JKAU: Mar. Sci., **Vol. 16,** pp: 45-56 (2005 A.D. / 1425 A.H.)

The Effect of Redox Potential on the Stability of Some Heavy Metals in the Bottom Sediments of the Gulf of Suez, Egypt

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Abstract. The relationship between pH and Eh values and the content of some heavy metals in 27 bottom sediments from the Gulf of Suez has been studied. The sediment samples are mainly composed of carbonate-sand and silt. Three main factors control the behaviour of the examined metals in sediments.

Factor 1 represents a pH-Eh factor that reveals the influence of redox potential on these metals in sediment. Carbonates are insoluble at high pH and Eh values and hence the metals in the carbonate debris are stable under such redox conditions. The strong positive loadings on mud (silt and clay), organic carbon, iron and manganese indicate to the close relationship of these components in the marine environment. The inverse relationship between these components and pH and Eh, indicates that the decay of organic matter tends to lower the pH of the sediments – but not far below pH 7.35 – and consumes the oxygen, and hence lowers the Eh too. The process of organic matter decay may release part of the iron and manganese content that is associated with organic debris.

Factor 2 is a pH factor that clearly reveals the relationship of pH with iron, copper, zinc and cobalt. The increase of pH is associated with similar increases in the content of these metals in sediments. This factor shows that these metals are more stable in the solid phase under more alkaline conditions.

Factor 3 is a metal-carbonate factor where cadmium, nickel, cobalt and lead are mainly present in the carbonate constituents of the sediments.

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Introduction

The heavy metals in sediments of the Gulf of Suez (GOS) have been studied by many authors, *e.g.* El-Moselhy and Gabal (2004), El-Moselhy *et al.*, (1999), Abd El-Azim, (1996) and Hamed (1992). Their investigations showed an increase in the concentrations of some heavy metals in the sediments with time. Such increase has been attributed to pollution due to increased dumping of sewage and industrial wastes into the Gulf (El-Moselhy and Gabal, 2004). The hazardous effect of a metal is determined by its instability in the marine sedimentary compartment (solid phase). The redox state of the sediment controls the solubility, or bioavailability of heavy metals (Kehew, 2001). The hydroxides, oxides, carbonates and phosphates of all of the trace metals are insoluble under alkaline conditions (Lindsay, 1979). The dissolution of these metal salts is strongly dependant on the pH of the system (McLean and Bledsoe, 1992). Also, the redox state can greatly affect the transport of a metal from the solid phase to the dissolved phase. Oxidizing conditions favor retention of metals in the solid phase (sediments) while reducing conditions contribute to the accelerated migration of metals from sediments to seawater (Clark *et al.*, 1998). The present work is focused on the distribution of pH and Eh (redox state) of GOS bottom sediments and their influence on the stability of some environmentally important metals.

Area of Study

The Gulf of Suez (Fig. 1) is a semi-enclosed basin that is 280 km long and its width varies between 20 and 40 km. It occupies a wide valley and lies between the wide plains of low relief of the Eastern Desert in the west and Sinai Peninsula in the east. It has no significant terrestrial input of water. The mean monthly air temperature at the Suez Meteorological Station, based on the average of records in the years 2001, 2002, and 2003, varies between 14ºC in January and 30ºC in August. The atmospheric pressure increases gradually from 1007mb in July to 1020mb in January and decreases afterwards until July. The mean wind speed is minimum (3.5-6 knot) in January and December and its maximum value recorded in August and September (7-11 knot). Local storms occur frequently. The direction of dominant wind on GOS is mainly north and northwest. The sea surface temperature in the Gulf, ranges between 19.3ºC in winter and 26.2ºC in summer. Horizontal decrease of water temperatures from south to north and from east to west is a pronounced feature of the Gulf that is due in part to the cooling effect of the north and northwest winds. The north-south increase in water temperature is associated with a decrease in water salinity (42.5 in the north and 40.5 in the south) (Rifaat *et al.*, 1996). According to Shepard *et al.* (1992), the rapid cooling of surface water in winter and the increased evaporation lead to a rise in the salinity causing a steep salinity gradient along the Gulf. The regional current system in the Gulf is characterized by northward flowing surface waters and a southward flowing bottom waters except near the shore where it has a gyratory character. The bottom topography of the Gulf is almost flat with a maximum depth of 70 m at its southern end. The near shore zone is mostly occupied by coral reefs. The Gulf appears to be spreading and exhibits normal faulting. The bottom sediments are predominantly carbonate-sands and -silty sands. The carbonates are composed of calcareous debris of corals, coralline algae, molluscan shell fragments and other organisms; terrestrial deposits are minor (Shepard *et al.*, 1992). The terrigenous component of the sediments is composed of quartz, orthoclase, plagioclase, micas, opaque minerals, and traces of heavy minerals (Nawar, 1981).

Materials and Methods

Figure (1) shows the locations of 27 bottom sediment samples collected from the Gulf of Suez. The pH and Eh of these samples were measured *in situ* using pH-Eh-meter (Model wtw pH 315i). Buffer solutions of pH 4, 7, 9 and Zobell's solution were used as standard solutions for testing the redox instruments. The detailed method for measuring pH and Eh is mentioned by Wild and Radtke (2004).

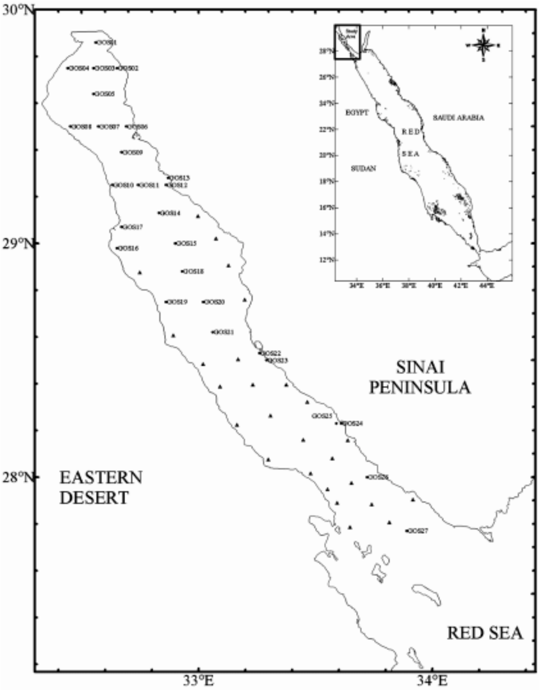

Fig. 1. The study area and locations of sampling stations.

The percentages of sand, silt and clay of collected samples were determined using Shimadzu SALD 3001 Laser Particle Analyzer. Total carbonates were determined using the method of Molnia (1974). Organic Carbon content was determined colourmetrically after the method of Sims and Haby (1971). The trace metals iron, copper, manganese, zinc, cadmium, cobalt, and lead were extracted from the collected samples using the method mentioned by Rifaat *et al.*, (1992) and their concentrations were determined using Atomic Absorption Spectrophotometer (Model Varian A250). The data obtained were analyzed statistically using the Varimax Rotated Factor Analysis technique (Davis, 1973) to decide upon the factors controlling the stability of these metals in the GOS bottom sediments.

Results and Discussion

The bottom sediments of the Gulf of Suez are mainly of carbonates that are composed of calcareous debris of corals and other marine shells and shell fragments. The carbonate content in the examined sediments ranges from 41.9% to 97.4% with an average of 69.3%. The distribution of carbonate content (Fig. 2) shows a relative increase towards west and south while the northern part of the GOS has a lower carbonate percentage. The distribution of organic carbon (Fig. 3) is inversely correlated with carbonate distribution. Organic carbon ranges between 0.92% and 6.84% with an average of 3.58%. The central and northern parts of the Gulf of Suez show the greatest amounts of organic carbon in sediments while the southern part sediment has a relatively low organic carbon content. Most of the examined samples are sand to sandy silt. The northern part of the GOS bottom is covered by sandy silt sediments whereas sediments of the southern part are mainly sands to silty sands (Fig. 4). Table (1) shows the data obtained including the values of pH and Eh, percentages of carbonate and organic carbon and the concentration of Fe, Cu, Mn, Zn, Cd, Ni, Co, Cr and Pb given in ppm.

The distributions of pH and Eh in the sedimentary environment of the GOS are presented in Fig. (5) and (6). The pH of the bottom sediments ranges from 7.35 and 8.05 with an average of 7.62 (slightly alkaline medium). It shows two pH zones. The northern and southern parts of the GOS are dominated by sediments having pH values between 7.35 and 7.75 while its central part is dominated by sediments of pH values greater than 7.75 indicating more alkaline conditions than that of the northern and southern parts (Fig. 5). The Eh values of the GOS bottom sediments vary between 112.74 and 470.24 mV (oxidizing) except at GOS24 at the southeastern part where Eh decreases to –76.81 (reducing). The four general ranges of redox conditions as suggested by Patrick and Mahapatra (1968), which may be encountered in soils are at pH 7, oxidizing > 400 mV, moderately reduced from +400 to +100 mV, reduced from +100 to –100 mV

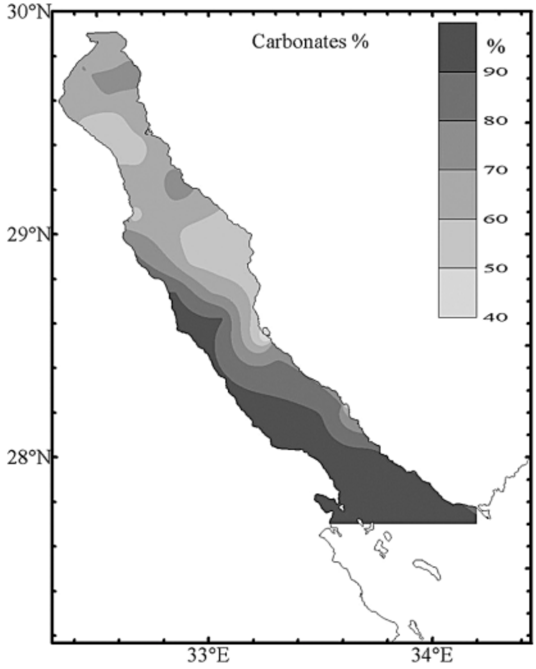

Fig. 2. Distribution of carbonate content in the bottom sediments of Gulf of Suez.

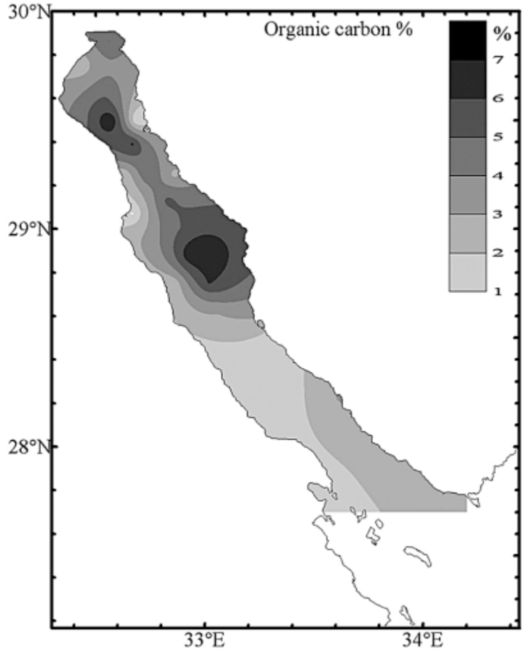

Fig. 3. Distribution of organic carbon in the bottom sediments of the Gulf of Suez.

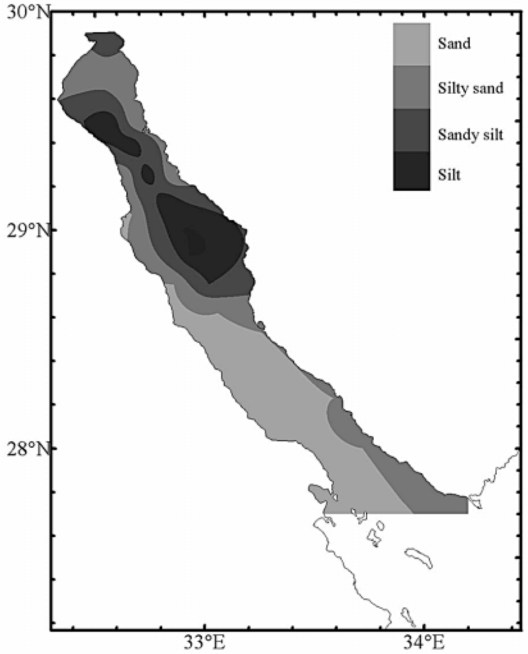

Fig. 4. Sediment type on the bottom of Gulf of Suez.

Table 1. The determined parameters in the bottom sediments of the Gulf of Suez.

					Concentration in ppm								
	pH	Eh	CO3 %	O.C. %	Fe	Cu	Mn	Zn	Cd	Ni	Co	Cr	Pb
GOS01	7.45	112.7	60.2	5.0	601.7	4.7	93.3	14.8	5.1	34.8	37.5	2.9	56.2
GOS02	7.70	211.6	72.1	3.4	527.7	3.6	54.1	8.9	4.7	37.2	43.3	3.6	73.6
GOS04	7.45	279.5	70.1	2.4	494.1	2.1	64.4	8.5	2.8	33.0	35.6	4.9	71.9
GOS05	7.40	413.5	71.5	4.8	725.7	3.1	100.3	16.6	4.6	45.6	39.9	1.6	51.9
GOS06	7.55	470.2	65.3	1.0	427.8	1.4	69.1	7.6	5.4	34.6	36.7	9.8	68.6
GOS07	7.55	423.0	53.7	6.8	768.3	4.4	146.0	20.3	3.4	39.5	37.1	14.8	53.2
GOS08	7.55	384.6	58.6	4.8	903.8	4.5	126.9	18.4	5.7	32.7	40.9	11.8	54.8
GOS09	7.65	419.5	55.6	6.1	829.0	4.2	151.6	24.3	4.3	30.1	36.2	7.9	59.4
GOS10	7.75	434.4	64.5	2.2	439.0	0.8	68.5	6.9	3.8	33.9	36.6	1.2	43.0
GOS11	7.35	463.5	61.6	4.9	826.3	2.8	140.8	19.5	4.1	31.5	40.6	16.9	52.5
GOS12	7.70	468.2	79.1	2.7	384.1	2.3	68.8	6.1	4.8	29.6	31.7	6.0	65.5
GOS13	7.60	224.4	70.0	3.1	365.9	3.2	113.9	7.7	4.0	26.3	40.7	2.4	55.0
GOS14	7.35	130.9	68.6	5.3	621.5	4.0	110.8	17.6	2.5	39.5	36.0	3.7	51.8
GOS15	7.70	184.4	57.9	5.1	902.6	8.7	157.0	25.9	2.5	23.5	48.0	3.5	57.5
GOS16	7.65	372.8	78.5	2.6	323.4	3.4	41.6	5.7	4.1	29.3	28.7	1.9	69.2

Table 1. Contd.

					Concentration in ppm								
	pH	Eh	CO3 %	O.C. %	Fe	Cu	Mn	Zn	Cd	Ni	Co	Cr	Pb
GOS17	7.75	347.4	57.7	0.9	174.3	2.6	38.4	3.1	3.1	24.9	25.2	3.0	36.8
GOS18	7.65	137.5	56.4	6.7	433.0	5.0	117.7	20.2	3.7	33.7	27.5	6.1	43.7
GOS19	7.85	430.1	89.2	2.3	388.3	4.9	70.9	5.6	4.6	39.1	39.4	2.1	67.7
GOS20	7.55	151.0	66.9	6.1	745.6	6.3	109.4	20.0	3.8	30.0	35.6	7.4	72.7
GOS21	8.05	421.6	90.9	3.1	885.5	6.2	91.5	48.6	5.2	45.2	47.4	10.2	52.1
GOS22	7.65	375.0	41.9	2.4	622.8	5.4	83.6	11.1	2.6	18.5	27.9	21.9	38.8
GOS23	7.90	467.6	77.0	1.1	245.5	3.6	28.8	4.3	3.9	32.3	29.7	6.1	46.8
GOS24	7.45	– 76.	56.2	3.2	512.6	5.0	62.1	14.3	3.0	24.2	30.8	10.9	40.8
GOS25	–	–	85.3	2.7	435.4	6.1	25.0	6.1	4.2	33.1	43.2	7.9	53.9
GOS26	7.70	389.3	95.5	2.2	198.2	4.6	17.9	4.8	1.9	29.3	40.1	5.4	37.1
GOS27	7.55	399.9	97.4	2.2	162.6	2.4	15.1	44.5	4.6	35.2	38.2	9.0	58.5
Average	7.62	321.4	69.3	3.6	536.3	4.1	83.4	15.1	3.9	32.6	36.7	7.0	55.1
Min.	7.35	– 76.8	41.9	0.9	162.6	0.8	15.1	3.1	1.9	18.5	25.2	1.2	36.8
Max.	8.05	470.2	97.4	6.8	903.8	8.7	157.0	48.6	5.7	45.6	48.0	21.9	73.6

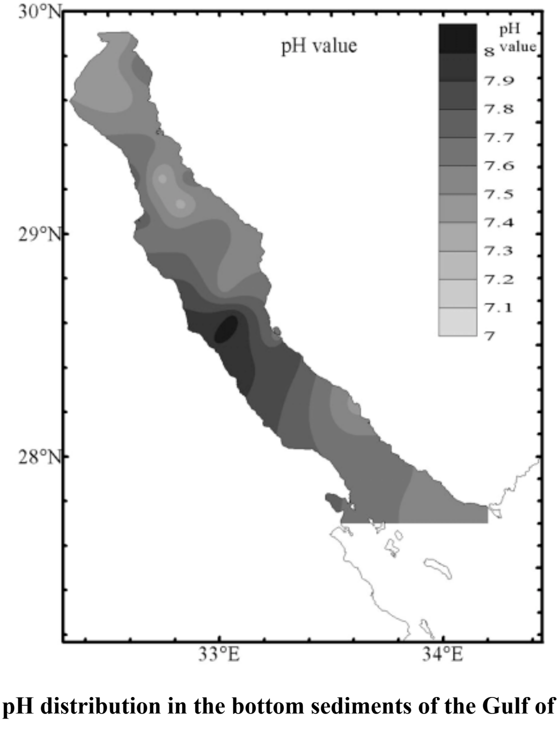

Fig. 5. pH distribution in the bottom sediments of the Gulf of Suez.

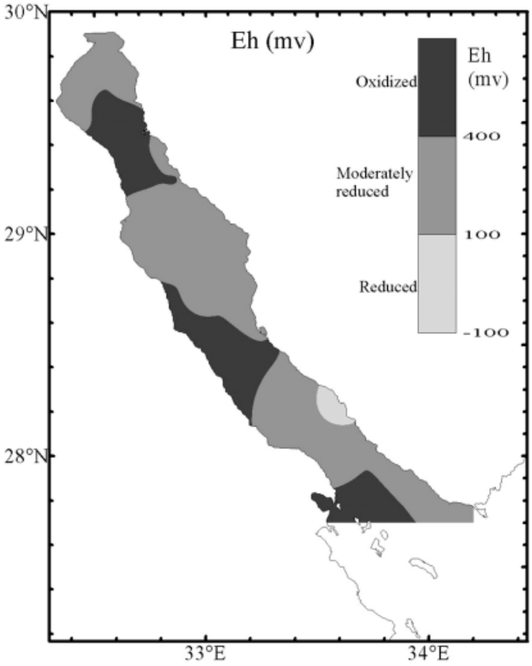

Fig. 6. Eh (mV) distribution in sediment of the Gulf of Suez.

and highly reduced from –100 to –300 mV. Clark *et al.*, (1998) considered all values of Eh greater than +100 mV as oxidizing and all Eh values lower than –100 mV as reducing environments. Accordingly, the entire GOS bottom is covered by oxidized sediments except in the southeastern part at station GOS24 where the Eh of sediments is –76.81 mV (Fig. 6). The prevailing pH and Eh conditions recorded in the bottom sediments of the Gulf of Suez favour trapping of the metal precipitates in the solid phase rather than releasing them to the surrounding seawater.

Table (2) shows the factors controlling the examined metals in the bottom sediments of GOS.

Factor 1 contains two associations; the first is a negative association of Sand (loading = –0.95), pH (loading = –0.67), Eh (loading = –0.40), and Carbonate content (loading = –0.67). The second one is an inverse association as indicated by the positive loadings on Silt (loading = 0.93), Clay (loading = 0.77), Organic Carbon (loading = 0.88), Iron (loading = 0.73) and Manganese (loading = 0.85). This factor represents the interaction of coarse-grained sediments that are composed of calcareous debris and fine-grained sediments that are associated with organic carbon and iron-manganese oxides. It denotes that the pH and Eh of the sediment are the fundamental influence behind this factor. Carbonates are insol-

Table 2. Factor Analysis of the obtained data in Table (1).

	Factor 1	Factor 2	Factor 3
Sand %	– 0.95		
Silt %	0.93		
Clay %	0.77		
Ph	– 0.67	0.49	
Eh	– 0.40		
Carbonate %	– 0.67		0.45
OC %	0.88		
Fe ppm	0.73	0.50	
Cu ppm	0.74	0.76	
Mn ppm	0.85		
Zn ppm		0.72	
Cd ppm			0.74
Ni ppm			0.77
Co ppm		0.64	0.46
Pb ppm			0.59

Insignificant values have been omitted

Eigen Value	5.68	2.37	2.36
% of Trace	35.52	14.83	14.73
Cum % of Trace	35.52	50.35	65.08

Kaiser-Meyer-Olkin Test = 0.6

uble at high pH and Eh values and hence the metals content of the carbonate debris are stable under such redox conditions. The strong positive loadings on mud (silt and clay), organic carbon, iron and manganese metals indicate the close relationship of these components in the studied marine environment as observed by many authors (Gibbs, 1973, Armstrong *et al.*, 1976, Rifaat *et al.*, 1992 and El-Sayed *et al.*, 2002). The inverse relationship between these components and both pH and Eh values indicates that the decay of organic matter tends to lower pH of the sediments, but not far below pH 7.35 and consumes the oxygen, and hence lowers the Eh too. The process of organic matter decay may release part of the iron and manganese content that is associated with organic debris (Förstner and Wittmann, 1981).

Factor 2 is a pH factor that reveals the relationship of pH with iron, copper, zinc and cobalt contents. The increase of pH is associated by similar increase in the content of these metals in the sediments (Galloway *et al*., 1975 and Dillon *et al*., 1977). This factor shows that these metals are more stable in the solid phase under more alkaline conditions.

Factor 3 is a metal-carbonate factor where cadmium, nickel, cobalt and lead are present in the carbonate constituents in the examined sediment which means that the carbonate minerals are the main host of such metals in the sediments as also noticed by Beltagy (1984) in his work on the sediments from the northern Red Sea.

Conclusion

The bottom sediments of the Gulf of Suez are mainly composed of carbonates-sand and -silt. The pH values of these carbonate sediments showed two distinctive zones. The northern and southern parts of the Gulf of Suez are dominated by sediments having pH values ranging between 7.35 and 7.75 while the central zone sediments have pH values greater than 7.75. The entire Gulf of Suez sediments are oxidizing except at the southeastern part. The prevailing redox potential in the Gulf of Suez sediments favours trapping of the metal precipitates rather than releasing them to the ambient seawater.

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تأثير الجهد الأكسدي-الاختزالي على ثبات بعض العناصر الثقيلة في رواسب قاع خليج السويس

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المستخلص. أوضحت الدراسة التى تمت على ٢٧ عينة من رواسب قاع خليج السويس بالبحر الأحمر، وجود علاقة وثيقة بين كل من الأس الهيدروجيني والجهد الأكسدي الاختزالي من جهة، ودرجة ثبات بعض العناصر الثقيلة في تلك الرواسب. تتكون رواسب قاع خليج السويس فى الغالب الأعم من الرمال والغرين الكلسي (الرمال والغرين المكونة من كربونات الكالسيوم والمغنيسيوم) وقد تم التوصل إلى أنه هناك ثلاثة عوامل رئيسية تتحكم في ثبات العناصر تحت الدراسة في الرواسب، العامل الأول هو درجة الأس الهيدروجيني - والجهد الأكسدي الاختزالي، وحيث إن معظم رواسب قاع خليج السويس تتكون من الرمال والغرين الكلسي، فإنها لاتذوب تحت معدلات عالية من الأس الهيدروجيني (الوسط القاعدي) والجهد الأكسدي الاختزالي (الوسط المؤكسد). وبما أن هذه الرواسب الكلسية تحتوي على معظم الفلزات، فإن انتقالها إلى الوسط المائى المحيط عن طريق الذوبان المباشر غير وارد. على الصعيد الآخر، فإن العلاقة العكسية بين المحتوى العضوي وكل من درجة الأس الهيدروجيني والجهد الأكسدي الاختزالي، توضح أن تحلل المواد العضوية في الرواسب يقلل من قلويتها ويستهلك الأكسجين مكسبا الرواسب جهداً اختزالياً أكبر. العامل الثانى هو الأس الهيدروجيني، والذى يتحكم فى وجود عناصر الحديد والنحاس والزنك والكوبلت، وهو يظهر علاقة هذه العناصر بدرجة قلوية الرواسب، بحيث كلما زادت قلوية الرواسب زادت درجة وجود هذه العناصر وثباتها. أما العامل الثالث فهو يوضح وجود العناصر فى صورة كربونات، كما هو واضح من علاقة الكادميوم والنيكل والكوبلت والرصاص بالكربونات الكلية في رواسب خليج السويس.