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Distribution and Significances of the Major Oxides in Recent Coastal Sabkha Sediments of the Al-Dafna Plateau, Northeast Tobruk, Libya

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ABSTRACT

Twenty sabkha samples were chemically analyzed by XRF technique for determination of their major oxides concentrations. Six cores penetrated both the intertidal and supratidal flat zones developed in six wadis mouths in the coastal stretch of the Al-Dafna plateau, northeast Tobruk city. The significance distribution and concentration of the major oxides are discussed and interpreted. Elements in the raw material of the study area reflect important evidence of geochemical weathering processes that affecting parent rocks as well as conditions of sedimentation, and rate of deposition. Correlation coefficients have been used to illustrate the abundance and distribution of these elements.

The distribution of major oxides are follows Si_2O > CaO > LOI > Al_2O_3 > SO_3 > MgO > Na_2O > K_2O. The vertical distribution of major elements is mainly controlled by the abundance and proportions of the clastics, carbonates and evaporite minerals. It was found that silica present in the form of detrital, subrounded to rounded silt- to sand-sized quartz grains, while the content of Al_2O_3 is associated with terrigenous argillaceous materials. On the other hand, the presence of Fe_2O_3 is related to the abundance of clastic materials in sabkha deposits. It was found that K_2O and Na_2O concentrations increase toward the sabkha surfaces.

1 Introduction

Sabkhas are widespread geomorphological features in the coastal landforms of the Mediterranean Sea of Libya Wadis sabkhas always subjected to flash floods during the rainy season in the main Wadis and/or recharge from tidal flow. A tidal pool partially filled with seawater during high tide flood seasonally and daily thus intertidal and supratidal sabkhas are developed. A marine sabkha is a near coastal salt dominated by marine-derived brines and processes; a continental sabkha is an inland salt flat dominated by continental brines and processes (Prudencio et al., 2007). The study area is characterized by the presence of many geomorphological coastal forms and bays. The coastline extends from the Wadi El-Shawash estuary in the west to the Ramla well in the east at the western border of the Arab Republic of Egypt. The sand dunes, the Sabkhas and the pockets are abundant in this area (Al-Haram, 1997). An attempt has been made herein to study the geochemical features regarding both abundance and vertical distribution of major elements in the raw sabkha samples of intertidal and supratidal zones. The chemical composition of the sabkha deposits provide important information in order to define and understand the basic processes involved in major elements transport during and after the deposition of the sabkha deposits. Also the chemical analysis is used to find out the general trend of

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the chemical composition as well as support the trend of mineralogical composition through the vertical profiles. Geologists may use geochemical information to improve understanding of geological processes, including the origin, formation, and composition of rocks and sediments (Rollinson et al., 2014). X-ray fluorescence is a non-destructive technique for analysis of elemental composition. XRF is a well-established analytical technique used for estimating the chemical composition of rocks and sediments both in the field and the laboratory (Potts et al., 1997).

The present work aims to determine the Significances and distribution of the major elements in the studied sabkha deposits.

2 Techniques of the study

Two field trips were conducted to the study area along the coastal stretch of the Al-Dafna plateau (150 km from northeast Tobruk city, Libya) where temperature ranging from 25C to 40C in the winter and summer 2018, respectively. Twenty samples of sabkha deposits were chemically analysed for determination of their major elements. X-Ray Fluorescence (Model ARL9900-X-Ray) at Al Arish Cement Company (ACC) was used for major chemical oxides determination in the raw sabkha samples. X-ray fluorescence is a nondestructive technique for analysis of element composition. Flame photometer instrument PFP7 was used for assurance of XRF results. The samples are irradiated by a strong X-ray beam which leads to emission of X-rays. XRF is a well-established analytical technique used for estimating the chemical composition of rocks and sediments both in the field and the laboratory (Potts *et al.*, 1997; Ramsey *et al.*, 1995). Wavelengths make it possible to detect which elements are present in the samples. The intensity of these characteristic X-rays give information about the abundance of different elements. A computer was utilized for gathering information. Wet analytical analysis was applied for chemical assurance of SiO_2, Al_2O_3, Fe_2O_3, CaO and MgO.

Percentages of silica (SiO_2), alumina (Al_2O_3), ferric oxide (Fe_2O_3), lime (CaO), magnesium oxide (MgO), sulfur trioxide (SO_3), sodium oxide (Na_2O), potassium oxide (K_2O) chloride content (Cl-) and loss on ignition (LOI) were determined.

2.1 Study area

The study area occupies the northeastern coast of Libya (Figure 1); where sabkhas are common in the coastal area of Al Dafna plateau which extends from the mouth of Wadi Umm El-Shawash in the west (east of Tobruk City), to Bir Al Ramla Weep in the eastern border of Libya with Egypt for about 130 km long. The area lies between Longitude 24° 00’ to 25° 08’ E and Latitude between 31° 45’ to 32° 21’ N (Figure 1). The study area has a Mediterranean climate where arid to semiarid conditions are dominant. The average temperature is ranging from 25 to 40° c in summer months and from 10 to 20° C during winter. The rainy season is limited and often concentrated in few showers from October to March. While December and January months are the wet. Al Dafna plateau in the north eastern side of Libya is characterized by different sabkhas developed at Wadis mouths, Wadi Al-Sawani sabkha, Wadi Rizk sabkha, Umm Rukbah sabkha, Wadi Alain sabkha, Alaqila sabkha, and Wadi Umm El-Shawash sabkha. Supratidal and intertidal sabkhas are developed in the Wadis mouths in the coastal area of Al Dafna plateau where desiccation in tidal flat areas causes precipitation of gypsum and halite.

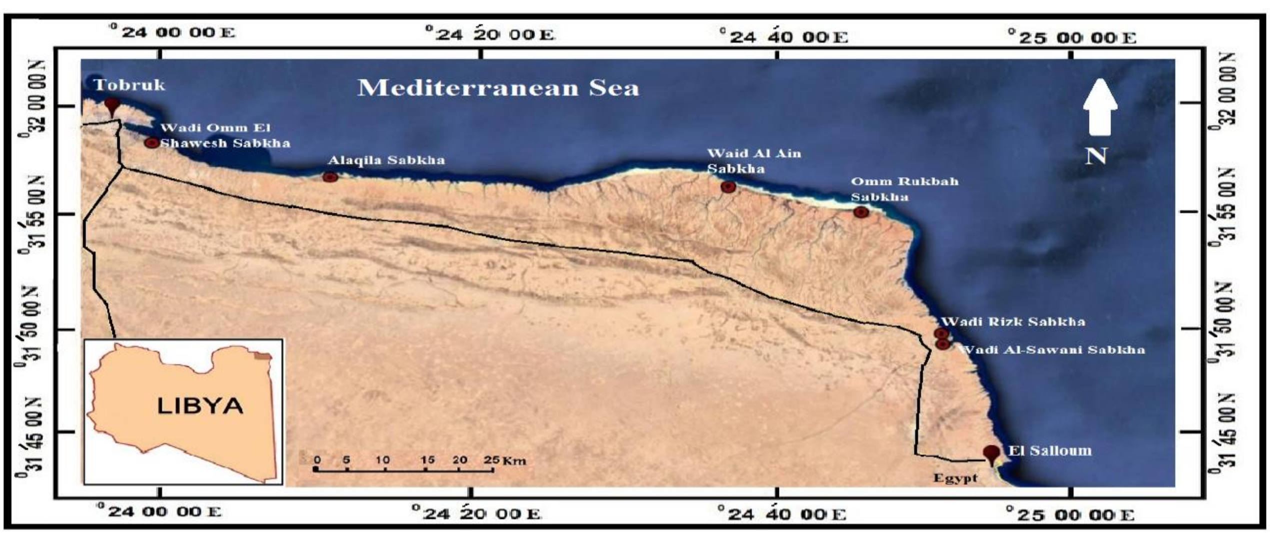

Figure 1: Satellite image showing the location of the studied coastal sabkhas in Al-Dafna plateau. **(.)**

3 Results

Major elements distributin

Data of the major oxides concentration is studied sabkhas are summarized below:

SiO_2

The silica content in the analyzed sabkha samples ranges from 43.8 to 50.83 % with an average of 46.51 % in intertidal zone (Table 1) (Figure 2), and varies between 37.31% and 49.11% with average of 44.82% in supratidal zone (Table 2) (Figure 3).

Al_2O_3

The content of Al_2O_3 in the analyzed sabkha of the intertidal zone varies between 7.01 % and 11.3 % with an average of 8.9 % (Table 1 and Figure 2), whereas in supratidal zone the content ranges from 4.54 % to 10.1 % with an average of 7.61% (Table 2 and Figure 3).

Fe_2O_3

The content of iron in the analyzed sabkhas varies between 1.21 and 3.83 % with an average of 2.47 % in intertidal sabkha (Table 1) and ranges from 0.19 % to 3.15 % with average of 1.90 % in supratidal sabkha (Table 2).

CaO

Calcium content fluctuated between 8.72 and 23.04 % with an average of 15.19 % in intertidal area (Table 1) and ranges from 10.84 % to 39.33 % with an average of 20.50 % in supratidal area (Table 2).

MgO

Magnesium oxide content in the examined sabkhas ranges from 0.089% to 5.24 % with an average of 3.31 % in intertidal zone (Table 1) and varies between 1.92 % and 5.68 % with average of 3.56 % in supratidal zone (Table 2).

SO_3

Contents of SO_3 in the studied sabkhas vary between 0.08 and 7.33 % with an average of 4.22 % in intertidal area (Table 1) and ranges from 1.02 % to 14.16 % with average of 5.63 % in supratidal area (Table 2).

Na_2O

The content of Na_2O in the studied intertidal sabkha varies between 0.15 % and 5.72 % with an average of 1.61 % (Table 1 and Figure 2), whereas the content of Na_2O in the studied supratidal sabkha ranges from zero to 5.29 % with an average 1.61 % (Table 2 and Figure 3).

K_2O

Trends of K_2O in the analyzed sabkhas show values ranging from 1.11 to 1.72 % with an average of 1.36 % in intertidal sabkha (Table 1) and varying between 0.68 % and 2.8 % with average of 1.36 % in supratidal sabkha (Table 2).

Cl^-

Chlorine concentration in the studied intertidal sabkha varies between 0.897 % and 6.39 % with an average value of 2.25 % (Table 1 and Figure 2), whereas the content in the supratidal sabkha ranges from 0.52 % to 5.36 % and its average value is 2.72 % (Table 2 and Figure 3).

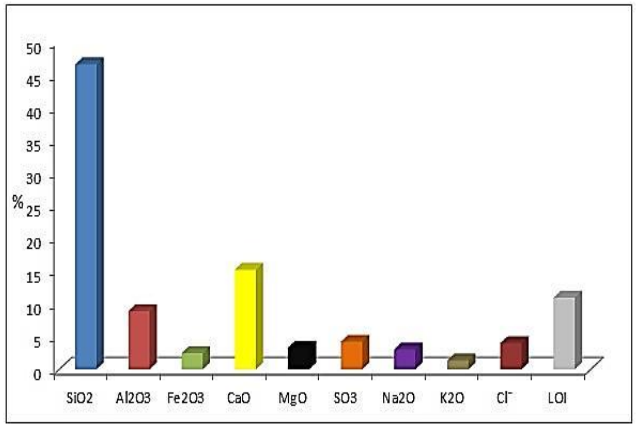

Figure 2. Histograms showing distribution of the average percentage of the major element contents of the sabkhas in intertidal.

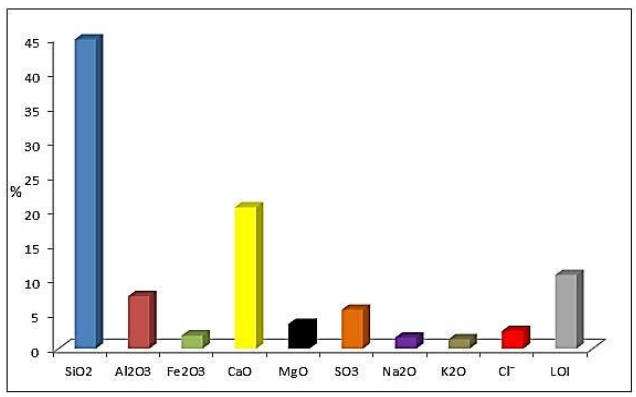

Figure 3. Histograms showing distribution of the average percentage of the major element contents of the sabkhas in supratidal

Table 1. Major oxides concentration in the studied intertidal sabkha sediment

S.no	Core No.	Depth cm	Sabkha	Location	Major Oxides												
					SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Cl^-	LOI	Organic matter %	Carbonate %	Mud %
1	1	0-5	Wadi Al-Sawani	Intertidal	47.91	8.48	2.23	14.5	2.5	1.05	2.89	1.29	3.61	15.54	21	39	53
3		15-20			50.83	7.73	1.71	12.59	2.09	1.08	0.15	1.16	0.897	21.763	0.1	40	38
6	2	0-4	Wadi Rizk		46.51	7.01	1.21	23.04	2.48	0.089	0.408	1.11	2.27	15.87	6	40	54
7		5-14			46.16	7.09	1.45	22.38	2.63	1.62	1.303	1.13	2.96	13.277	8	42	55
9		25-28			46.76	7.84	1.91	18.21	2.59	3.911	1.66	1.19	2.94	12.989	7.6	42	49
10	3	0-5	Omm Rukbah		46.16	7.09	1.45	22.38	2.63	1.62	1.303	1.13	2.96	13.277	8	42	55
11	4	0-5	Wadi Al Ain		48.31	9.44	2.77	8.72	3.67	4.95	5.24	1.39	5.09	10.42	6	28	55
16	6	0-5			43.8	9.19	2.81	16.46	3.42	12.60	5.72	1.31	4.41	0.28	15	45	54
17		20-30			45.03	11.3	3.83	12.25	3.83	2.76	4.73	1.72	6.39	8.16	11.4	48	49
18	7	0-5	Alaqila		44.52	10.3	3.39	12.99	5.24	5.56	4.5	1.61	6.26	5.63	14	58	41
20		20-25			44.87	9.99	3.06	14.42	4.24	7.33	3.67	1.53	4.86	6.03	13	39	60
Average					46.51	8.90	2.47	15.20	2.32	4.23	3.04	1.36	4.03	10.94	10	42.18	51.18
Min					43.80	7.01	1.21	8.72	2.09	0.09	0.15	1.11	0.90	0.28	0.1	28	38
Max					50.83	11.30	3.83	23.04	5.24	12.60	5.72	1.72	6.39	21.76	21	58	60

Table 2. Major oxides concentration in the studied supratidal sabkha sediment

S.no	Core No.	Depth cm	Sabkha	Location	Major Oxides												
					SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Cl^-	LOI	Organic matter %	Carbonate %	Mud %
4	2	0-5	Wadi Rizk	Supratidal	43.09	4.54	0.19	39.33	1.92	2.81	0	0.68	0.52	6.92	2.64	64	27
5		5-15			43.54	5.05	0.36	37.01	2.28	0.63	0	0.81	0.75	9.57	4.5	83	16
6	3	0-5	Omm Rukbah		46.58	9.94	2.95	14.57	3.49	1.02	2.43	1.57	3.09	14.36	9.9	45	54
8		20-25			46.77	10.1	3.15	10.84	5.11	1.34	5.29	1.51	5.36	10.53	16.3	37	60
9	4	0-5	Wadi Al Ain		49.11	9.46	2.66	12.61	2.66	0.15	0.336	1.51	0.919	20.585	7.2	43	55
14	5	0-5	Alaqila		44.83	8.15	1.95	15.93	4.35	14.16	2.01	1.19	3.42	4.01	6.4	50	49
17		30-35			44.65	9.13	2.71	16.04	5.68	8.85	1.68	1.36	2.79	7.11	9.2	46	53
18	6	0-10	Wadi Omm El-Shawesh		47.46	6.11	1.07	19.39	2.09	7.31	0.46	0.88	2.243	12.987	4.2	51	36
21		30-35			37.31	5.97	2.1	18.8	4.53	14.4	2.31	2.8	3.89	10.2	9.9	48	10
Average					44.82	7.61	1.90	20.50	3.57	5.63	1.61	1.37	2.55	10.69	7.80	52	40
Min					37.31	4.54	0.19	10.84	1.92	0.15	0.00	0.68	0.52	4.01	2.64	37	10
Max					49.11	10.10	3.15	39.33	5.68	14.40	5.29	2.80	5.36	20.58	16.3	83	60

Table 3. Correlation coefficients of major oxides for the studied intertidal sabkha sediments.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Cl^-	LOI	Organic matter %	Carbonate %	Mud %
SiO_2	1.0												
Al_2O_3	-0.466	1.0											
Fe_2O_3	-0.503	0.995	1.0										
CaO	-0.229	-0.710	-0.700	1.0									
MgO	-0.623	0.821	0.834	-0.477	1.0								
SO_3	-0.602	0.465	0.526	-0.258	0.536	1.0							
Na_2O	-0.567	0.814	0.848	-0.573	0.728	0.730	1.0						
K_2O	-0.469	0.975	0.964	-0.654	0.852	0.355	0.717	1.0					
Cl^-	-0.656	0.902	0.914	-0.497	0.885	0.469	0.868	0.904	1.0				
LOI	0.873	-0.656	-0.705	0.174	-0.749	-0.869	-0.851	-0.595	-0.774	1.0			
Organic matter %	-0.564	0.398	0.434	-0.043	0.353	0.334	0.537	0.373	0.521	-0.531	1.0		
Carbonate %	-0.561	0.348	0.382	0.098	0.486	0.167	0.146	0.419	0.372	-0.370	0.312	1.0	
Mud %	-0.353	0.000	-0.004	0.217	0.036	0.268	0.239	0.004	0.189	-0.346	0.301	-0.483	1.0

Table 4. Correlation coefficients of major oxides for the studied supratidal sabkha sediments.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Cl^-	LOI	Organic matter %	Carbonate. %	Mud %
SiO_2	1.0												
Al_2O_3	0.560	1.0											
Fe_2O_3	0.284	0.937	1.0										
CaO	-0.375	-0.862	-0.920	1.0									
MgO	-0.209	0.592	0.730	-0.622	1.0								
SO_3	-0.576	-0.173	0.030	-0.196	0.452	1.0							
Na_2O	-0.006	0.627	0.721	-0.634	0.752	0.100	1.0						
K_2O	-0.516	0.262	0.571	-0.513	0.546	0.433	0.468	1.0					
Cl^-	-0.128	0.534	0.683	-0.688	0.791	0.383	0.943	0.562	1.0				
LOI	0.502	0.341	0.325	-0.353	-0.338	-0.549	-0.124	0.193	-0.206	1.0			
Organic matter %	0.047	0.726	0.838	-0.704	0.766	-0.036	0.940	0.574	0.853	0.116	1.0		
Carbonate %	-0.298	-0.780	-0.865	0.908	-0.587	-0.183	-0.651	-0.506	-0.672	-0.294	-0.686	1.0	
Mud %	0.780	0.897	0.720	-0.703	0.386	-0.267	0.453	-0.135	0.338	0.238	0.482	-0.690	1.0

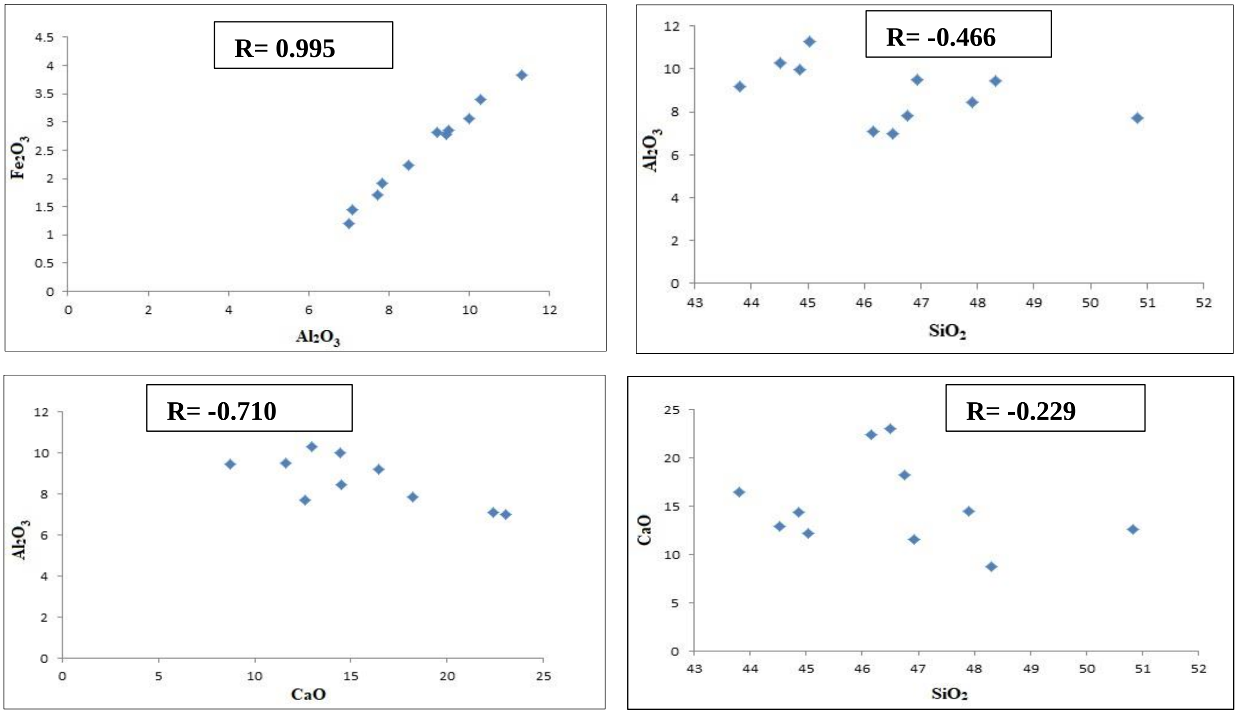

Figure 4. Diagrams showing the correlations of some major elements with each other in the studied intertidal sabkha

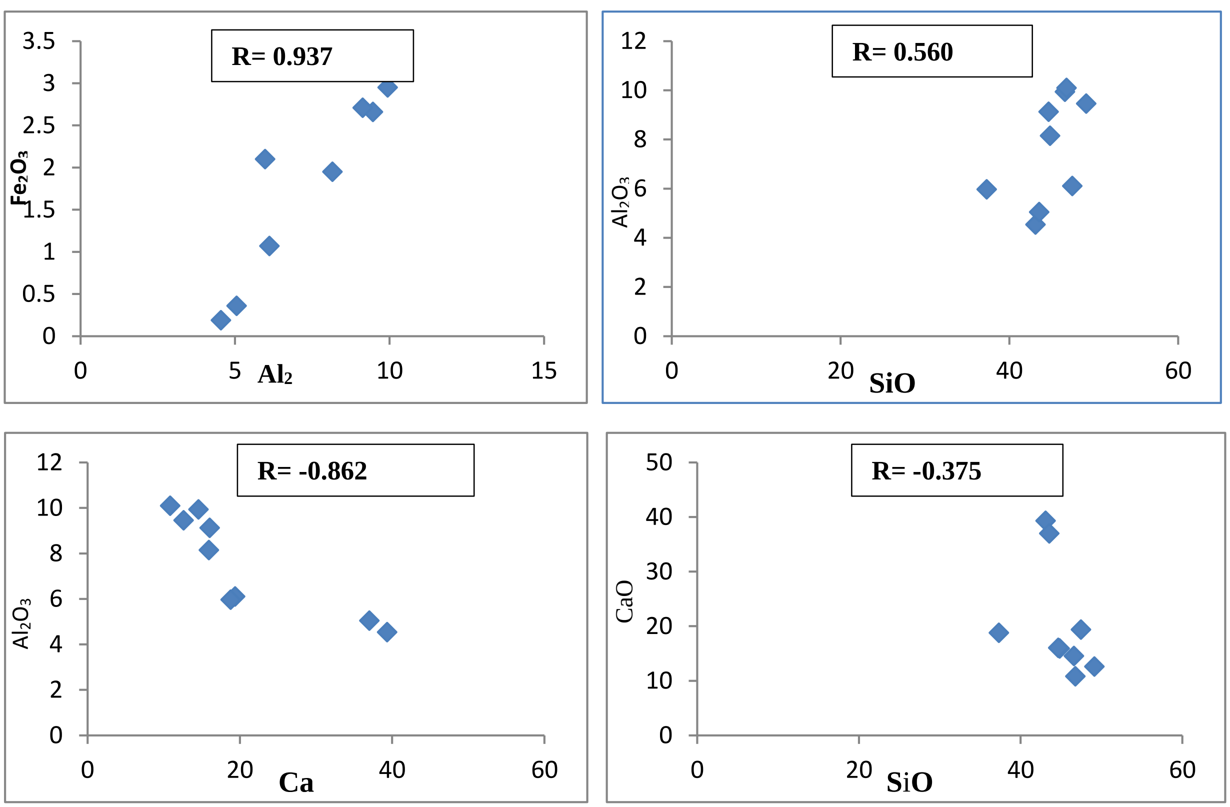

Figure 5. Diagrams showing the correlations of some major elements with each other in the studied supratidal sabkhas

4 Discussion

Significances distributions of the major oxides in both types of studied sabkhas are summarized in the following:

Silicon dioxide, also known as silica, silicic acid or silicic acid anhydride is an oxide of silicon with the chemical formula SiO_2. Calculations of correlation coefficients of major element concentrations in the studied sabkha samples are shown in (Table 3) and illustrated in (Figure 4). In intertidal sabkha, SiO_2 is positively correlated with LOI (r = 0.873) and negatively correlated with Fe_2O_3, MgO, SO_3, Na_2O, Cl^-, organic matter and carbonate contents (r = -0.503, -0.623, -0.602, -0.567, -0.656, -0.564 and -0.561, respectively). In supratidal sabkha, high positive correlation exists between silica, Al_2O_3, LOI and mud content (r = 0.56, 0.502 and 0.78, respectively) (Table 4). In contrast, SiO_2 is strongly negatively correlated with SO_3 and K_2O (r = -0.576 and -0.516, respectively) (Figure 5). Silica in the studied sabkha occurs in the form of detrital, rounded to subrounded sand to silt-sized quartz grains.

Aluminum is an important component of particulate matter derived from continents (Taylor & McLennan, 1985), so it is used to trace the abundance of the terrestrial components. Alumina in intertidal zone has a strong positive correlation with Fe_2O_3, MgO, Na_2O, K_2O and Cl^- (r = 0.995, 0.821, 0.814, 0.975, and 0.902, respectively, Table 3 and Figure 4). In addition Al_2O_3 has negative correlation with CaO and LOI (r = -0.71 and -0.656, respectively). In supratidal zone, Al_2O_3 has strong positive correlations with Fe_2O_3, MgO, Na_2O, Cl^-, organic matter and mud contents (r = 0.937, 0.592, 0.627, 0.534, 0.726 and 0.897, respectively, Table 4). Alumina has strong negative correlation with CaO and carbonate content (r = -0.862 and 0.897, respectively) (Figure 5). This trend indicates its association with terrigenous argillaceous materials as evidenced by (Murray *et a*, 1992). Aluminum is mainly hosted in clay minerals and occasionally in detrital feldspars (Albarede, 2003). Aluminum solubility in hydrous fluids is low, except at very high temperature and high pH (Hem, 1970; Albarede, 2003).

In intertidal zone, **Ferric oxide** has a strong positive correlations with MgO, SO_3, Na_2O, K_2O and Cl^- (r = 0.834, 0.526, 0.848, 0.964 and 0.914, respectively) (Table 3 and Figure 4) and a negative correlation with LOI (r = -0.7). In supratidal zone, Fe_2O_3 has a strong positive correlation with MgO, Na_2O, K_2O, Cl^-, organic matter and mud content (r = 0.730, 0.721, 0.571, 0.683, 0.838 and 0.72, respectively Table 4). In contrast, Fe_2O_3 strongly negatively correlated with CaO and carbonate content (r = -0.920 and -0.865) (Figure 5).

The presence of iron is related to the increase of clastic materials in sabkha deposits (Mohamed, 1993).

The vertical distribution of CaO and MgO and the correlation matrix show that MgO correlates negatively with CaO (r = -0.477) (Tables 3 and 4 and Figures 4 and 5) in the studied sabkhas.

The antipathetic behavior between Ca and Mg is attributed to the dolomitization process (Brand and Veizer, 1980). The XRF Data analyses show that dolomite in the studied sabkha is very rare so that MgO contents are very low. In the intertidal zone, MgO has a positive correlation with SO_3, Na_2O, K_2O, Cl^- and organic matter (r = 0.452, 0.752, 0.546, 0.791, and 0.766, respectively, Table 3 and Figure 3) and negative correlation with LOI. In the supratidal zone, MgO has positive correlations with SO_3, Na_2O, K_2O, Cl^- and organic matter (r = 0.452, 0.752, 0.546, 0.791 and 0.766, respectively, Table 4 and Figure 5).

Sulfur trioxide is the chemical compound with the formula SO_3, with a relatively narrow liquid range. In the gaseous form, this species is a significant pollutant, being the primary agent in acid rain (Loerting *et al.*, 2000). It is prepared on an industrial scale as a precursor to sulfuric acid. In perfectly dry apparatus, sulfur trioxide vapor is invisible, and the liquid is transparent. However, it fumes profusely even in a relatively dry atmosphere (it has been used as a smoke agent) due to formation of a sulfuric acid mist. This vapor has no odor but is extremely corrosive (Lerner, 2011). Sulfur trioxide has a strong positive correlation with Na_2O and Cl^- (r = 0.730 and 0.469, respectively, Table 1.3 and Figure 4) in intertidal area, whereas in supratidal area, SO_3 has a strong positive correlation with K_2O (r = 0.433, Table 4 and Figure 5) and negative correlation with LOI (r= -0.549).

Sodium oxide content shows upward increase through the different cores taken in the studied sabkhas where its maximum values occur at the surface. Na_2O represents the most abundant cations in the sea water and should be a good indicator of salinity (Moore and Billings, 1971). If Na_2O content is less than 0.05%, this indicates contribution of freshwater, while if it is higher than 0.3%, this denotes marine influence (Ernest, 1970). In the intertidal sabkha, Na_2O has positive correlations with K_2O, Cl^- and organic matter content (r = 0.717, 0.868 and 0.537, respectively) (Table 3 and Figure 4), whereas it has a negative correlation with LOI (r = -0.851). While the supratidal sabkha, Na_2O has positive correlations with K_2O, Cl^-, organic matter and mud contents (r = 0.468, 0.943, 0.940 and 0.453, respectively) and a negative correlation with carbonate content (r = -0.651) (Table 4 and Figure 5). The slightly high content of the Na_2O in the studied sabkha is mainly due to the presence of the halite at the sabkha surface.

Potassium oxide in intertidal sabkha, has a strong positive correlation with Cl^- (r = 0.904, Table 3) and a negative correlation with LOI (r=-0.595) (Figure 4). In supratidal sabkha K_2O exhibits strong positive correlations with Cl^- and organic matter content (r =

0.562 and 0.574, respectively, Table 4) (Figure 5) and a negative correlation with carbonate content (r = -0.506). Like Na_2O, potassium oxide values increase upward in the studied sabkha.

In intertidal sabkha, **chloride** has a positive correlation with organic matter content (r = 0.521) and a negative correlation with LOI (r = -0.774) (Table 3 and Figure 4). In supratidal carbonate, Cl^- has a strong positive correlation with organic matter content (r = 0.853) and a negative correlation with carbonate content (r= -0.672) (Table 4 and Figure 5).

5 Conclusion

The studied coastal sabkha were subdivided into two types; intertidal and supratidal sabkhas. Geochemical analyses in the recorded sabkha deposits reveal enrichment of SiO_2, Al_2O_3, and Fe2O3 due to abundance of clastic materials that are dominated by silt- to sand-sized quartz grains. CaO and MgO oxides are recorded with limited distribution due to the presence of chemically precipitated some calcite and dolomite in the analyzed sabkha deposits reflecting the weak supplied sea water to the studied sabkha.

Conflict of interest: The authors declare that there are no conflicts of interest.

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