Fossil Shell Color and Trace Element Concentration as Indicators of the Paleoenvironments of the Piney Point Formation at the Pamunkey River, Virginia Coastal Plain

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Abstract: The minor and trace inorganic elements may contribute to different colors of fossilized shells, depending on the environmental conditions of the sea water, differential fossilization process and diagenesis, even though the original color of the living biocalcifers' shell is primarily developed by a variety of organic pigments. The sediments of the Piney Point Formation that crop up along the Pamunkey River are made up of blue glauconitic sand and clay with scattered, distributed enormous shell fossil fragments. Shattered fossil fragments of differing color from two exposures along the Pamunkey River were studied in terms of minor and trace element concentration to comprehend the relation between the color of fossil shells and paleoenvironments. The fossil fragments were grouped and sorted according to color independently of each of the other samples. Total 35 groups of fossil fragments resulted after sorting. The samples were organized by place in the stratigraphic column, then sorted into 5 similar color groups for analysis: Light, dark, gray, coated and black. Fossil fragment samples from the Piney Point Formation exhibited apparently lower concentrations of Barium than those in the Woodstock Member of the Nanjemoy Formation. Magnesium and strontium values were also higher in the Piney Point Formation. There was a higher level of strontium at the Piney Point-Old Church boundary, this could be due to an increased salinity in the Old Church Formation. Concentrations of sulfur and phosphorous in the partitioned fossil fragments were mostly anomalous, though the black and dark fossil fragments of Old Church Formation had significantly higher concentrations of sulfur. There were no linear and explicit relationships between the colors of the fossil shells fragments and trace metals concentration. Ba/Ca ratios tended to be higher in the fossil fragments of the Piney Point sediments. The higher Ba/Ca ratios in the Piney Point samples probably demonstrate an increase in biogenic activity. At the time of deposition of Piney Point sediments, the water probably had higher temperatures and the Piney Point-Old Church contact had an increased salinity condition.

Key words: Pamunkey River, Piney Point Formation, fossil fragments, paleoenvironments, trace elements, salinity

INTRODUCTION

The original color in fossil shells is very rarely preserved in the geologic record due to the differential fossilization processes and diagenesis (Kobluk and Mapes, 1989; Kidwell, 1998). Fossilized shells are often turned a dull, medium gray color following the loss of original pigmentation (Nitecki and Sadlick, 1968). Sometimes, even within a single sedimentary layer fossils occur with different color, ranging from light to dark with hues of gray, brown and red (Brett, 1983), even though the original color of the shell of living biocalcifers is primarily developed by a variety of organic pigments. The minor and trace inorganic elements may contribute to different colors of fossilized shells (Dauphin et al., 2011; Dauphin, 2002; Fox, 1966; Kolbe et al., 2011; Zhao, 1990).

It has been well established for years that marine biocalcifers develop skeletons predominantly in accordance with the seawater chemistry of the time when that particular group came into existence (Clarke and Wheeler, 1922; Wilkinson, 1979; Constanz, 1986;

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Railsback and Anderson, 1987). Since, calcium ions are taken up from seawater, it is likely that other elements would be taken in during shell formation (Furuhashi *et al.*, 2009).

Therefore, if mollusks use the elements in the water in which they live to form their shells, then their shells should be representative of the trace elements that were present in the water at the time of formation. Trace elements are in higher and lower concentrations depending on the environmental conditions of the water (Hahn *et al.*, 2012). However, the case with fossil shells is not that obvious, as the fossils are further modified due to burial diagenesis.

Scattered and extensively distributed fossil fragments of Pamunkey River stratigraphic sequences were studied to verify whether paleoenvironmental conditions had an effect on the differing fossil colors and trace element concentrations. The researchers of the present study assumed that the different colors of fossilized shells existing in the sedimentary layers may represent different concentrations of trace elements, reflecting the water chemistry and therefore differing conditions in the paleoenvironments of the Atlantic Ocean at Salisbury embayment where the modern day Pamunkey River lies.

Geologic and stratigraphic background: Well preserved tertiary marine sequences in the Virginia Coastal Plain present a magnificent opportunity to study the sedimentary sequences of the fossiliferous Nanjemoy, Piney Point and Old Church Formation along the Pamunkey River. Furthermore, the sedimentary sequences along the Pamunkey River provide geological evidence of 3 distinct time periods, more specifically 3 epochs: The Eocene, Oligocene and Miocene, all preserved in one place.

Shattered fossil fragments of differing color from 2 exposures along the Pamunkey River (Fig. 1) were studied in terms of minor and trace elements distribution and concentration to comprehend the relation between the color of fossils and paleoenvironments. At first exposure (Fig. 2), the Piney Point Formation is unconformably underlain by the Nanjemoy Formation, a definite boundary event that demarcates the bottom of the Piney Point Formation. The second exposure (Fig. 3) was located at Horseshoe, the exposure had a definite boundary feature where the Piney Point Formation is unconformably overlain by the Old Church and Calvert Formation.

The area around the modern day Pamunkey River was a part of the Salisbury embayment. During the Eocene, Eastern Virginia was dominated by the Salisbury embayment and the Norfolk arch. The water of the Salisbury embayment was broad and shallow with a mild-to warm-temperature marine environment while South of the Norfolk arch the water was a subtropical to tropical environment (Ward, 1985). The stratigraphy of Eastern Virginia includes the Nanjemoy Formation and the Piney Point Formation during the early and Middle Eocene, respectively. There is then no layer present until the Old Church Formation which is most likely late Oligocene (Ward, 1985; Bybell and Gibson, 1994).

The Nanjemoy Formation consists of 2 members: The Potapaco Member and the Woodstock Member. Only the younger Woodstock Member will be discussed in this study, as it is the only part of the Nanjemoy Formation that is exposed in Fig. 2. The Woodstock along the Pamunkey River is typically olive-black, very fine, well-sorted and silty, glauconitic sands and it is directly overlain by the Piney Point by an easy to recognize

Fig. 1: Location map (google map)

Fig. 2: Horseshoe of Pamunkey River with the distinct unconformity surface between Piney Point and Old Church Formation

Fig. 3: The bone bed between Old Church and Calvert Formation

Fig. 4: PM section, the Woodstock Member of Nanjmoy Formation is unconformably underlaying the Piney Point Formation

Fig. 5: Fossil shell fragnments in PM section

unconformity (Ward, 1985). There is an abrupt change in the lithic, faunal and floral characteristics that makes it easy to distinguish between the 2 stratigraphically. Both the Piney Point and the Woodstock are extensively fossiliferous, even though they have no species in common (Ward, 1985).

The most important stratigraphic unit of the present study is the Piney Point Formation. The sediments of the Piney Point Formation that crop up along the Pamunkey River are made up of blue, glauconitic sand and clay with scattered, distributed enormous shell fossil fragments. The Piney Point formation unconformably overlies the Woodstock member of the Nanjemoy Formation. The unconformable contact between the 2 units is exposed almost continuously along the Pamunkey River and is easily identifiable due to the unique salt pepper appearance of the Piney Point sediments and intense burrowing in the Woodstock surface (Fig. 4 and 5).

According to Ward (1985), the Piney Point Formation is much lighter in appearance than the Woodstock member, he attributed this is in part due to the higher shell content in the Piney Point. Ward states that around 150 species of well preserved molluscan fossils are present and the fossil assemblages make up a large portion of the strata which is the focus of the present study.

The Piney Point is overlain by the Old Church Formation and Calvert Formation. The unconformable contact between the Piney Point and Old Church is sharp

and is marked by a basal lag of shell, bone and pebble. Otton (1955) first encountered the Piney Point sediments in the subsurface of Maryland and assigned an upper eocene age to the formation. Brown (1972) examined the Piney Point sediments and suggested the formation be assigned a Middle Eocene (Claiborne) age. The age determination was based on the presence of characteristic Claibornian ostracod species.

Olsson *et al.* (1980) studied the Piney Point in Maryland and based on the presence of characteristic Oligocene planktonic foraminifera, assigned the Oligocene age for the Piney Point Formation, they also suggested early to middle eocene age for the Nanjemoy Formation. Ward (1985), however remarked that Olsson *et al.* (1980) wrongly termed Old Church Formation as Piney Point since their description of the layer fits the Old Church beds from the Pamunkey River, except for the amount of glauconite. Ward (1985) assigned the age for the Piney Point formation to Middle Eocene, principally based on presence of *Cubitostrea sellaeformis.*

The Old Church Formation is grayish-olive, clayey, quartz sands containing small amounts of reworked glauconite. There is also a high amount of shell fragments. The Old Church distinctively overlies the Piney Point Formation and is distinctively overlain by the Calvert Formation. According to Ward (1985) at Horseshoe, the Old Church is burrowed with the overlying Calvert Formation sediment that is spread horizontally along the Piney Point Old Church contact.

The exposed sequences along the Pamunkey River were not examined paleontologically in this study. However, since there are definite unconformities between the three formations, the fossil shells are all from different species and times in the different formations.

MATERIALS AND METHODS

Collection of samples: It is rare to find geological evidence of 3 distinct epochs, preserved all in one place, particularly in a coastal plain setting. The 2 exposures studied along the banks of the Pamunkey River are excellent examples of 3 distinct Cenozoic epochs. The unconformities present at the 2 locations are distinguished by distinct boundary features between the formations. The boundary events are termed PM-B and HS-B. In the PM section (Fig. 2), the bottom of the Piney Point Formation is marked by the PM-B event and below this is the Woodstock Member of the Nanjemoy Formation. The PM-B event is made up of hard fossiliferous sandstone with calcareous cementations that serve as the distinctive boundary in the exposure between Nanjemoy and Piney Point. The HS section

is at Horseshoe (Fig. 3) on the Pamunkey River, similar to the PM exposure the only distinct feature is the HS-B boundary event between the overlaying Calvert Formation and underlying Old Church Formation. The Old Church is also burrowed with the Calvert Formation. Many shark teeth can be found at the HS exposure and the large hiatus concretions at its foot.

Sediments containing the fossils fragments were collected from 2 specific locations, i.e., Fig. 2 and 3 along the Pamunkey River. The samples were collected in regular intervals from different stratigraphic units in a vertical column at the 2 sites. Prior to sampling, selection of sampling sites was finalized through detailed field investigations, in order to obtain representative samples from each stratigraphic unit. The exposures were thoroughly unsoiled to remove the weathered and slumped materials and to obtain the clean and unweathered vertical exposures. Finally, intact and undisturbed sediments samples were collected, in PVC pipes by penetrating perpendicularly into the exposure in both fixed intervals and following significant geological features.

Sorting and selection of samples: About 10 sediments samples were selected and washed through a 106 μm sieve and allowed to dry in an oven at 70°C overnight. The dried samples were filtered again through a 500 μm sieve in order to discard the smaller fragments. The fractions larger than 500 μm were screened again through a 2000 μm sieve and kept aside. The pieces larger than 2000 μm were sorted to make sure all were fossils, rocks, plant debris and other non fossil material were removed carefully. The remaining fossils were grouped and sorted according to color independently of each of the other samples. About 35 groups of fossils resulted after sorting.

In order to obtain sediment-free and clean fossil shells fragments, samples were thoroughly washed with a method modified after De Deckker *et al.* (1988). The modified method is described as follows: The color sorted samples were put in different glass beakers with deionized water and sonicated for approximately 10 min. When the water of the beaker appeared cloudy, the samples were rinsed with water and allowed to soak again. This process was continued until the water of the beaker remained clean. The samples were then oven dried for 24 h at 70°C. After the samples were completely dry they were sonicated again with methanol for 10 min. The methanol was removed and the samples were dried overnight in an oven at 60°C.

Partitioning of the samples by color and physical properties: The cleaned samples were verified for

color and were resorted if needed. The samples were photo-cataloged for additional evidence of their physical appearance. A list and description of the color sorted samples is summarized in Table 1, according to the stratigraphic position (Fig. 6).

Bulk chemical analysis: About 35 of the fossil color group samples were crushed to a fine powder with an agate mortar and pestle, then immediately transferred to airtight vials for later analysis with ICP-MS and ICP-OES to determine the trace element concentration.

Table 1: Summery of partitiionary of fossil shell fregments

Stratigraphic unit	Sample code	Colors	Munsell color code	Texture	Weight (mg)	Weight (%)
Calvert Formation	HS2A1 black	Black		Hard	1637	100.00
	HS2B shell	Light gray	2.5YR7/1	Brittle	18	6.45
	HS2B brown	Black-brown to red-orange-brown		Fragile	15	5.38
	HS2B black	Black		Hard	246	88.17
Old Church Formation	HS2C fragments	Gray to tan		Fragments, chalky	193	28.34
	HS2C white	Dark gray		Thin, britlle, shiny	110	16.15
	HS2C dark	Dark gray		Brittle	216	31.72
	HS2C light	White to yellow-tan		Thin, brittle	162	23.79
Piney Point Formation	HS2D1 light	Light gray		Chalky	524	50.63
	HS2D1 black	Black	5YR3/1	Thin	66	6.38
	HS2D1 gray	Gray		Crystallized	113	10.92
	HS2D1 darker (1)	Dark gray	10YR4/1	Crystallized	197	19.03
	HS2D1 dark (2)	Dark gray		Brittle	135	13.04
	HS2D2 gray brittle	Gray	7.5YR7/2	Brittle	94	10.97
	HS2D2 light brittle	Light gray		Very brittle, shiny	200	23.34
	HS2D2 light	Light gray		Brittle, chalky	563	65.69
	PM1A2 gray no-white	Gray no-white		Chalky	377	7.56
	PM1A2 gray striped	Gray striped		Chalky	269	5.40
	PM1A2 gray crystallized	Gray crystallized	2.5Y5/2	Crystallized, pyrite	158	3.17
	PM1A2 coated	Black coating, white	5Y4/1	Pyrite, chalky	629	12.62
	PM1A2 light	Light gray	7.5YR8/3	Chalky	3025	60.67
	PM1A2 dark	Dark gray	7.5YR6/3	Brittle	528	10.59
	PM1B light	White to tan	7.5YR8/3	Chalky	16464	70.58
	PM1B light crystallized	White to dark tan		Crystallized, brittle	550	2.36
	PM1B gray	Dark gray		Coated, chalky	1381	5.92
	PM1B dark crystallized	Black gray	10YR3/1	Crystallized and hard	4465	19.14
	PM1B black complete	Black		Brittle	82	0.35
	PM1B black	Tan with black streaks		Very hard	384	1.65
Nanjemoy Formation	PM1C1 green	Green, white green		Chalky	1382	15.95
	PM1C1 light	Light gray	7.5YR8/3	Chalky	5722	66.04
	PM1C1 dark	Dark gray	10YR8/4	Brittle	153	1.77
	PM1C1 gray	Gray coating	10YR6/2	Chalky	1163	13.42
	PM1C1 gray crystallized	Gray	10YR5/2	Crystallized and hard	245	2.83
	PM1C2 light	Light gray	7.5YR8/3	Chalky	3847	100.00
	PM1E light	Light gray	7.5YR8/3	Chalky	102	100.00

10 mm	8 mm	20 mm	15 mm
HS2B black	HS2C light (2.5YR7/1)	PM1C1 gray crystallized (10YR5/2)	HS2D black (5YR3/1)

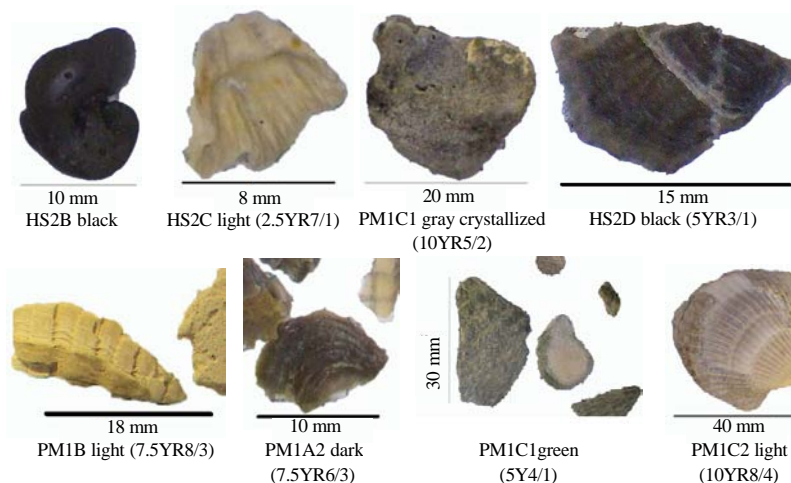| 18 mm	10 mm	30 mm	40 mm
PM1B light (7.5YR8/3)	PM1A2 dark (7.5YR6/3)	PM1C1green (5Y4/1)	PM1C2 light (10YR8/4)

Fig. 6: Photographs of representative fossil fragments

A nominal mass of the crushed powder fossil shell fragments were weighed using a microbalance. The samples were, then digested with aqua regia and volumetrically diluted with trace metal grade nitric acid. A Varian 820 ICP-MS and Varian Vista-MPX Axial Simultaneous ICP-OES were used for sample analysis. The ICP-MS used a chilled spray chamber, micromist low flow nebulizer and standard glass torch. The ICP-OES system used a glass cyclonic-action spraychamber with glass concentric nebulizer and one-piece quartz torch with an extended outer tube that excludes atmospheric gases. Standards were prepared using multielement solutions obtained from Inorganic Ventures (Christiansburg, VA, USA) allowing for minor and trace metals to be analyzed for each sample. Excess sample dilution would have needed to be done to be able to analyze the concentration of Ca and Sr via ICP. Thus an XRF analysis with Bruker Tracer SD III was also conducted to determine the concentration of Ca and Sr of those samples that had enough crushed material left to be turned into pressed pellets. In addition to that portion of intact fossil shells of *Venericardia ascia* and *Cubitostrea sellaeformis* were analyzed with the XRF, as controls.

RESULTS AND DISCUSSION

The biogenic pigments, along with a number of trace elements and metals, probably play the dominant role in the development of color in the fossilized shells of marine bivalves (Dauphin *et al.*, 2011; Dauphin, 2002; Fox, 1966; Kobluk and Mapes, 1989; Kolbe *et al.*, 2011; Nitecki and Sadlick, 1968; Zhao, 1990). The relation is not straightforward, as the incorporation of different types of minor and trace elements during the shell formation is influenced by a number of factors, such as concentration of elements in the ambient water, salinity, temperature and the mineralogy of the shells and diagenesis (Hautmann, 2006; Huanxin *et al.*, 2000; Carriker *et al.*, 1991; Zhao, 1990; Frazier, 1975; Dodd, 1966; Harriss, 1965; Pilkey and Goodell, 1963; Rucher and Valentine, 1961). The primary purpose of the present study was to recognize whether there is any relation between minor and trace element concentrations and different color groups of fossil shell fragments. The samples were organized by place in the stratigraphic column than sorted into 5 similar color groups for analysis: Light, dark, gray, coated and black.

There were no-linear relationships observed between the colors of the fossil shells fragments and trace element concentrations. However, the concentration of Iron (Fe) and Sulfur (S) was comparatively high in some of the dark and black colored specimens. The close relation between

the dark color in the fossil fragments and the higher concentration of Fe and S is either due to the diagenetic uptake from the host sediments or higher availibity in the ambient seawater (Zhao, 1990). Though, the mechanism was not well understood other than the pyritization of the fossilized shell. Further detailed, analysis will be necessary to ascertain the relation between the presence of high quantity of S in black and dark colored of fossil shell fragments (Fig. 7a, b).

One of the most important chemical proxies to understand the environments of the paleocean is Barium (Ba). An increased amount of Ba in ostracod shells has been observed to reflect an increase in biogenetic activity and export productivity (Lazareth *et al.*, 2003; Carre *et al.*, 2006). The sources of Strontium (Sr) to the marine environment primarily include riverine inputs (Elderfield and Schultz, 1996), thus indicative of terrestrial controls over the paleocean. Sr/Ca ratios are related to salinity and Mg/Ca ratios are affected by both temperature and salinity (Hull and Norris, 2011; Schenau *et al.*, 2001; Gonneea and Paytan, 2006). When Sr/Ca ratio values are comparatively low and Mg/Ca ratio values are comparatively high, temperature fluctuation can be indicated and when both Sr/Ca and Mg/Ca ratio values are low, salinity and temperature were most likely constant (Chivas *et al.*, 1986; De Deckker *et al.*, 1988, Vasiliev *et al.*, 2007).

Overall, Ba concentration was the highest in the coated group. The light group also had generally high Ba values. The black group had both the highest and lowest Ba values. On the other hand, PM1A2 light had the highest values for Sr and Mg. PM1B light also had slightly higher values than the baseline in Ba and Mg.

In the light group, samples from the Piney Point Formation exhibited apparently lower concentration of Ba than those in the Woodstock Member of the Nanjemoy Formation (below PM-B). Mg values were also higher in the Piney Point then in the Nanjemoy Formation.

In the dark group, Ba values were higher in Piney Point samples. Sr was highest in HS2D1 dark (2) but there was no trend around it. Mg was significantly higher in PM1A2 dark and significantly lower in HS2D1 dark (2) than the baseline. Otherwise, it did not seem like there was much variation in the dark group of trace element concentrations.

In the gray group, Ba was highest in PM1A2 gray no-white with a slight increase above and below it in the baseline values. Sr was notably higher in the HS boundary level but then fairly consistent elsewhere in the column. Mg was much lower in the Nanjemoy samples.
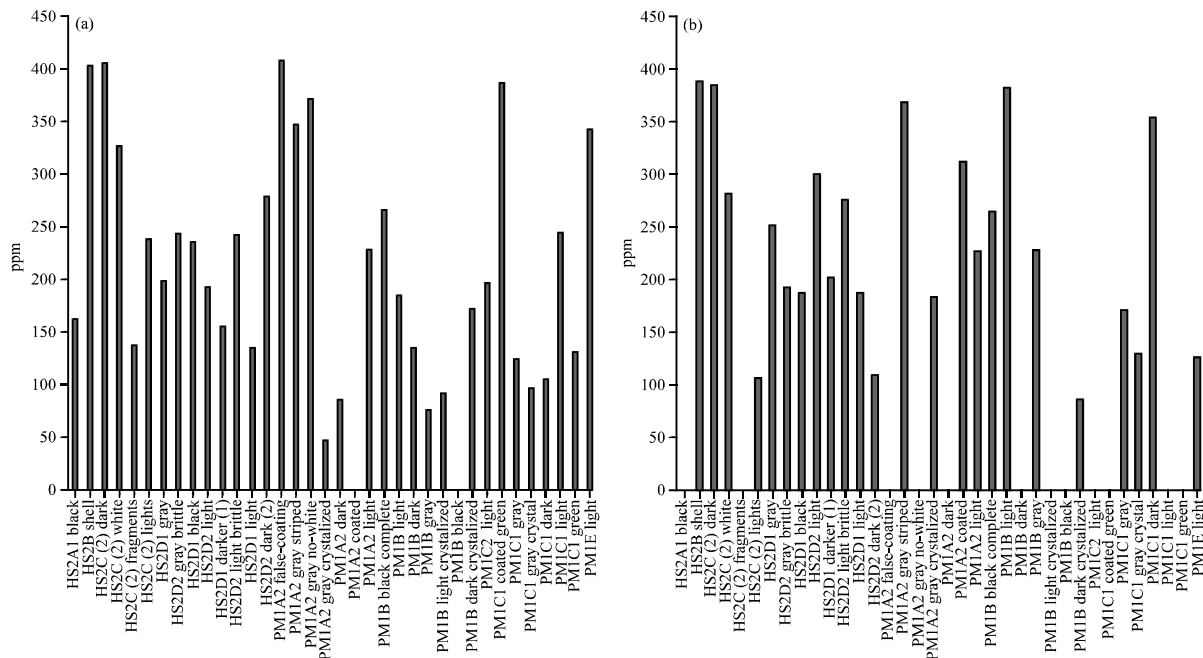
Fig. 7: Plots of: a) S; b) Fe concentration (ppm) versus color partitioned fossil fragments

Fossil fragments with coating were encountered in the PM exposure only. The coated group had consistently higher Ba values than other color groups. Otherwise, there did not appear to be any noteworthy trends in this color group. The black group had the lowest and highest values for Ba. Sr had a higher value in the samples from Piney Point Formation. The PM1B black complete sample had the overall highest Mg concentration but there appeared to be no trend otherwise (Fig. 8a-d).

Since, the light group showed relatively higher values of Ba in the Woodstock Member (PM1C and E), there may have been more biogenetic activity than in the younger formations, i.e., Piney Point and Old Church. Hull and Norris (2011), Schenau *et al.* (2001) and Gonneea and Paytan (2006) all confirm a similar relationship between Ba and biogenetic activity in their studies. Since, Mg values were higher for the light group in the Piney Point there could have been elevated temperature as long as salinity was constant.

The dark group's higher Ba values in the Piney Point could indicate an increase in biogenetic activity. The gray group also reflected similar increase in Ba concentration at PM1A2, moreover indicating an increase in export productivity and biogenic activity. The gray group also indicated a higher level of Sr at the Piney Point-Old Church Boundary (HS2B), this could be evidence for an increased salinity in the Old Church Formation. Lower Mg values in the Nanjemoy samples of

the Gray group (PM2E) could indicate lower temperature, as long as salinity was constant (Chivas *et al.*, 1986; De Deckker *et al.*, 1988).

There was only one color sample from the Piney Point in the black group, however Sr was higher in the Piney Point and this could indicate increased salinity. Ba was also higher above and below the Piney Point Formation in the black group but since there was only one data point it would be interesting to conduct further study.

Differing diagenetic conditions could have prevailed at the 2 locations, since only fossils with coating were encountered in the PM exposure. Since, the coated group had comparatively higher Ba concentration, this could indicate an increase in biogenic activity but could just as likely be contamination from their coating. Further, investigation into the effects coating has on trace element values is necessary. Since, the coated group was covered in pyrite, diagenetic changes may have affected the shell chemistry.

Presence of Manganese (Mn) is indicative of the persistence of original oxygenated bottom water circulation in the paleocean. The apparent absence and/or very low concentration in the HS exposure samples signify a more shallow depositional setting in contrast to PM samples.

Since, XRF analysis was only conducted on samples with enough material to be formed into pellets, these
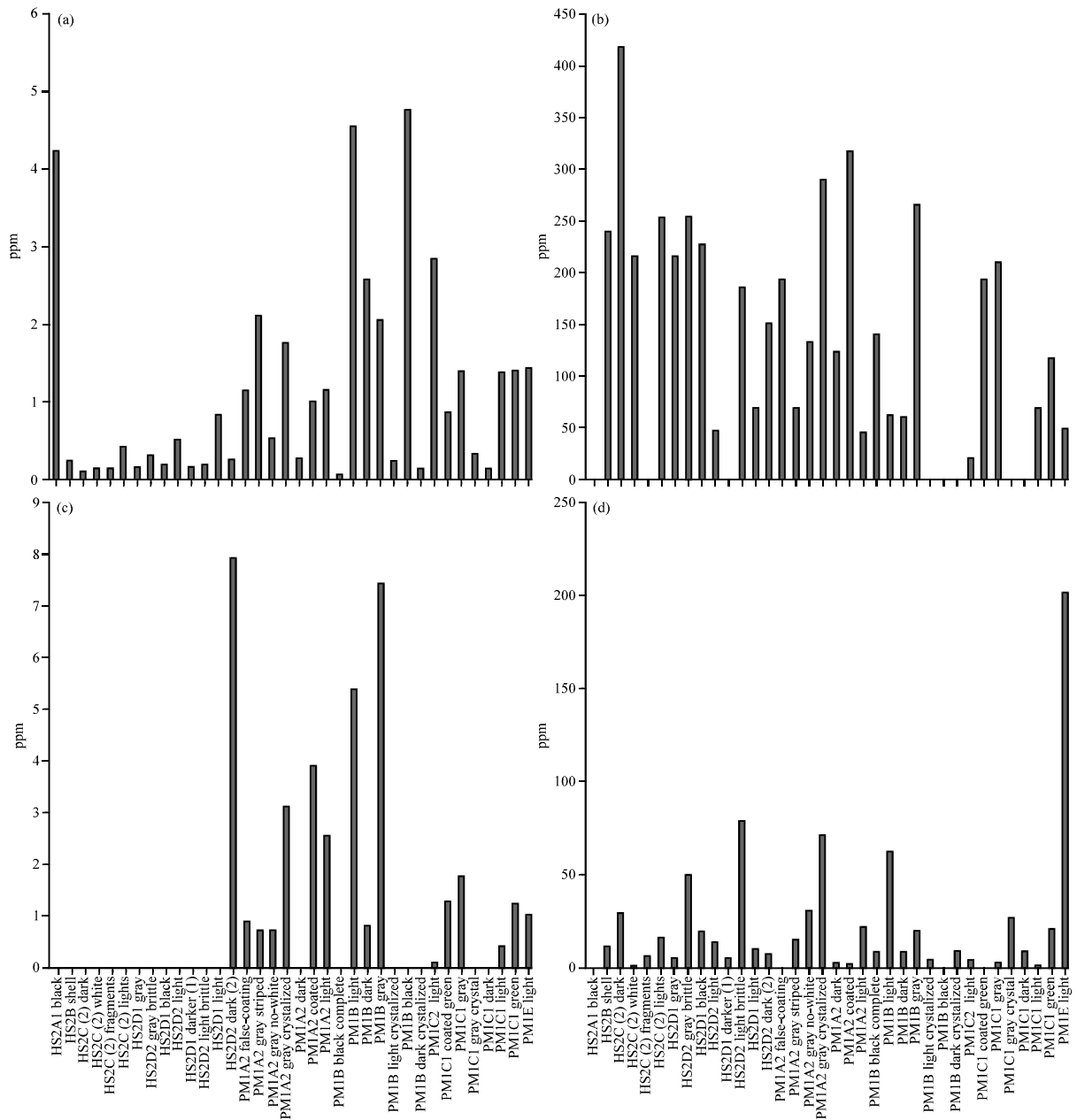
Fig. 8: Plots of: a) Ba; b) Mg; c) Mn ; d) P concentration (ppm) versus color partitioned fossil fragments

results were not put in color groups. In general, Sr/Ca ratios were higher in the fossils of Woodstock Member. Ba/Ca ratios tended to be higher in the fossil of the Piney Point sediments at the HS exposure. The Ba/Ca ratio of PM1B dark crystallized was also significantly lower (Fig. 9a-d).

Surprisingly, the PM1B light fragments at the bottom of the Piney Point Formation contain higher concentration of Zinc (Zn), Copper (Cu), Chromium (Cr) and Nickel (Ni) (Fig. 10a-d). Higher concentration of Zn and Cu is apparently indicative of terrestrial influence in the marine biocalcifers. These higher concentrations of metals in the shell were probably taken up diagentically from the host sediments (Mierzwa, 2011), as Ni is mainly accumulated in the tissues to smaller degree in the shell (Nicolaidou and Nott, 1998). Verifying further the comparatively higher concentration of Cr and Ni is beyond the scope of the present study.

Fig. 9: Plots of: a) Ba/Ca; b) Mg/Ca; c) Mn/Ca; d) Sr/Ca versus color partitioned foshsil fragments
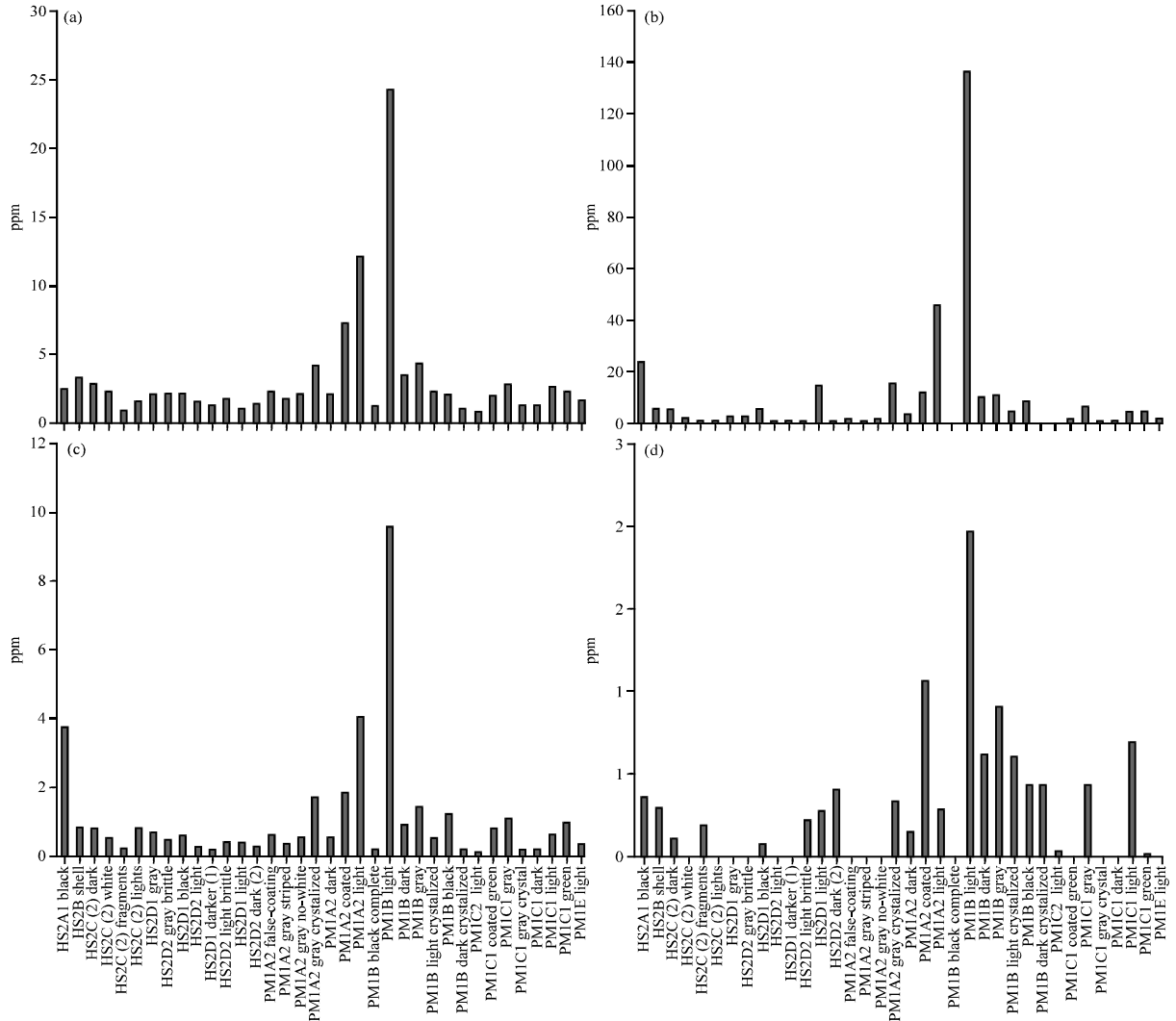

Fig. 10: Plots of trace metal concentrations: a) Ni; b) Zn; c) Cr; d) Cu (ppm) versus color partitioned fossil fragments
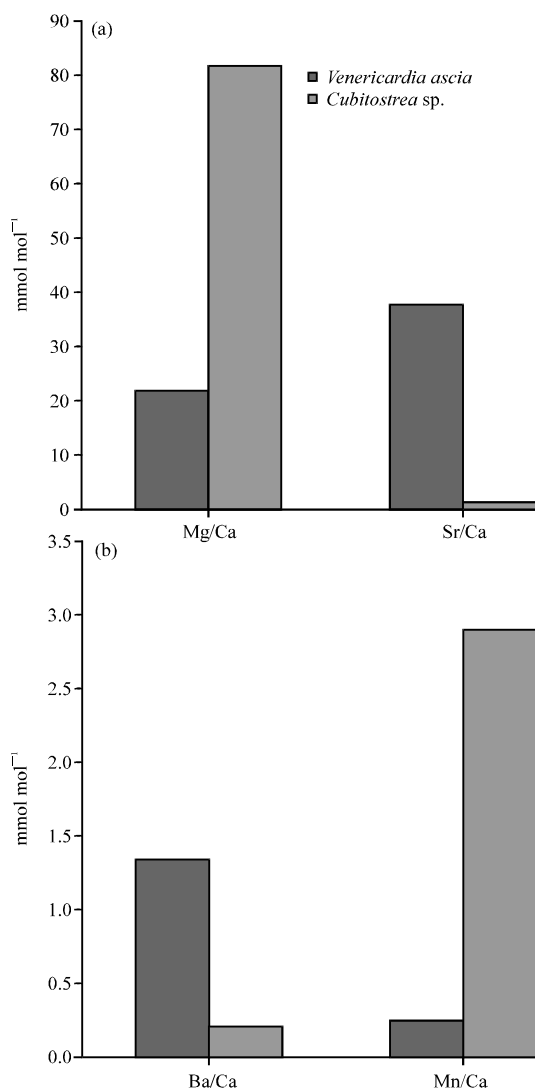
Fig. 11: Plot of Mg/Ca, Sr/Ca, Mn/Ca and Ba/Ca versus

Fe and S. Other than that no-linear relation between the different color fragments of fossil shell and other trace elements concentration were observed. Geochemical environment of ambient seawater may not be the only factor that influences concentration of trace elements in the fossil shell, diagenetic alteration of the fossil shell and the mineralogy and chemistry of the sediments that host fossil shells for long geological period might also played an important role (Zhao, 1990).

The higher Sr/Ca ratios, based on XRF analysis in the Woodstock member of the Nanjemoy probably indicate *Venericardia ascia* and *Cubitostrea* sp. increased salinity. The higher Ba/Ca ratios in the Piney Point samples probably demonstrate an increase in biogenic activity (Hull and Norris, 2011).

Therefore, from the minor and trace elements analysis, researchers can conclude that the Woodstock Member probably had a lower water temperature during deposition and both Woodstock and Piney Point environments probably had higher biogenic activity. At the time of deposition of Piney Point sediments, the water probably had higher temperatures and the Piney Point Old Church contact had an increased salinity condition. It is not possible to determine the accurate salinity values based on shell chemistry of marine bivalves, especially from Mg/Ca ratios because the uptake of Mg is controlled by both the water Mg/Ca ratio and temperature (Chivas *et al.*, 1986; De Deckker *et al.*, 1988). Further, detailed study combining chemical analyses of fossil shells and of authigenic, non-biogenic carbonates within the same samples, fossil shell mineralogy and isotopic analysis is required to confirm these postulations.

Most of the samples studied were in shattered in pieces so it was usually not even possible to identify the species of the fossils. But, the results of XRF analysis explicitly show a number of positive correlations between some species, e.g., *Venericardia ascia* with light color and *Cubitostrea* sp. with dark color (Fig. 11a, b). It is also possible that the different fossil colors could be indicators of different species. The large difference in the Ba/Ca, Mn/Ca, Mg/Ca and Sr/Ca ratio in the control fossils also supports this. An alternative hypothesis is that different species are affected by paleo-water chemistry differently.

CONCLUSION

Only the dark and black color of the fossilized shell fragment has close relation with higher concentration of

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