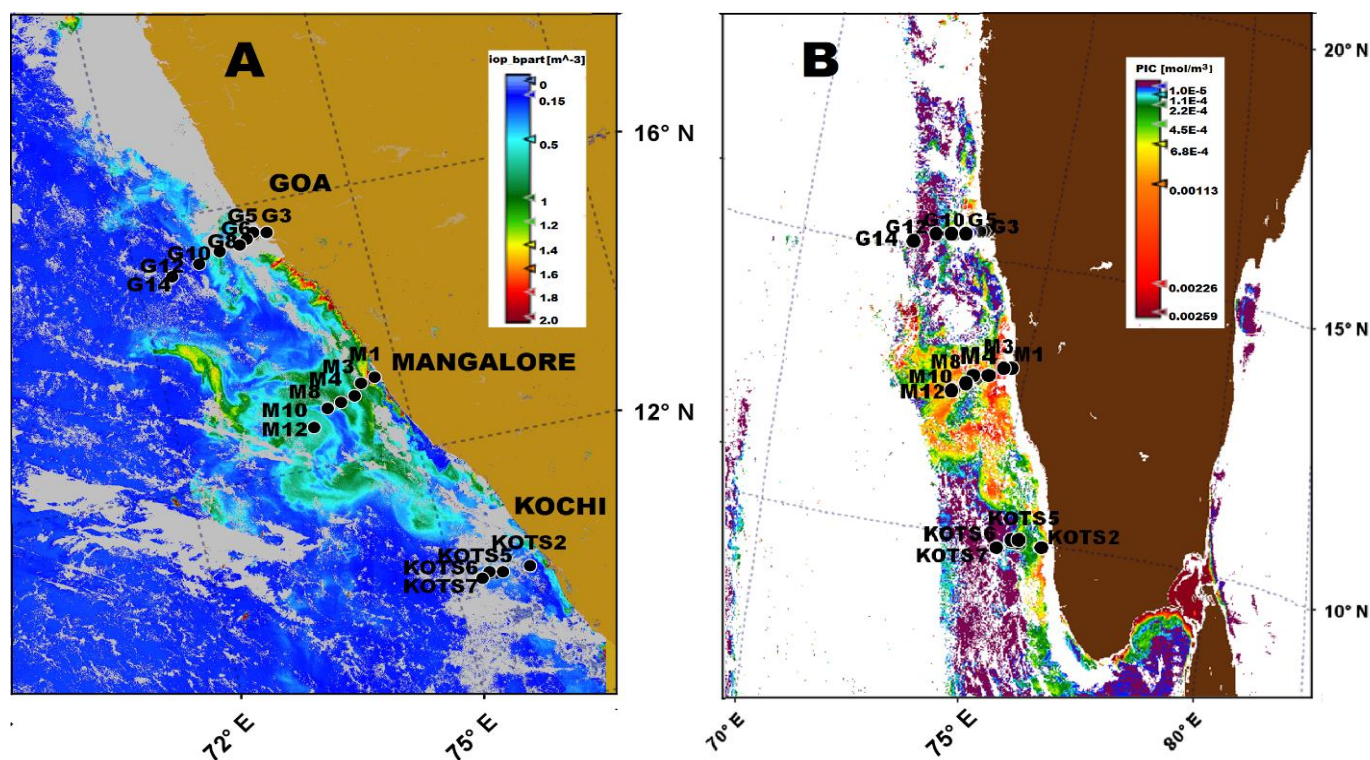


Fig. 1 Map showing (A) backscatter and (B) PIC, overlaid on the sample locations along the west coast of India during the late SWM of 2017

2.2 Analysis

2.2.1 Physicochemical parameters

Dissolved oxygen (DO) was measured following the Winkler titrimetric method (Grasshoff et al., 1983) with a precision of $<1 \mu\text{M}$. Inorganic nitrogen species (NO_3^- , NO_2^- , NH_4^+ , SiO_4^{4-} , and PO_4^{3-}) were analyzed using an Auto analyzer (SKALAR) with a precision of ± 0.06 , ± 0.006 , ± 0.01 , ± 0.003 , and $\pm 0.06 \mu\text{M}$, respectively (Grasshoff, 2009).

DMS was analyzed using the purge and trap method as detailed in Shenoy et al. (2012). The GC was calibrated using DMSP standards (Santa Cruz Biotechnology, Asia), which gave a precision ranging from 1 to 1.5 % for the DMSP standards. For natural samples, a precision of 2.8% was obtained for DMS ($n=10$). Direct measurements of pH_T were made onboard spectrophotometrically using purified *m*-cresol purple as an indicator (Patsavas et al., 2013). Analytical precision was ~ 0.002 for pH_T . Alkalinity was analyzed by potentiometric titration using Vindta 3S. The precision was $2.5 \mu\text{mol/Kg}$. CO_3^{2-} and Ω_{Ca} were calculated from alkalinity and pH using the CO_2SYS program by Lewis and Wallace (1998).

2.2.2 Coccolithophore analysis

The analysis of the samples was done using a Scanning Electron Microscope (SEM) (JEOL SEM Model- JSM 5800 LV (at CSIR-NIO) and 6360 LV (at ESSO-NCPOR)). A quarter piece of the filter membrane was cut and mounted onto the aluminum stubs using double-sided adhesive tape. The samples were coated with approx. 2 nm of platinum to provide optimal conductivity and were then analyzed under SEM at 6-10 KV accelerating voltage and 2000X magnification. Coccolithophores in the samples were counted for abundance from 400 fields. Coccolithophore identification was done following Young et al. (2003) and Mikrotax website (<http://mikrotax.org>).

2.2.3 Pigments

Chl *a* and other pigments were analyzed using high-performance liquid chromatography (Agilent Technologies) using an Eclipse XDB C8 column following the modified method of Van Heukelem (2002) as described in Kurian et al. (2012) and Shetye et al. (2021). Calibration standards were procured from DHI, Denmark. The 19'-hexanoyloxyfucoxanthin (19'HF) is a marker pigment of prymnesiophytes such as coccolithophores (Jeffrey and Veski, 1997).

2.3 Satellite Data

2.3.1 Particulate Inorganic Carbon (PIC)

Daily MODIS level-2 (netCDF4) cloud-free data with 1 km resolution were downloaded from the NASA ocean color website (<http://oceancolor.gsfc.nasa.gov>) for September 2017. The data products have been processed using the recent updates and algorithms using the l2gen software by the NASA ocean biology processing group (O'Reilly et al., 2000). The land and clouds were masked using the standard available level-2 flags. PIC is one of the standard products in the Level-2 OC product suite and was used in this study. The PIC algorithm, used by NASA is a hybrid of two independent approaches based on normalized water-leaving radiances in two bands near 443 and 555 nm (Balch et al., 2005) and spectral top-of-atmosphere reflectance at three wavelengths near 670, 750, and 870 nm (Gordon et al., 2001). The average PIC over the years 2003 to 2019 in the EAS region (71.6- 75.94 °E, 9.48- 19.9° N) was acquired using MODIS from the NASA's Ocean Biology Processing Group.

2.3.2 Backscatter

We used the Sentinel-3 satellite data in this study. Sentinel-3, Level-1C data was downloaded for September 2017 from the publicly available Sentinel Scientific Data Hub. The Case 2 Regional Coast Color algorithm gives the scattering coefficient of marine particles at 443 nm ($b_{\text{part}443}$) as one of the outputs. PIC shows a very good correlation with the scattering coefficient. Hence we have used the same to show the presence of highly scattering calcareous scales of coccolithophores in this study.

2.3.3 Ekman Pumping Velocity (EPV)

The daily wind speed with 25 km resolution was obtained from ASCAT (<http://manati.star.nesdis.noaa.gov/products/ASCAT.php>). Using the above data Ekman pumping velocity (EPV) was calculated following Smith (1968).

$$\text{EPV} = \frac{1}{\rho f} \nabla \times \tau$$

where $\nabla \times \tau$ is the curl of the daily wind stress vector, ρ is the density of the seawater, and f is the Coriolis parameter.

2.4 Statistics

2.4.1 ANOVA

ANOVA analysis and a Tukey post-hoc test were conducted using SPSS software to determine whether the variations in biogeochemical parameters during different seasons are statistically

significant. The Tukeys test was conducted for different seasons and also between the Goa, Mangalore, and Kochi transect. Statistical significance was accepted for $p < 0.05$.

2.4.2 Spearman Rank Correlation

The Spearman Rank Correlation was conducted using SPSS software to check the correlation between various biogeochemical parameters.

3. Results

3.1 Physicochemical factors

On a spatial scale, the Ekman Pumping Velocity (EPV) clearly showed higher upwelling intensity along the Kochi coast as compared to Mangalore and Goa coast, while on the temporal scale the EPV increased from July to September (Fig. S1). Fig. 2 shows the variation of temperature, salinity, pH, and turbidity in the coastal waters of Goa, Mangalore, and Kochi. In general, temperature, turbidity, and pH were low during late SWM, while salinity was low during peak SWM. The average temperature in the top 100 m during the late SWM was 23.8°C (± 3.1) as compared to 26.5°C (± 2.9) during peak SWM, with a difference of nearly 3°C (Fig. 2a & b). The average temperature in the top 40m was 27.8°C (± 0.11) during the NEM (Fig. 2c). The salinity averaged 34.89 (± 0.75) in the top 100 m during the late SWM as compared to 33.96 (± 1.44) during peak SWM and 34.03 (± 0.19) during the NEM (Fig. 2d-f). pH and turbidity were low during late SWM as compared to peak SWM and NEM (Fig. 2g-i). pH in the top 100 m decreased from 7.94 (± 0.13) during peak SWM to 7.82 (± 0.18) during late SWM, while the average pH in the top 40m during the NEM was 8.05 (± 0.03) (Fig. 2g-i). During the peak SWM pH decreased from north to south with Goa having a pH of 7.97 (± 0.1), Mangalore 7.94 (± 0.13), and Kochi having an average pH of 7.89 (± 0.14) (Fig. 2g). During the late SWM, Mangalore had the lowest average pH (7.78 ± 0.18), in comparison to Goa (7.84 ± 0.18) and Kochi (7.83 ± 0.2) (Fig. 2h). The lowest pH (7.53) was found at 100m at station M10 during the late SWM. Carbonate concentration in the top 100 m varied between 70 and $268 \mu\text{M}$, while the carbonate saturation constant (Ω_{calc}) ranged from 1.65 to 6.2 during the late SWM (Fig. 3a & b).

Similarly, Fig. 4 shows the variations of DO, nutrients, N/P and Chl *a* during the peak SWM, late SWM, and NEM. DO vary between 0.3 and 4.4 mL L^{-1} during the peak SWM, between 0.1 and 4.7 mL L^{-1} during the late SWM, and between 3.6 and 4.5 mL L^{-1} during the NEM (Fig. 4 a-c). Fig. 4 (d-k) shows the availability of nutrients during the late SWM as compared to peak SWM and NEM. The average concentrations of nutrients (NO_3^- , PO_4^{3-} and SiO_4^{4-}), in the top 100 m were higher ($12.4 \pm 9.8 \mu\text{M}$, $1.2 \pm 0.6 \mu\text{M}$, and $13.5 \pm 8.7 \mu\text{M}$) during late SWM as compared to peak SWM ($7.3 \pm 8.8 \mu\text{M}$, $0.8 \pm 0.6 \mu\text{M}$, and $11 \pm 6 \mu\text{M}$), respectively. The average concentration of nutrients (NO_3^- ,

PO_4^{3-} , and SiO_4^{4-}) in the top 40m, during NEM, was $(0.25\pm 0.3 \mu\text{M}, 0.3\pm 0.1 \mu\text{M}, \text{ and } 6.6\pm 2.3 \mu\text{M})$ respectively (Fig. f, i, l). N/P was low during peak SWM as compared to late SWM and NEM (Fig. 4 m-o). The N/P was lower than Redfield's ratio of 16 in the top 50m during all the 3 seasons (Fig. 4 m-o). A comparison between the transects (Fig. 4 n) shows N/P was lowest in Goa, followed by Kochi, and greatest in Mangalore during late SWM. The seasonal variations in all the above physicochemical parameters are significant (Table 1). The Tukey's test shows that the variations in NO_3^- , PO_4^{3-} , and DO are significant between all the 3 seasons, while temperature, salinity, pH, and SiO_4^{4-} are significant between peak SWM and late SWM, and between late SWM and NEM (Table 2). Among the three transects (Goa, Mangalore, and Kochi), NO_3^- , temperature, salinity and N/P show significant variations (Tables 3 and 4).

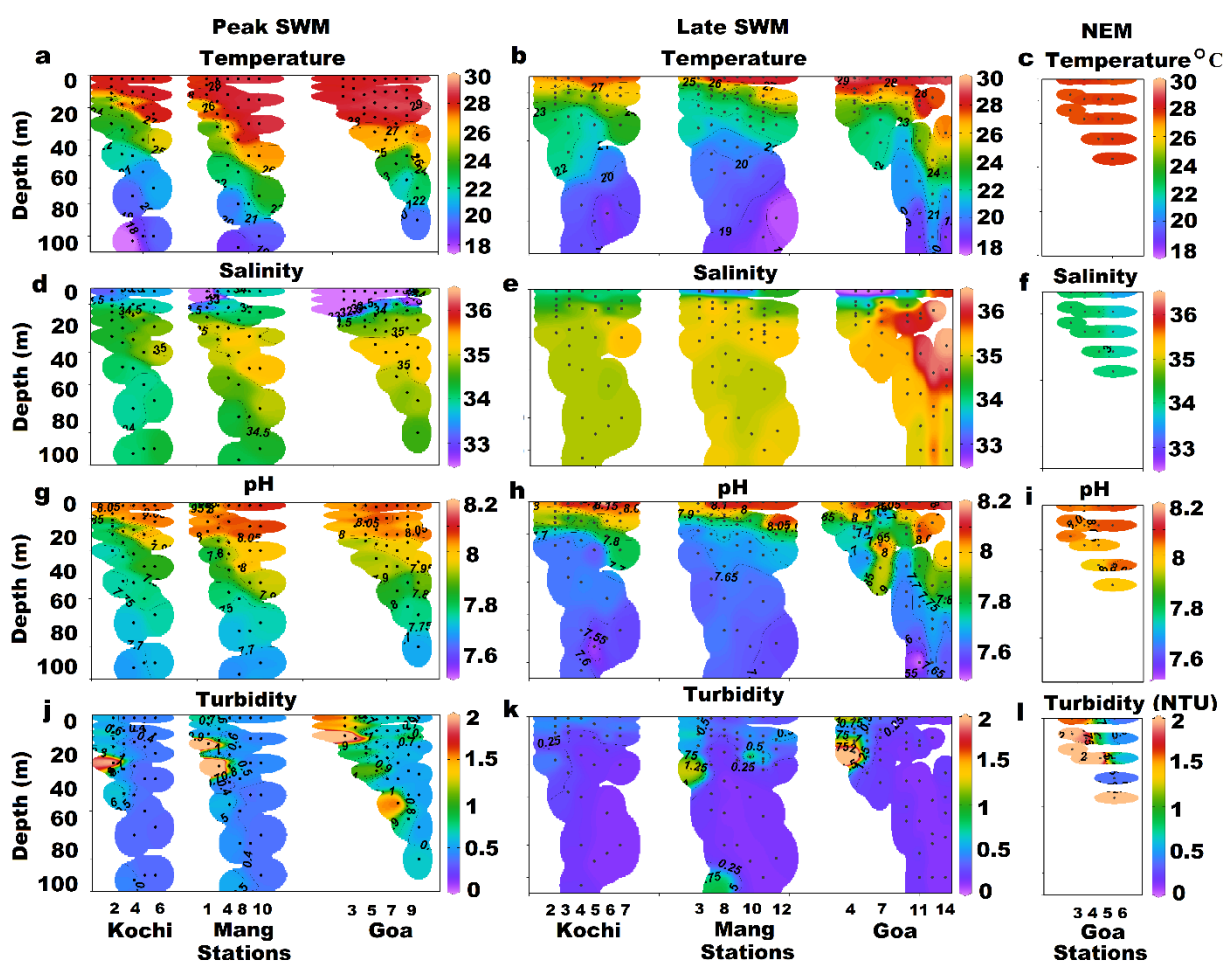


Fig.2 Variability in physicochemical parameters such as Temperature (a-c), Salinity (d-f), pH (g-i), Turbidity (j-l) during peak SWM, late SWM, and NEM along the Kochi, Mangalore, and Goa transects in the EAS

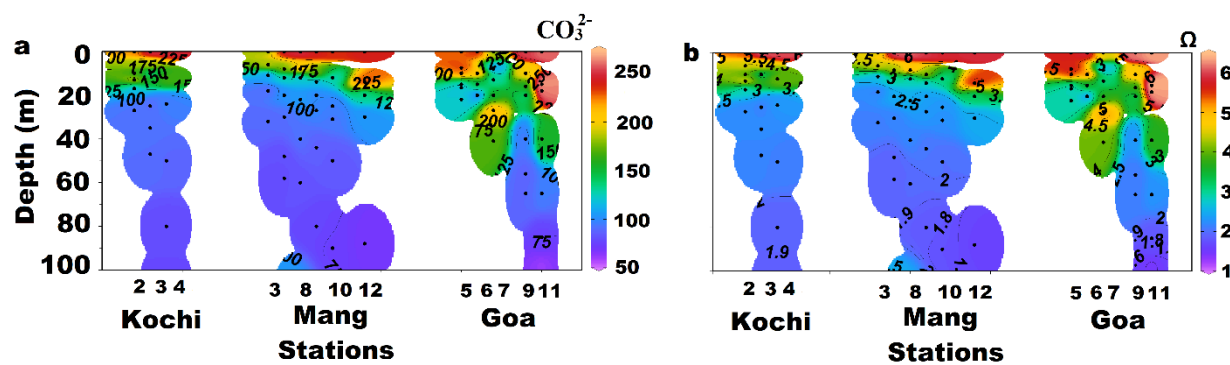


Fig. 3 Spatial distribution in (a) CO_3^{2-} ($\mu\text{mol/kg}$) and (b) carbonate saturation constant (Ω_{calc}) along the Kochi, Mangalore, and Goa transects in the EAS during late SWM

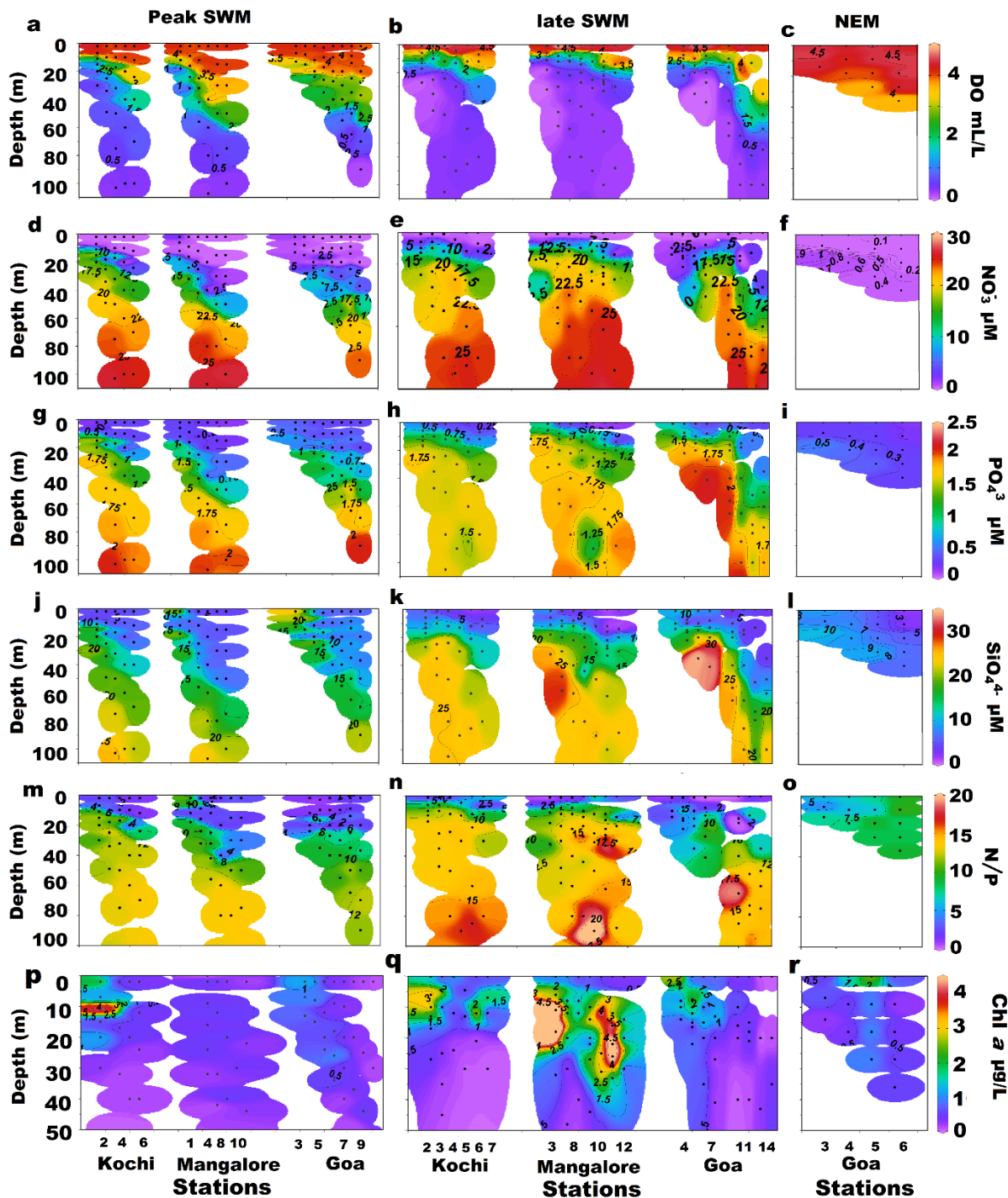


Fig.4 Variability in biogeochemical parameters such as DO (a-c), NO_3^- (d-f), PO_4^{3-} (g-i), SiO_4^{4-} (j-l), N/P (m-o) and Chl *a* (p-r) during peak SWM, late SWM, and NEM along the Kochi, Mangalore, and Goa transects in the EAS

Chl *a* was also high during the late SWM reaching up to $4 \mu\text{g L}^{-1}$ as compared to peak SWM and NEM (Fig. 4 p-r). While the marker pigment of dinoflagellates (peridinin) was high along the Kochi transect, its concentrations were low along the Mangalore and the Goa transect (Fig. 5a). The marker pigment of coccolithophore (19'HF) was similar in concentration to that of peridinin along the Mangalore and

the Goa transect, while it was much lower than peridinin at the Kochi transect (Fig. 5a & b). The surface DMS concentrations varied between 3.3 to 52.6 nM (± 13.8) during the late SWM (Fig. 5c). The surface DMS concentrations were highest along the Mangalore transect reaching up to 53 nM during the late SWM (Fig. 5c).

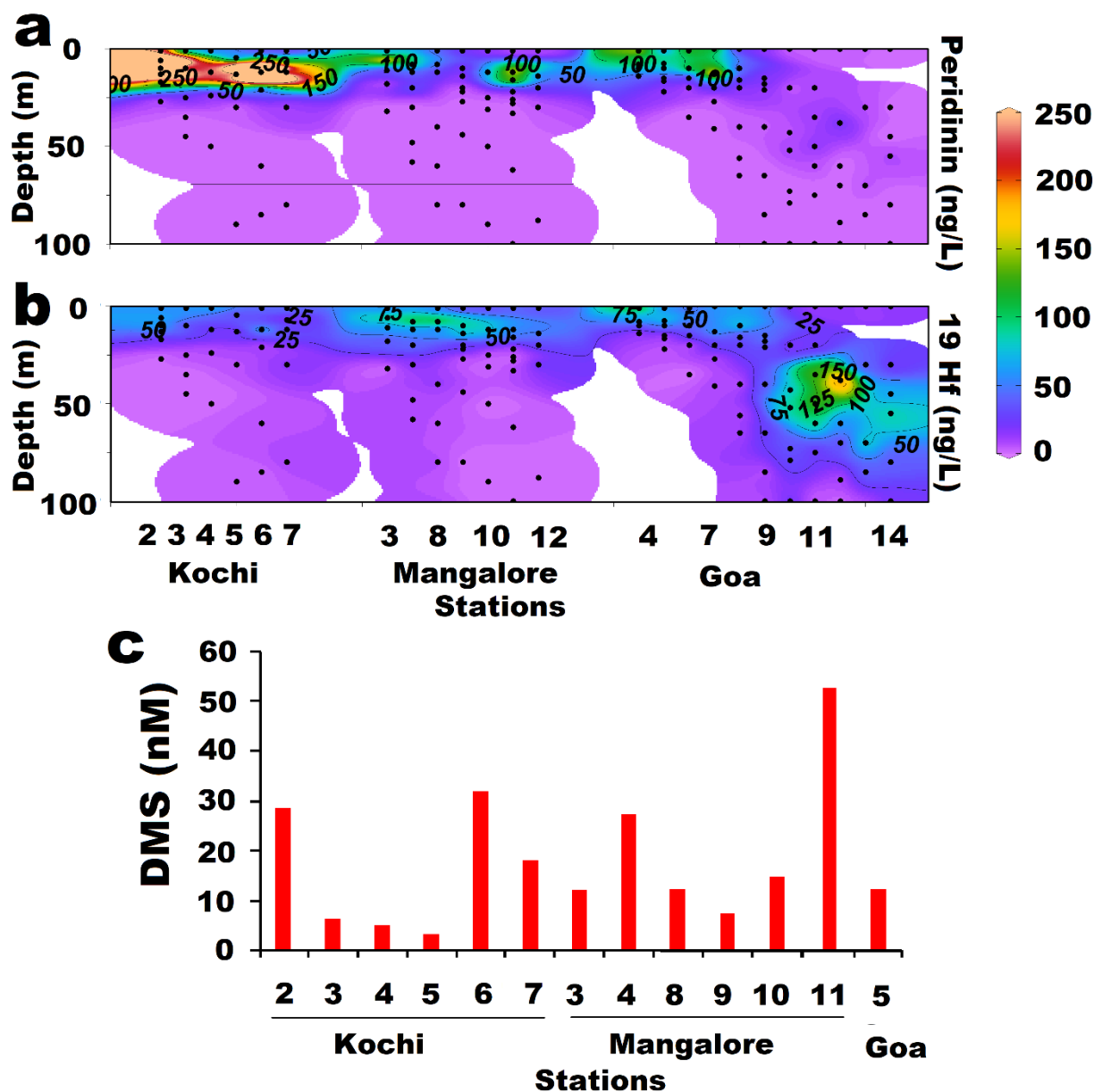


Fig. 5 Spatial distribution of (a) Peridinin, (b) 19'hexanoxyfucoxanthin (19'HF), and (c) DMS along the EAS during late SWM

3.2 Spatial and seasonal abundance of coccolithophores

Coccolithophores exhibited variation in abundance during both seasons. Our study showed an increase in the number of both coccolithophores during late SWM as compared to peak SWM or NEM. The maximum number of coccolithophores (up to $\sim 1800 \times 10^3 \text{ cellsL}^{-1}$) was found at station M-10 (12 m

depth) followed by station M-3 (up to $\sim 1100 \times 10^3$ cells L^{-1}) at 18 m depth (Fig.6a). High numbers of free coccoliths were also reported at the same stations as that of coccolithophores with a count of 1800×10^3 coccoliths L^{-1} and 670×10^3 coccoliths L^{-1} at M-10 and M-3, respectively (Fig. 6c).

Gephyrocapsa oceanica was the most abundant coccolithophore species in the study area. Apart from *G. oceanica* the numbers of other species were not significant, however, free coccoliths were found in other species and are reported in supplementary Fig. S2. *G. oceanica* had its highest abundance at M-10 (12m depth) reaching up to 1450×10^3 cells L^{-1} (Fig. 6b). The other most common coccolithophore species found was *Calcidiscus leptoporus* with a maximum abundance of only 67×10^3 cells L^{-1} .

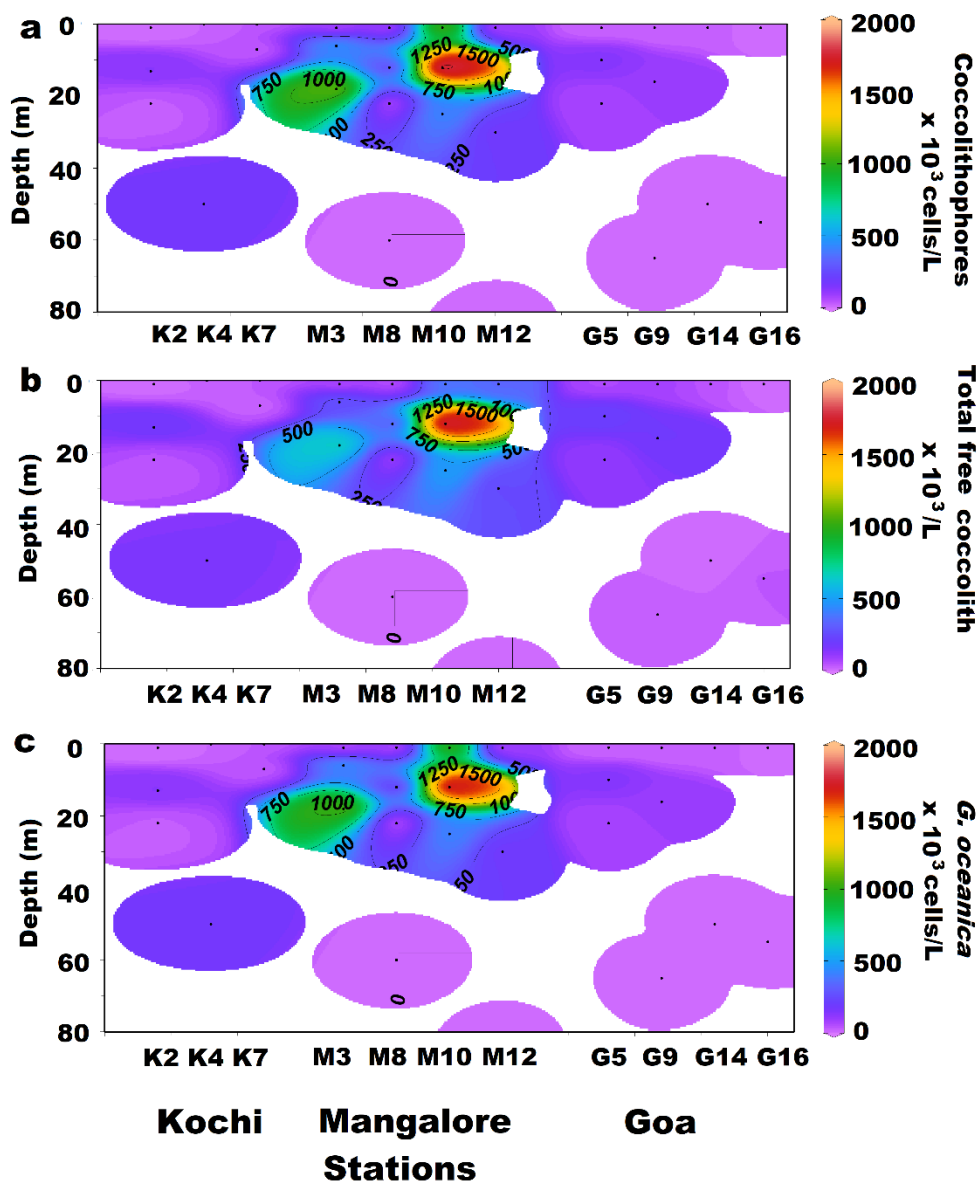


Fig.6 Vertical and spatial distribution of (a) coccolithophores, (b) total free coccoliths, and (c) *G. oceanica* during late SWM along the EAS

While comparing the late SWM and NEM, the abundance of coccolithophores was found to be less during the NEM. The abundance of coccolithophores showed large seasonal variation, with the highest abundance at Goa transect during the late SWM ($136 \times 10^3 \text{ cells L}^{-1}$) (Fig.7a), whereas it was only $8.5 \times 10^3 \text{ cells L}^{-1}$ during peak SWM (Fig.7b), while during NEM abundance was $73 \times 10^3 \text{ cells L}^{-1}$ (Fig.7c),

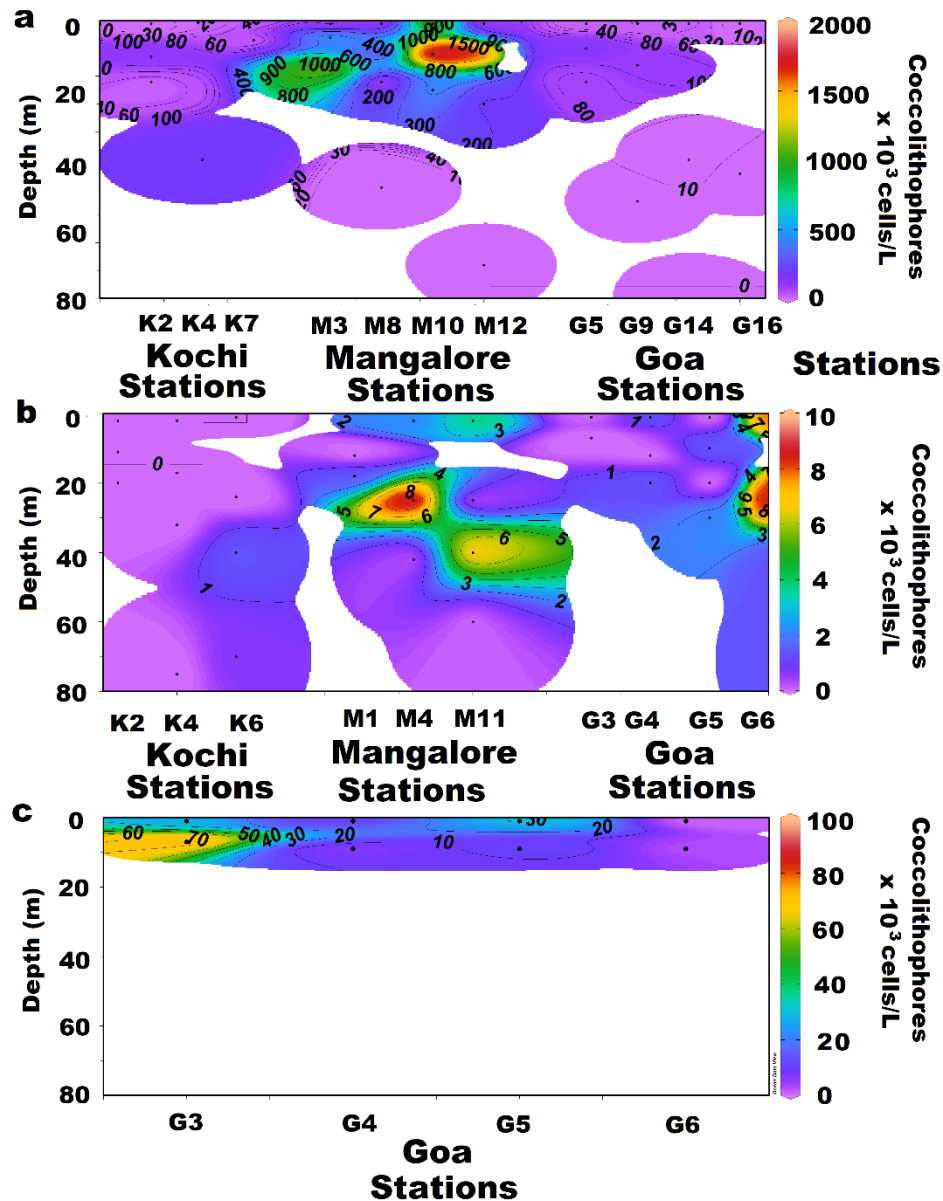


Fig. 7 Seasonal variation of coccolithophores during (a) late SWM (b) SWM and (c) NEM along the EAS. Please note that the scales are not matched due to high abundance at 2 stations during late SWM

3.3 Malformation

One of the most striking findings was the presence of malformed coccolithophores during peak and late SWM. We found 2 types of malformation, one in which the bridge was absent, the lack of the central tube, and a distal shield; however the coccosphere structure was intact (Fig.8 a, b & c). While

in the second case the coccolithophore structure was distorted, and the central tube was solid calcite (Fig.8 d, e & f). The second type of malformation in *G. oceanica* was observed only at station M10 (12m) during the late SWM. During the NEM the coccolithophores exhibited normal calcification (Fig.8 g, h&i).

3.4 Spearman rank correlation

Spearman rank correlation between coccolithophore abundance and various physico-chemical and biological factors shows that the coccolithophore abundance was positively correlated with salinity ($r=0.3$), while it showed a negative correlation with pH, temperature, and SiO_4^{4-} (Table 5). However, the correlations with all these factors were either very weak or weak and $p>0.05$.

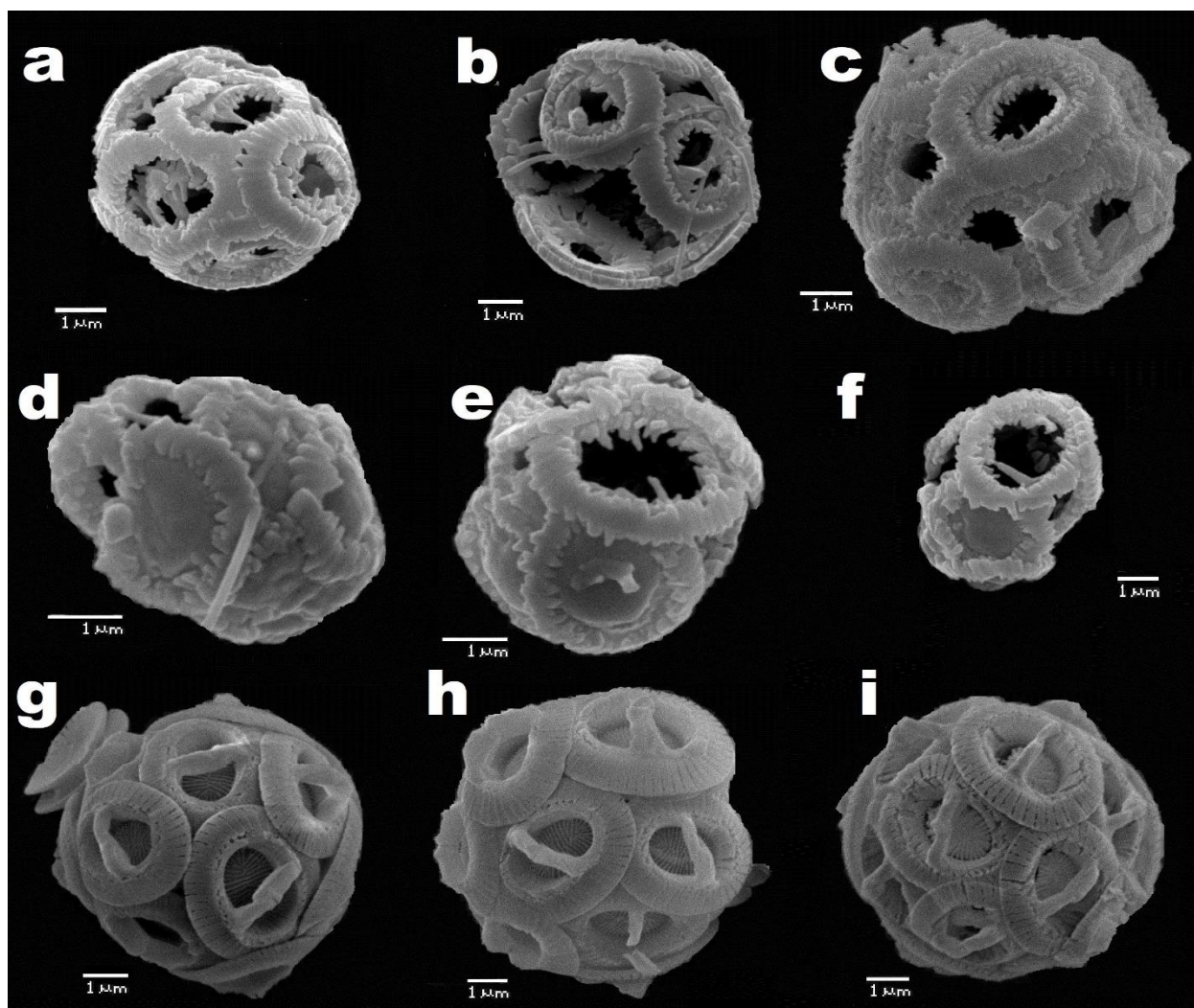


Fig.8 Coccolithophores of *G. oceanica* showing malformation during late SWM (a-c) malformation with empty central area, (d-f) malformation with solid calcite in the center during late SWM, and normal calcification during NEM (g-i). The scale bar length is not the same as images were observed at different magnifications.

4. Discussion

The Arabian Sea is characterized by upwelling and this brings low-pH subsurface waters to the surface (Raven et al., 2005). Recently, Shetye et al. (2020) presented results from the first long-term pH data from the coastal Arabian Sea, indicating that the EAS exhibits large variations on a seasonal scale (7.81 to 8.12) with low pH waters during the SWM. Earlier, Kanuri et al. (2017) showed that the mean pCO₂ along the southwest coast of India (EAS) has increased at a rate of 5.3 $\mu\text{atm}\text{y}^{-1}$. Prior to that, Sarma et al. (2000) showed that the coastal waters along the EAS contained high pCO₂ reaching up to 685 μatm during the SWM. These studies indicate that the EAS is prone to low pH and high CO₂ waters that are expected to affect calcification and calcifying plankton such as coccolithophores. In the following sections, we discuss the distribution of coccolithophores and their controlling factors in the EAS.

4.1 High abundance of coccolithophores during late SWM

A high abundance of coccolithophores was observed during the late SWM despite low pH conditions. The high abundance can be related to high N/P as compared to peak SWM. For eg., the N/P ratio along Goa transect is 5.6 and 7.4 during peak SWM and late SWM. The average N/P ratio across the Mangalore transect increases from 7.6 to 11.5 from peak SWM to late SWM. Ekman pumping velocity shown in fig. S1 clearly shows a rise in upwelling velocity from peak SWM to late SWM. Upwelling brought the required nutrients to the surface waters that were required for coccolithophores (Fig.4). A recent study by Shetye et al. (2019) from the EAS has clearly shown that the concentrations of inorganic nutrients drop from SWM to the NEM. As nutrients are essential for the growth of phytoplankton (Arrigo, 2005) and vary due to physical forcing, we can see their influence on coccolithophore abundance. Few experimental studies have shown that under nutrient-replete conditions coccolithophores show better adaptation to high CO₂ conditions and maintain higher calcification rates (Lohbeck et al., 2012; Benner et al., 2013; Schluter et al., 2014). Coccolithophore distribution and community composition are suggested to be most affected by pH (Charalampopoulou et al., 2011). However, a recent study by Vazquez et al. (2022) has suggested that it is the high-CO₂ levels rather than low pH that restrict the growth and performance of coccolithophores such as *E. huxleyi*. The high abundance of coccolithophores can also be related to their ability to utilize different sources of nitrogen (for eg., Benner and Passow, 2010).

Compared to Goa and Kochi, the abundance of coccolithophores was high off Mangalore, which had high N/P. Mangalore also had high concentrations of DMS. The dominant coccolithophore species was *G. oceanica*. This is known to be the most abundant species in monsoon-influenced marginal seas

and shelf areas (Giraudeau, 1993). However, their abundance was very low during peak SWM which may be attributed to nitrogen limitation and low salinity (Fig. 4 m-o & 2 d-f). The high abundance observed during late SWM requires special adaptations to counter the stress resulting from low pH conditions (Fig. 2h). Coccolithophores are known to exhibit a wide array of adaptation strategies, e.g. *G. oceanica* increases substrate uptake efficiency and decreases light requirement under high CO₂ levels (Gafar et al., 2019). On the other hand, some species maintain a constant pH at the calcification site, irrespective of the pH in the surrounding seawater (Liu et al., 2018). D'Amario et al. (2017) suggested that a haplo-diploid life cycle could provide a way to adapt to environmental changes. Díaz-Rosas et al. (2021) reported the occurrence of *E. huxleyi* in naturally low pH- Ω_{cal} environments and suggested that it is capable of adaptation. Experimental evidence reveals the potential for adaptation and rapid microevolution; however, they need to be monitored in the field as also suggested by Lohbeck et al. (2012).

4.2 Malformation in coccolithophores

The present field study found malformation in coccolithophores (Fig.8), indicating that the prevailing environmental conditions on the western continental shelf of India during the SWM can affect the coccolithophores. The malformation may be the result of incomplete calcification, due to a deficiency in the metabolism induced by particular environmental conditions (Kleijne, 1990). Except at station M10, coccospheres have their normal shape and only the coccoliths seem to be affected. However, at station M10, the coccosphere was also found to be malformed as seen in Fig.8 (d-f) and is not reported earlier. Interestingly, this station had a maximum abundance of coccolithophores and experienced low pH conditions during late SWM (average pH=7.7 and bottom water pH=7.53). The average Ω_{calc} was also low (2.85) at this station, with minimum values of 1.75. The malformed cells of *G. oceanica* during late SWM (Fig.8 a, b & c) are identical to those collected in the South China Sea, Indonesian Sea, and Benguela upwelling system as reported by Okada and Honjo (1975), Kleijne (1990), and Giraudeau (1993), respectively. On the other hand, normal coccolithophores were found during non-upwelling conditions with high pH during the NEM.

Each malformed coccosphere contains multiple (malformed) coccoliths indicative of an intact cellular mechanism for initiating coccolithogenesis and expulsion, despite the significant malformation (Rickaby et al., 2010). Malformation of coccoliths can be the result of either dissolution (Roth and Berger, 1975; Schneidermann, 1977) or incomplete calcification (Kleijne, 1990). Faucher et al. (2020) suggested that malformations are unlikely to be the consequence of an ecological adaptation to environmental stress because there is no ecological advantage to producing malformed coccoliths. Okada and Honjo (1975) considered nitrogen deficiency and Kleijne (1990) considered nitrogen

deficiency and low salinity as responsible factors for coccolith malformation in the Red Sea and the Indonesian waters, respectively. Yang et al. (2004) suggested nitrate deficiency as the reason for the malformation of coccolithophores in the East China Sea. Although Oviedo et al. (2014) reported that phosphorus limitation did not lead to malformations in the Mediterranean strains of the coccolithophore *E. huxleyi*, Batvik et al. (1997) reported that phosphorus and nitrogen stress caused significant changes in coccolith size and evidence of malformation was clear in the low-phosphate conditions. Langer et al. (2022) showed that coccolithophores exhibited defects in coccolith formation under both nitrate and phosphate limitation only in the heavily calcified heterococcolithophore phase and not in holococcolithophore phase. Also, an increase in coccolith malformations was observed when nitrate was replaced with urea as the nitrogen source (Benner, 2008). All these studies report nutrient limitation as a cause for malformation, however, Giraudeau et al. (1993), suggested that nutrient deficiency is not the main cause of coccolith malformation. Even the limitation of Si impacts crystal morphogenesis and led to malformation (Langer et al., 2021). However, the requirement for Si in heterococcolith formation has been lost in certain coccolithophore lineages, such as the *Emiliana* and *Gephyrocapsa* (Durak et al., 2016).

Some studies reported that changing seawater carbonate chemistry induced malformations, and malformation increases in some species with phosphate limitation (Gerecht et al., 2015; Faucher et al., 2020). Earlier, Ziveri et al. (2014) observed malformed coccolithophores close to CO₂ seeps, which indicated that those were affected by low pH conditions. D'Amario et al. (2020) also reported malformations in the Mediterranean Sea coccolithophores under OA conditions. A recent study by Kottmeier et al. (2022) reported that low pH prevents removal of H⁺ generated by the calcification process, leading to specific coccolith malformations. From all the above studies the possible factors for coccolith malformation appear to be low pH and nutrient limitation, however considering that late SWM had higher N/P as compared to peak SWM, we rule out role of nutrient limitation in malformation. When the pH is low during the late SWM, the abundance of *G. oceanica* was still high due to sufficient nutrient availability, but the calcification can shift from normal calcification to malformation.

4.3 Implications of changes in coccolithophores

Coccolithophores account for a significant proportion of ocean productivity and are the main producers of biogenic calcite, making major contributions to global biogeochemical cycles, including the long-term export of both inorganic and organic carbon from the ocean photic zone to deep waters (Balch et al., 2018; 2019). As plankton communities influence sinking velocities of organic matter by providing ballast minerals and modifying aggregate porosity (Balch et al., 2016), any changes in the abundance

of coccolithophores will affect many biogeochemical processes. Changes in coccolithophore calcification such as malformation will affect their ingestion by predators. Harvey et al. (2016) reported that predators had, on average, a 60% slower growth rate on calcified strains of coccolithophore relative to naked strains. Changes in coccolithophore abundance will affect the production of climatically important gas such as DMS as seen in this study (Fig.5) as coccolithophores are one of the major producers of DMS along with dinoflagellates (Keller et al., 1989; Liss et al., 1993). Although OA is expected to decrease DMS production (Archer et al., 2018), global warming overturns the effect of increased pCO₂ (Arnold et al., 2013). The smaller phytoplankton will be favored under low nutrient availability (Wang et al., 2018) and climate change is expected to increase coccolithophores in the low latitudes (Tyrrell et al., 2007; Cermeño et al., 2008). The satellite data of PIC in the eastern Arabian Sea indicates a high abundance of coccolithophore in recent years, especially during the warm Elnino years (2015 and 2018) (Figure S3). These changes in coccolithophores will in turn play an important role in DMS production under future warming scenarios. Although their abundance may increase, the malformation in coccolithophores due to low pH will reduce the PIC and the settling fluxes and thus result in the disruption of the organic carbon pump.

We suggest that in the Arabian Sea, low pH conditions play an important role in the calcification process while nitrogen limitation regulates the abundance of coccolithophores. Our results are important considering that both low pH and nitrogen-limiting conditions are expected to rise in the future (Sreeush et al., 2019; Buchanan et al., 2021) with CO₂ uptake and ocean warming. D'Amario et al. (2020) have predicted that coccolith malformations will increase with ocean warming and OA until they develop adaptation to these climatic stressors. They also suggested that OA is expected to exacerbate effects due to the rise in temperature in coccolithophore communities. Faucher et al. (2020) through laboratory experiments have suggested a more global occurrence of malformation in modern coccolithophore species under OA. Von Dassow et al. (2018) suggested that the coccolithophores may be near the limit of their capacity to adapt to the ongoing OA. Therefore, evolutionary processes are key to the success of phytoplankton in a future ocean (Schlüter et al., 2014). Niu et al. (2020) suggested that a greater disruption of the organic carbon pump can be expected in response to the combined effects of environmental stressors in the oceans of the future. Therefore regular and long-term monitoring of coccolithophores is needed as the coverage of coccolithophore bloom will influence the atmospheric chemistry and potentially the climate.

5. Conclusion

The present study provides the first detailed information on the abundance and calcification of living coccolithophores from the eastern Arabian Sea. *G. oceanica* was the most abundant species found in

the study. Mangalore had the highest abundance of coccolithophores during the late SWM despite having the lowest pH. The high abundance off Mangalore was also captured in the PIC and particle backscatter data. Our study shows that coccolithophore abundance was regulated by nitrogen availability. Coccolithophores showed malformation in low-pH waters during the late SWM. The malformation reported in this study is the first evidence from the Arabian Sea and would influence settling fluxes of PIC and organic matter in future high CO₂ waters. Long-term in-situ monitoring of coccolithophores and their controlling factors is required for the northern Indian Ocean, especially in the Arabian Sea to assess the decadal changes in their abundance, including a rise in their bloom formation in the Arabian Sea.

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Statements & Declarations

Ethics approval

We approve that this manuscript is part of research studies on ocean biogeochemistry.

Consent to participate and for publication

We give consent to publish our work on coccolithophores in the Arabian Sea and this work is jointly contributed by all authors.

Competing interests

The authors declare no competing interests.

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Author Contribution

Suhas Shetye: Planning and Execution of study, sample collection, analysis, manuscript writing

Sahina Gazi: Analysis of Coccolithophores

Arundhathy M: Analysis of Coccolithophores

Damodar Shenoy: Analysis of Dimethyl Sulphide, manuscript writing

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Nandakumar K: Sample collection and processing for Coccolithophore analysis

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Competing Interest

The authors have no relevant financial or non-financial interests to disclose

Availability of data and materials section

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