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MINERALOGICAL STUDIES AND TRACE METALS IN FOUR RECENT MOLLUSCAN SHELLS FROM ROSETTA NILE BRANCH SEDIMENTS - EGYPT

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ABSTRACT

Molluscan shells collected from the recent Rosetta Nile branch sediments were investigated by X-ray diffraction. The carbonate mineral phases include aragonite and calcite. The early diagenetic processes in the carbonate mineral include the calcitization of originally aragonite skeletons by transformation and recrystallization. This was affected by environmental factors and activity of organisms.

The chemical analysis of the recent molluscan shells proved that the contents of Fe, Cu, Mn, Zn and Cd increase generally northwards, while Pb increase in the mid-stream region. The relative order of abundance of elements in the bivalve shells is in the order as follows: Mn> Fe> Zn> Cu> Pb> Cd, while in gastropod shells: Fe>Mn>Zn>Cu>Pb>Cd. The distribution of elements proved due to mineralogy of shells, secondary alteration, ecological parameters and activity of organisms.

Zonal distribution of trace metals proved that the northern zone are enriched with relatively Fe, Mn, Zn, Cu and Cd and the mid-stream shells are enriched with Pb.

INTRODUCTION

Relatively few studies have been done on the mineralogy of the bottom sediments of the Rosetta Nile branch. The mineralogical and geochemical study of recent molluscan shells was dealt by several authors (Lowenstam, 1954; Turekian and Armstrong, 1960; Pilkey and

Goodel, 1962; Dodd, 1963; Chave, 1964; Aliev, 1971; Clark and Lutz, 1980, Ismail and Abdel Aal, 1986 and Lotfy 1997).

There are numerous types of pollutants in the aquatic environment such as organic compound, major and trace metals contribute to both natural and anthropogenic sources. Natural sources include storm dust-fall, erosion or crustal weathering and decomposition of the biota in water, whereas the anthropogenic sources include sewage, industrial and automobile waste as shipwrecks and dumping of war materials (FAO, 1994; Al-Saad, 1995 and Lotfy, 2001).

As a result of direct discharges of wastes containing trace metal to the environment, their levels increased in water column, while sediments act as archive for many pollutants (Forstner and Wittman, 1981). As a part of the aquatic environment, recent shells accumulate trace metals and act as indicators of pollution (Lotfy, 1997). In the Rosetta Nile branch few studies were done on mineralogy and trace metals accumulation by different molluscan shells.

This study aimed to determine the mineralogical composition of shells and distribution of trace metals in molluscan shells to illustrate the relation between chemical composition, mineralogy, metabolism, secondary alteration and ecologic interpretation.

The Rosetta Nile branch extends north of Al-Kanater Barrage along the western boundary of the Nile Delta and it opens into Rosetta Estuary through the gates of Edfina Barrage. It varies in width from 250 to 800m. The branch represents shallow water stream with a depth fluctuating between 4.5 and 16.0m (Fig. 1).

MATERIALS AND METHODS

Sampling: Nine stations were selected as representing the different habitats. Each station is represented by five samples (i.e. two from eastern and two from western beach and one from the mid-stream) (Fig. 1).

The bottom samples were collected by Petersen dredge from the different locations. Water samples from each station of Rosetta Nile branch were taken for measurement of temperature, salinity, chlorosity pH value, dissolved oxygen, and alkalinity.

Water analysis: Water temperatures were recorded using Hand Thermometer graduated up to 100°c.

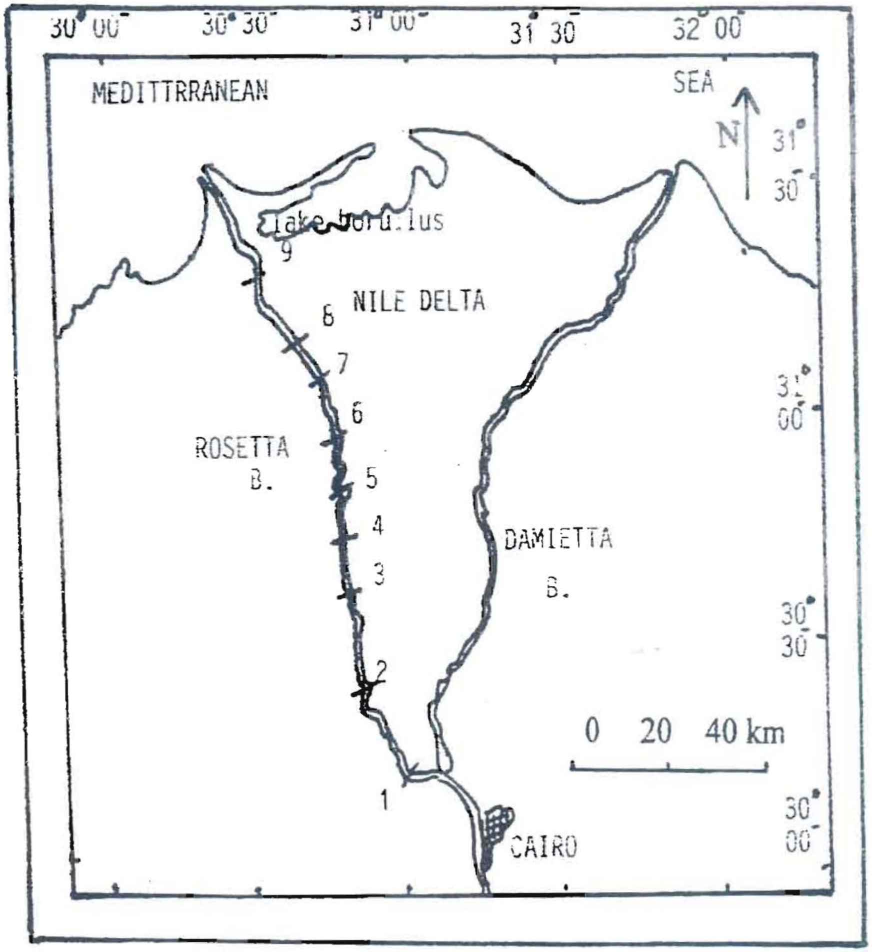

Fig. 1. The Rosetta Nile branch map position of stations
1- Alkanater. 3- El-Khatatba. 5- Kafr El-Zayat.
8- Dessuq. 9- Edfina.

Dissolved oxygen and salinity were determined according to the methods described by strickland and Parsons (1972) and was measured using Packman induction salinometer. The PH values were measured by a pocket pH meter directly in the field. The total chlorides were determined following the method of Mohr's titration. The total alkalinity was determined by titration versus standard HCl, using methyl organe indicator.

Mineral analysis: Thirty six shells of bivalves, namely Anodonta implicat, a corbicula consobrina and also thirty six shells of gastrods, namely Bellaniya unicolor, cleopatra bulimoides were picked from Rosetta Nile branch sampler which collected by petersen dredge from different locations (Fig. 1).

The mineral analysis was carried on the studied shells by using X-ray differaction (Shomatzo model XD-510-X-ray Lab. Fac. Of Scie. Cairo Univ.). The aragonite content was determined according to the method of Turekian and Armstrong, 1960.

The aim of the present study was to exhibit the distribution of trace metals Fe, Cu, Mn, Zn, Pb and Cd in the studied species. The analysis was done using the Atomic Absorption Spectrophotometer Flame (Perkin Elmer model 2380 AAS) in the Lab. of Inst. of the Earth's development, El-Mansoura, according to the method of Hendrik, 1968.

RESULTS AND DISCUSSION

General characteristics of Nile Water of the study area :

The average values of pH values, chlorosity, dissolved oxygen and total alkalinity of Rosetta Nile branch water during April – May 2001 are represented in (Fig. 2).

The Nile water temperature was subjected to both diurnal and seasonal variation. The monthly variation of the water temperature ranged between 14.6°c (in January) and 31.60°c (in June). The pH value of the investigated area lies mostly on the alkaline side. It fluctuated between 6.89 and 9.10 in the Nile water and 7.40 and 8.2 in the estuary of Rosetta (Fig. 2).

The chlorosity of the Nile water ranged between 30.25 and 109.9 mg cl/L near to the bottom. The average values of chlorosity increased gradually northwards. The salinity of the Rosetta estuary water ranged between 35.57 and 42.76%.

The dissolved oxygen varies in the Nile and Estuary water at different sites and the water is completely oxygenated from surface to bottom. The average oxygen content of the Nile water ranged between 7.5 and 10.2 mg/L) and increased gradually northwards (Fig. 2).

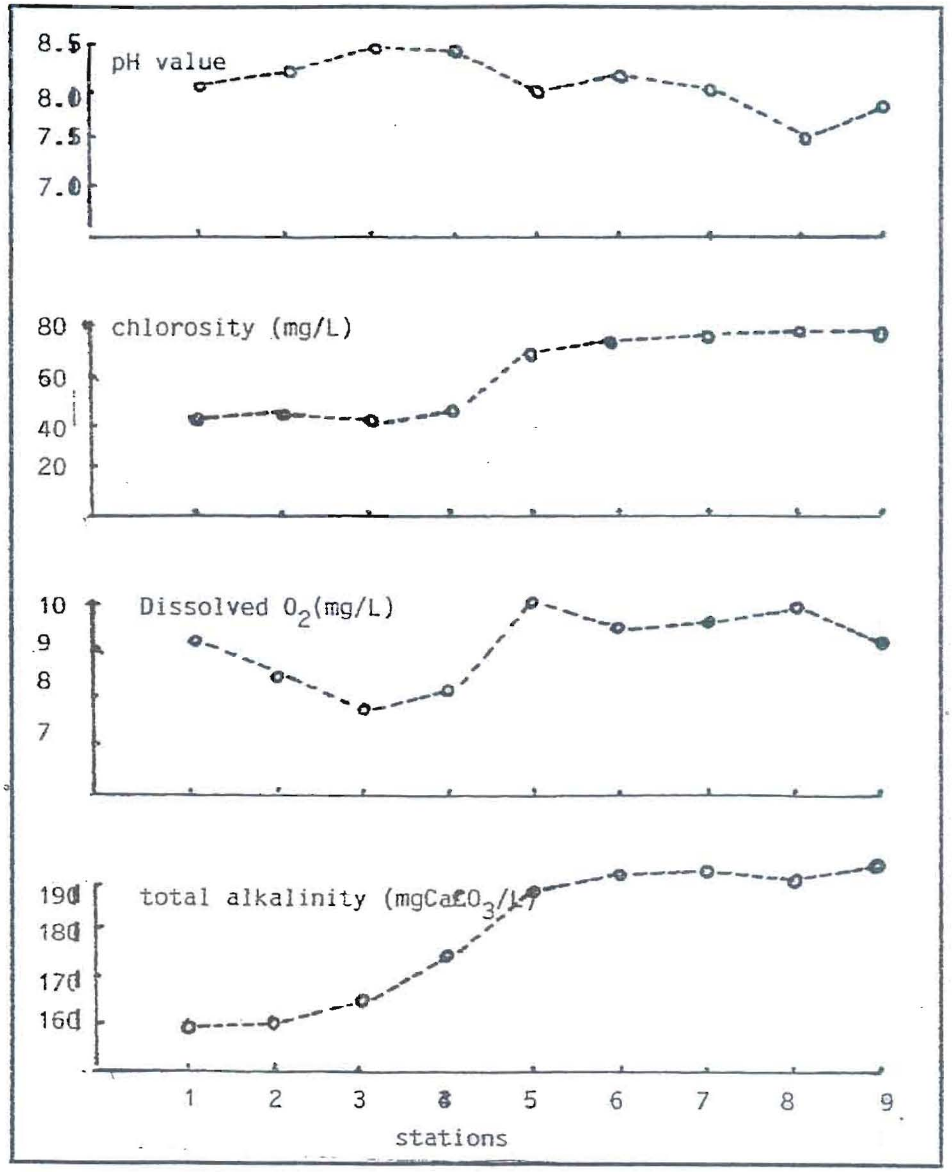

Fig.2. General characteristics of Rosetta Nile branch Water.

The minimum values of the total alkalinity were recorded southwards (average 157.67 mg $CaCO_3$/L. This was followed by a slight increase northwards 192.33 mg $CaCO_3$/L).

Mineralogy of shells

X-ray diffraction was carried out for identification of carbonate mineral phases in the shells of the four species, Anodonate implicata, Corbicula consobrina, Bellaniya unicolor and Cleopatra bulimoides shells. The identification was based on the scheme proposed by Warshow and Roy (1961), and Smith (1967).

X-ray diffraction patterns for Anodonta implicata (i.e. bivalve shells) from southern part sediments (Table 1 and Fig. 3) gave aragonite peaks at 3.40°A, 3.27°A, 2.71°A, 2.48°A, 2.41°A, 2.34°A, 2.34°A, 2.19°A, 2.14°A, 1.97°A, 1.87°A and 1.81°A. The aragonite content in the shells occurred an average 96.5%. Weak intensive peaks of calcite are recorded at 3.35°A to 3.02°A. The calcite contents reached to 3.5% (Fig. 3 and Table 1). The aragonite contents in the specimen of Anodonata implicata from the mid-stream region reached to average 97%, while the calcite contents occurred average 3%.

The X-ray diffraction patterns for Anodonta implicata from the northern region gave aragonite and calcite peaks. The aragonite content reached to average 75%, while the calcite content occurred average 25%.

Fig.(3) and Table (1) recorded the X-ray diffraction patterns of Corbicula consobrina (i.e. bivalve shells) from the southern, mid-stream and northern regions gave aragonite and weak calcite peak. Aragonite contents vary from average 97%, 95% and 85%, respectively related to the regions, while the calcite content ranges between, 3%, 5% and 15%, respectively.

Generally, the semiquatitative approximation based on peak heights suggests that the carbonate mineral phases of bivalve shells from the recent sediments of Rosetta Nile branch consist mainly of aragonite with a minor amount of calcite. Maximum value of aragonite occurs in the southern region that of calcite takes place in the northern zone.

As shown in Fig. 3 and Table 1, X-ray diffraction patterns of Bellaniya unicolor (i.e. gastropod shells) from the southern region gave aragonite and weak calcite peaks. Aragonite contents occurred 95%, while the calcite content reached 5%.

X-ray diffraction patterns of Bellaniya unicolor from the mid-stream region gave also aragonite and calcite peaks (occurred 91% and 9%, respectively).

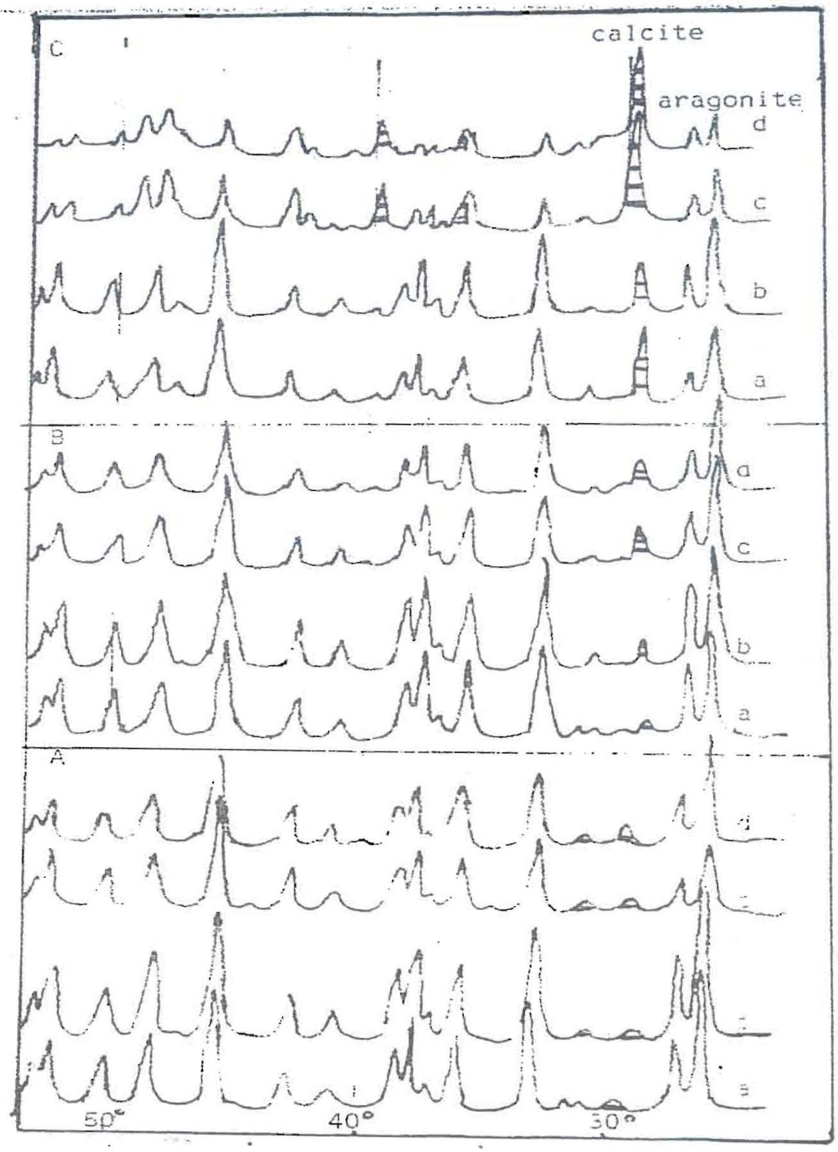

Fig.3. X-ray diffraction patterns of selected carbonate mineral phases of Bivalve.
A – Anodonta implicate. B – Corbicula consobrina.
C – Bellaniya unicolor. D – Cleopatra bulimoides

Similarly, X-ray diffraction patterns for Bellaniya unicolor from the northern region gave aragonite and calcite peaks with an average 25% and 75%, respectively.

Table (1): The mineral composition of the carbonate mineral phases (Bivalve, Anodonta implicata, Corbicula consobrina and Gastropod, Bellaniya unicolor, Cleopatra Bulimoides from Rosetta Nile branch sediments).

Type of shells	Zone	Carbonate minerals %	
		Calcite	Aragonite
A1	Zone I Southern zone	3.5	96.5
A2		3	97
B1		5	95
B2		4	96
A1	Zone II Mid-stream zone	3	97
A2		5	95
B1		9	91
B2		6.5	93.5
A1	Zone III Northern zone	25	75
A2		15	85
B1		75	25
B2		60	40

As shown in (Fig. 3 and Table 1), X-ray diffraction patterns of Cleopatra bulimoides (i.e. gastropod shells) from the southern, mid-stream and northern regions gave aragonite and calcite peaks. Aragonite contents occurred 96%, 93.5% and 40%, respectively related to the region while the calcite contents ranged between 4%, 6.5% and 60%, respectively.

Generally, X-ray diffraction patterns of gastropod shells indicate that carbonate mineral phases of shells consist mainly of aragonite and calcite, aragonite contents increase southwards while calcite contents increase northwards.

The Distribution of Trace Metals:

The contents of Fe, Cu, Mn, Zn, Pb and Cd in the studied shells of Anodonta implicata and Corbicula consobrina (i.e. bivalve shells) show a general increase starting from the south to the north (Fig 4). On the other hand, the content of iron in the shell of Corbicula consobrina decreases from south to north. The mean concentration of total iron in the bivalve shells varied between 46 ppm in the Corbicula consobrina shells from the northern region at Edfine station and 130 ppm in the Anodonta implicata shells at station No 8.

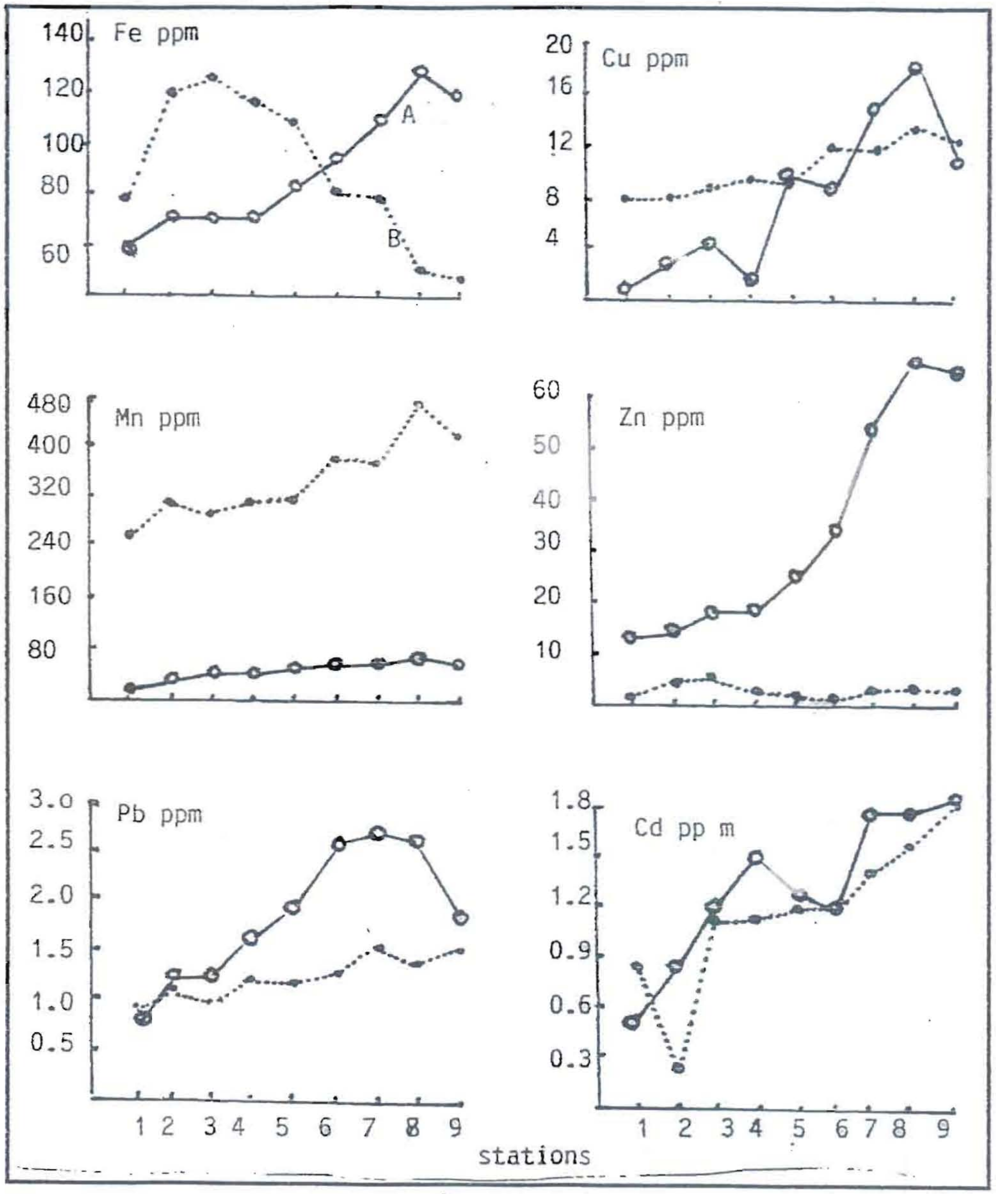

Fig. 4: The average distribution of Fe, Cu, Mn, Pb and Cd in Rosetta Nile branch of bivalve shells.
A – Anodonta implicate. B – Corbicula consobrina.

However, the iron content in the Anodonta implicata, the stream is nearly divided into northern rich (81-130 ppm) and southern poor basins (60-70 ppm). On the contrary, Fe in the Corbicula consobrina, the river is divided into northern poor (46-80 ppm) and southern rich basins (80-125 ppm).

From the value of copper contents in the Anodonta implicata and Corbicula consobrina shells at the corresponding stations, relation was drawn (Fig. 4). According to the distribution of the copper contents, the northern zone proved to have a high content reaching on the average 18 and 14 ppm respectively. Towards the southern zone, this value becomes very low (1 and 8 ppm respectively). However, the copper content in Corbicula consobrina is more abundant southwards and in Anodonta implicata northwards.

According to the distribution of the manganese contents (Fig. 4), the northern zone proved to have a maximum values (68 and 474 ppm) in the Corbicula consobrina and Anodonta implicata shells, respectively. This value becomes very low (25 and 250 ppm) towards the southern zone. The Mn content is more abundant in Corbicula consobrina shells.

Shifting the attention, the contents of zinc in the Anodonta implicata shells are higher than those of Corbicula consobrina. The northern zone proved to have a high zinc content, reaching as high as 68 ppm. Towards the southern zone, this value becomes very low 14 ppm especially in Anodonta implicata shells. While zinc contents in the Corbicula consobrina shells are quite regularly distributed between different station where most samples fall in the range of 1-4 ppm (Figure 4).

However, the gradient of lead and cadmium contents variation in Anodonta implicata and Corbicula consobrina shells has a uniform pattern, the shells of Anodonta implicata of the northern zone have a high contents, reaching on the average 1.9 and 2.7 ppm respectively. Generally, their contents are more abundant in Anodonta implicata shells northwards.

The contents of Fe, Cu, Mn, Zn, Pb and Cd in the studied gartropod shells of Bellaniya unicolor and Cleopatra bulimoides species show a general increase northwards (Fig.5). From the view of iron concentration, the stream is nearly divided into northern rich basin and southern-poor basin. The maximum value of iron (420 and 467 ppm) was observed in the Cleopatra bulimoides and Bellaniya unicolor shells, respectively, in the midstream and northern zone, and decreasing southwards reached to 144 and 380 ppm respectively.

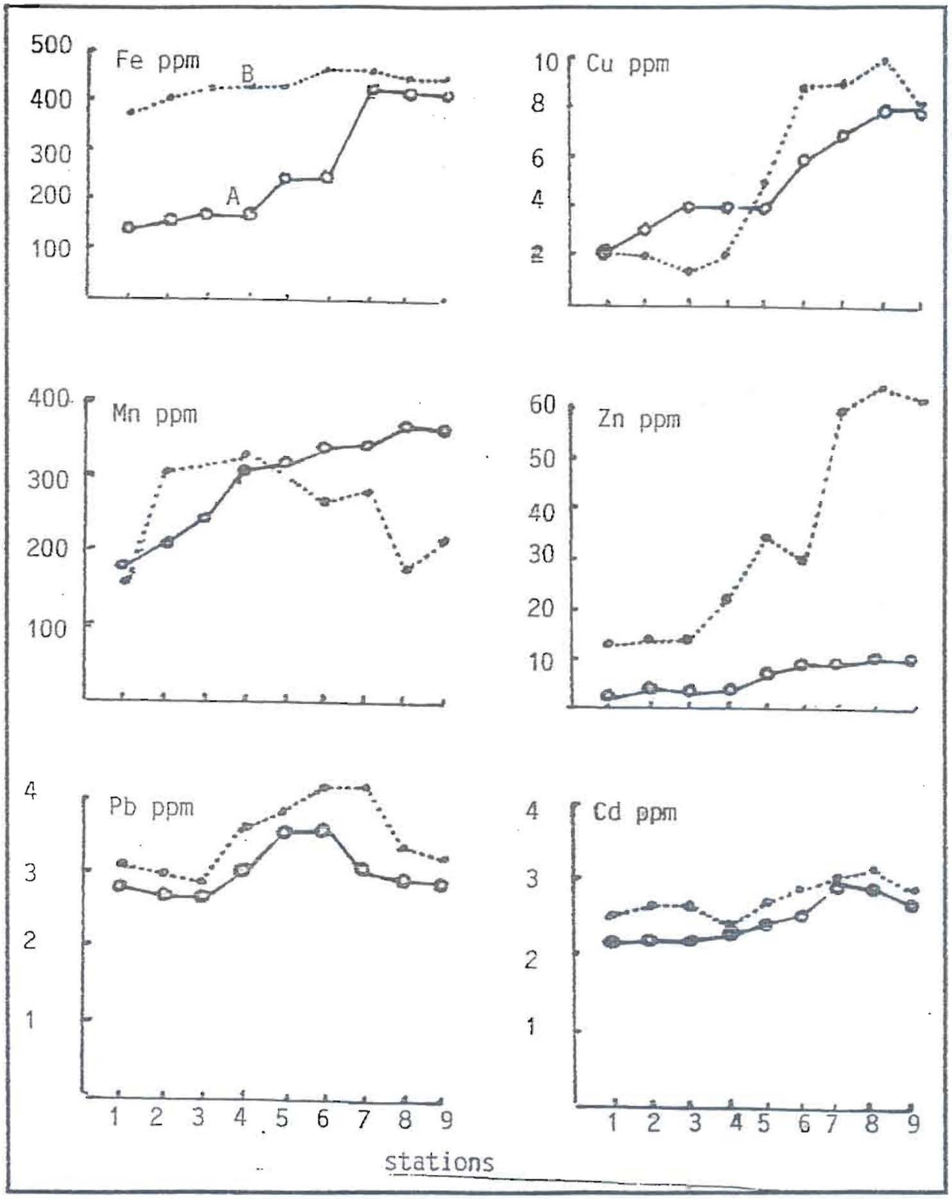

Fig. 5: The The average distribution of Fe, Cu, Mn, Pb and Cd in Rosetta Nile branch of bivalve shells.
A – Bellaniya unicolor. B – Cleopatra bulimoides.

Concerning the distribution of copper (Fig. 5), the highest levels (8 and 10 ppm) were observed in the northern side of river in Bellaniya unicolor and Cleopatra bulimoides shells respectively, and decreasing southwards. Iron and copper contents are more abundant in Cleopatra bulimoides shells.

The maximum value of manganese (376 ppm) was observed in the Bellaniya unicolor shells in the northern region. The values decreases southwards. In the Cleopatra bulimoides shells the maximum concentration of manganese 332 pmm occurred in the mid-stream. Meanwhile the concentration decreases south and northwards.

From the distribution of zinc view, the river is divided into northern – rich region (10 and 65 ppm) in the Bellaniya unicolor and Cleopatra bulimoides shells respectively, and then decreased southwards (1 and 12 ppm, respectively).

On the otherhand, the gradient of lead and cadmium contents variation in Bellaniya unicolor and Cleopatra bulimoides shells has a uniform pattern. In the mid-stream zone have a high Pb and Cd contents reaching on the average (Pb value, 3.6 and 4.2 ppm, respectively (the Cd value is 2.8 and 3.1 ppm, respectively). Generally the values of lead and cadmium are more abundant in Cleopatra bulimoides shells in the mid-stream regions.

The relative order of abundance of elements in the bivalve shells is as follows: Mn>Fe>Zn>Cu>Pb>Cd and most of elements increase northwards. Zn, Pb and Cd are more abundant in Anodonta implicata shells. Copper and manganese are more abundant in Corbicula consobrina.

The relative order of abundance of elements in gastropod shells is as follows: Fe>Mn>Zn>Cu>Pb>Cd and most of elements increase northwards and in the mid-stream region. Fe, Zn, Pb and Cd values are more abundant in Cleopatra bulimoides shells.

Relationships between Trace metals, Minerals and Environmental Parameters:

The relationship matrix among Fe, Cu, Mn, Zn, Pb, Cd contents and aragonite and calcite contents and the environmental parameters of water (Table 2 and Fig. 6) gave the following: the combined values show strong pathitic and antipathetic relations. Chlorosity, dissolved oxygen, alkalinity, salinity, calcite, Fe in gastropod shells, Cu, most of Mn, Zn and Cd value are positively correlated with each other. Conversely, they exhibit negative relationships with pH value and aragonite. So, Fe, Cu, Mn, Zn and Cd are associated with calcite mineral, while Pb are more associated with aragonite mineral. This depends on metabolism, activity of organism and early diagenesis and with increasing of alkalinity, salinity, dissolved oxygen and temperature. On the other hand, Pb and sometimes Fe associated with aragonite minerals which concentrate in bivalve shells by depending on increasing of the pH value.

Thus as expected most of the element are incorporated into carbonate mineral phases (Beltagy et al, 1986, Lotfy, 1997, Kostka et al 1999 and Vital et al, 1999). The term neomorphism includes all transformation between one mineral and itself or a polymorph (Folk, 1965). There are two aspects to neomorphism: the wet polymorphic transformation of aragonite to calcite and the wet recrystallization of calcite to calcite. The diagenetic environments are always wet, most early diagenesis in carbonates is the aggrading type, leading to a coarse mosaic of crystals, such early diagenesis includes the calcitization of originally aragonitic skeletons (Bathrust, 1972). This hypothesis (i.e. transformation and recrystallization processes) is confirmed (Leader, 1986).

There are several factors, of which the most important are temperature, salinity, water depth and siliclastic input, that control carbonate minerals deposition (Wilson, 1975).

The remobilization of metals from sediments is mainly controlled by the absorbed processes. Remobilization is mostly caused by four types of chemical changes in water (Forstner and Wittman, 1981): 1) elevated salt concentrations; 2) changes in the redox conditions; 3) lowering of pH; and 4) presence of natural complexing agents. In addition, there are probably other biochemical processes by means of which metals adsorbed on surficial sediments are transferred to aquatic organisms to be further concentrated along the food chain or excreated directly as composition products into water.

For sake of simplicity in data presentation the Rosetta Nile branch was subdivided ecologically into three regions (northern, mid-stream and southern). Zonal average of the elements (Fig. 6) showed high changes, northern zone is characterized by elevated averages of elements Cu, Mn, Zn and Cd and Fe in gastropod shells, while the mid-stream zone shells are enriched in Pb. Southern zone records the lowest average in nearly most elements. The aragonite mineral concentrates in southern and mid-stream zone, while the calcite mineral is more abundant in northern zone in gastropod shells.

However, in the Rosetta Nile branch sediments, the carbonate phases of Mollusk shells consist mainly of aragonite mineral by variation of environmental factors of water (i.e. increasing of alkalinity, salinity, chlorosity and dissolved oxygen and decreasing of pH value, high temperature, transformation and recrystallization of aragonite to calcite occurs depending on the activity of organisms (i.e. bivalve shells are easily transformed and recrystallized from aragonite to calcite).

Table (2): Average concentration factors of water (1) and minerals (2) and Trace metals (3) in the studied shells of A) Anodonta implicata B) Corb icula consobrina C) Bellaniya unicolor D) Cleopatra bulimoides

Factors of water,minerals and Trace elements inshells		Region I Southern zone		Region II stream zone	Regio III Northern zone
(1)	pH	8.25		8.07	7.60
	chlorosity	4.5		74.33	79.5
	O2	8.43		9.8	9.6
	alkalinity	164.5		192.3	192.5
(2)	Aragonite %	AA	A 96.5	97	75
			B 97	95	85
			C 95	91	25
			D 96	93.5	40
	Calcite %	A	A 3.5	3	25
		B	B 3	5	15
		C	C 5	9	75
		D	D 4	6.5	60
(3)	Fe ppm	A	A 67.5	95.33	125
		B	B 110.25	90.00	48
		C	C 154.75	364.33	409.5
		D	D 406	455	453
	Cu	A	A 2.75	11.33	14.5
		B	B 8.75	11.33	13.5
		C	C 3.25	5.67	8
		D	D 1.88	7.67	9
	Mn	A	A 35	54	61
		B	B 294	358.33	447
		C	C 251.5	349	368
		D	D 281.25	289.33	205
	Zn	A	A 16.25	38.67	67.5
		B	B 2.5	1.33	2
		C	C 2	8.67	10
		D	D 15.25	41.6	63
	Pb	A	A 1.20	2.40	2.2
		B	B 1.05	1.33	1.45
		C	C 2.83	3.43	2.9
		D	D 3.15	4.03	3.2
	Cd	A	A 1	1.43	1.85
		B	B 0.8	1.27	1.75
		C	C 2.23	2.27	2.65
		D	D 2.5	2.73	2.95

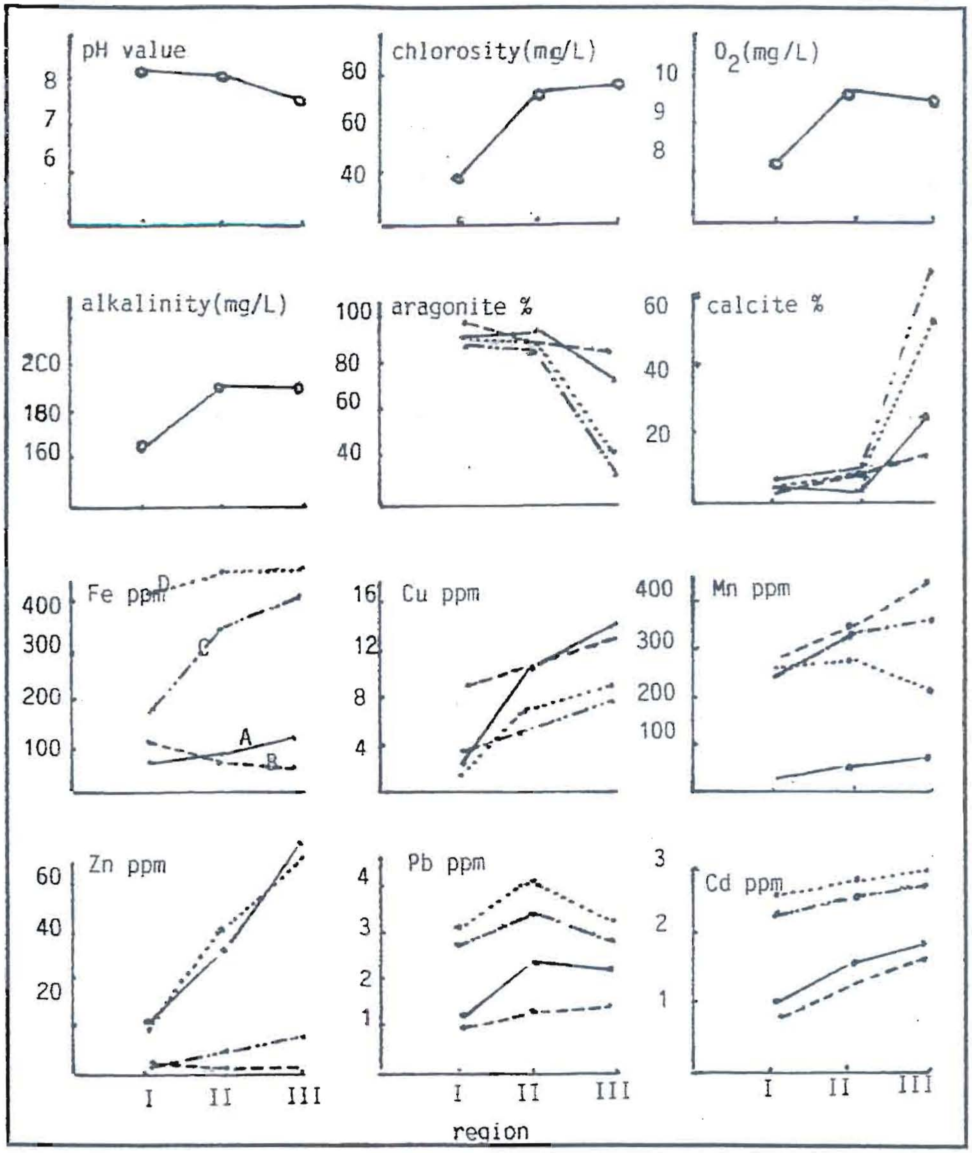

Fig. 6: The The average distribution of environmental factors of water and minerals and Trace metals in The Rosetta Nile branch shells.

A – Anodonta implicate. B – Corbicula consobrina.

C – Bellaniya unicolor. D – Cleopatra bulimoides

CONCLUSIONS

The chemical analysis of the recent fossil mollusk shells collected from Rosetta Nile branch sediments proved that the contents of Fe, Cu, Mn, Zn and Cd increase generally northwards while Pb increase in the mid-stream region.

The relative order of abundance of elements in the bivalve shells is given as follows: Mn>Fe>Zn>Cu>Pb>Cd. Zn, Pb and Cd contents are more abundant in Anodonta implicata shells, while Cu and Mn are more abundant in Corbicula consobrina.

The relative order of abundance of metals in the gastropod shells is as follows: Fe>Mn>Zn>Cu>Pb>Cd. Fe, Zn, Pb and Cd are more abundant in Cleopatra bulimoides shells, while the Cu value have a uniform distribution in the Bellaniya unicolor and Cleopatra Bulimoides shells and increased northwards.

The relationship matrix Fe, Cu, Mn, Zn, Pb, Cd contents and mineral composition of shells and environmental factors of water show a strong pathitic relations between alkalinity, salinity, dissolved oxygen, chlorosity, calcite minerals, Fe in gastropod shells, Cu, most of Mn, Zn and Cd value are positivelly correlated with each other. Conversely, they exhibit antipathitic relations with pH value and aragonite minerals.

Thus the distribution of trace metals in the Rosetta Nile branch sediments is mostly controlled by the mineral composition of the shells, the environmental factors of water and activity of organisms in addition to large amounts of metals introduced into the Nile through agricultural, domestic or industrial wastes discharge.

In the Rosetta Nile branch sediments, the carbonate mineral phases of mollusk shells consist mainly of aragonite and under the effect of increasing temperature, the transformation of aragonite to calcite occurs northwards by depending on the activity of organisms, i.e. the gastropod shells are easily transformed from aragonite to calcite.

Fe, Mn, Cu, Zn and Cd are more abundant in the gastropod shells and increasing northwards associated with calcite minerals. This is attributed to variation of environmental factors, activity of organisms and secondary alteration.

Zonal distribution of the elements proved that the northern zone are enriched with relatively Fe, Mn, Zn, Cu and Cd, while, the mid-stream sediments are enriched with Pb, and the southern zone are poor in most elements.

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