

A STUDY ON CARBONATE FORMS OF SOME CALCAREOUS SOILS NORTH AND SOUTH SINAI, EGYPT

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ABSTRACT

Eighteen soil samples were collected from the subsequent layers of nine soil profiles representing the calcareous soils of El-Arish and Ras Sudr. Field evidence showed the different forms of soil carbonates, crust, concretions, nodules and soft powdery (diffused). The collected soil samples were analysed to determine some of their physical and chemical characteristics, then X-rayed to determine the crystalline soil carbonate minerals.

The obtained results showed that total soil carbonates varies widely from 2.98 to 50.21% and 32.49 to 59.85% in El-Arish and Ras Sudr soils, respectively. The depthwise distribution of carbonates follows nearly two patterns characterized by a tendency of increase and irregular distribution downward the soil profiles with no distinctive formation of pedogenic calcic horizon.

The carbonate mineralogy revealed the dominance of calcite, ankerite and monohydrocalcite in both soils with slight occurrence of other eleven crystalline carbonate minerals, of which gaudefroyite was identified in both soils forming about 4-6% of carbonate minerals. Minrecordite, dolomite and northupite were also identified in traceable amounts (average 4.09 and 4.80% of soil carbonate), while other minerals constitute an average weighted means in soil profiles, not exceeding 4% of carbonates for each mineral.

The results of carbonate mineralogy were interpreted in light of soil origin, genesis and formation which clarified that most carbonate minerals are geogenic or lithogenic, derived from the limestone-enriched rocks of El-Tih and Egma plateau. But this does not deny the authogenic or pedogenic origin of some carbonates due to weathering and chemiprecipitation enhanced by the increasing concentrations of soluble Ca^{++} , Mg^{++} and HCO_3 ions and CO_2 from biotic origin as well as the links between abiotic and biotic CaCO_3 whose interactions are also discussed. However, the biogeochemical interaction is seemingly slow, weak and needs long time to reach distinguishable calcic horizon under the prevailing arid environment.

INTRODUCTION

The calcareous soils cover a considerable portion of agricultural desert lands in Egypt, particularly in the northwestern coastal zone and Sinai. The accumulation of carbonates in these soils is closely connected to soil genesis and formation. (Soil Survey 2011). The observed forms of soil carbonates depend as much on their contents and specific soil characteristics. Among these forms, calcareous crust, encrustation, concretions, nodules and diffused carbonates which are pedologically recognized and investigated (Ismail *et al.*, 1986). Undoubtedly, the high content of CaCO_3 and its forms affect soil physical, chemical and nutritional properties and consequently reflected on cropping pattern and productivity.

Previous studies have been focused on the effect of CaCO_3 on soil solution chemistry and physical characteristics rather on actual identification of carbonate minerals. This is expected due to practical application in reclamation and land use planning of calcareous soils which are widely distributed in arid and semi-arid regions. However, little attention is paid to carbonate minerals constitution which contributes to soil properties especially the physic-chemical behaviour.

The present work is therefore conducted to investigate the carbonate minerals in some calcareous soils of Sinai Peninsula with special emphasis on the role of biotic and abiotic factors of the ecosystem in their occurrences.

MATERIALS AND METHODS

Eighteen soil samples were collected from nine soil profiles representing the soils of El-Arish and Ras Sudr, Fig. (1). These soil samples were subjected to the following analyses:

- Particle size distribution by the pipette method, Syvitski and James (2007).
- Calcium carbonate content was determined using Collin's calcimeter, Cottenie *et al.*, (1982).
- Soil reaction (pH) was determined in the soil saturation extract using a pH meter, 3320 Jenway, Black (1986).
- Total soil salinity (EC_e) was measured in the soil extract (1:2.5) using a conductivity meter (YSI model 35) and soluble cations and anions were determined, according to Page *et al.*, (1982) and Black (1986).

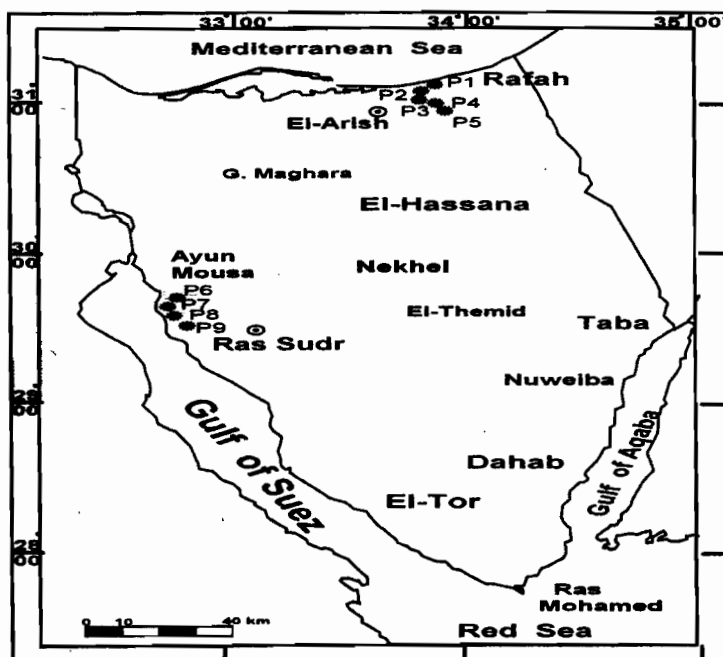


Fig.(1): Location of the studied soil profiles representing El-Arish & Ras Sudr.

-The bulk soil samples were X-rayed by a Philips PW 3710 installation supplied with a horizontal goniometry and a vertical object plane, using Ni-filtered Cu radiation (40 Kv operating voltage and current of 35 mA).

-Identification of carbonate minerals was carried out following the criteria established by Brown and Brindley (1980) and Moore and Reynolds (1989).

RESULTS AND DISCUSSION

Soil characteristics.

1-EI-Arish soils.

The studied soil profiles (Nos. 1 to 5) which represent EI-Arish soils are classified as Typic Torriorthents. The soils are loam to sandy clay textured (table 1) with a dominant medium (SCL) texture. Profiles 2 and 3 have uniform texture throughout their depth but with variable particle size distribution while other profiles displayed apparent discontinuity of grain size distribution (lithologic) and textural classes.

Table: (1) Particle size distribution and textural class of the studied soils.

Location and profile No.	Depth, (Cm.)	Mechanical fractions without CaCO ₃ (%)				Textural Class	
		Coarse sand	Fine sand	Silt	Clay		
EI-Arish	1	0-30	5.90	64.10	8.00	22.00	SCL
		30-60	5.50	52.50	8.00	34.00	SC
		60-90	1.05	62.95	6.00	30.00	SCL
		90-120	0.80	67.20	4.00	28.00	SCL
	2	0-30	70.0	6.00	2.00	22.00	SCL
		30-60	12.7	47.30	18.00	22.00	SCL
		60-90	26.80	37.20	12.00	24.00	SCL
		90-120	45.90	16.10	8.00	30.00	SCL
	3	0-30	70.00	4.00	4.00	22.00	SCL
		30-60	43.00	27.00	4.00	26.00	SCL
		60-90	46.30	19.70	2.00	32.00	SCL
		90-120	15.00	55.00	2.00	28.00	SCL
	4	0-30	63.50	4.50	2.00	30.00	SCL
		30-60	24.50	31.50	12.00	32.00	SCL
		60-90	8.40	9.30	73.80	8.50	SiL
		90-120	20.30	30.40	43.70	5.60	SL
5	0-30	50.60	7.20	23.70	18.50	SL	
	30-60	18.80	1.00	59.80	20.40	SiL	
	60-90	7.80	3.20	63.40	25.60	SiL	
	90-120	21.40	20.10	39.90	18.60	L	
Ras Sudr	6	0-25	40.40	25.00	13.80	20.80	SCL
		25-50	39.90	24.40	15.90	19.80	SL
		50-70	19.30	29.30	47.00	4.40	L
		70-100	20.60	30.40	43.60	5.40	SL
	7	0-30	22.20	21.10	36.80	19.90	L
		30-70	21.70	32.20	39.90	6.20	SL
		70-90	51.80	8.80	19.90	19.50	SL
		90-110	21.70	31.50	40.40	6.40	SL
	8	0-40	25.80	32.20	19.60	22.40	SCL
		40-70	60.00	3.50	7.50	29.00	SCL
		70-80	6.55	60.40	6.60	26.45	SCL
		80-100	21.20	22.20	36.50	20.10	L
	9	100-125	22.80	33.30	37.00	6.90	SL
		125-140	61.60	4.50	3.90	30.00	SCL
		0-20	21.90	31.30	38.60	8.20	SL
		20-40	5.55	61.60	7.90	24.95	SCL
	40-80	21.90	31.20	38.50	8.40	SL	
	80-100	6.60	35.20	48.30	9.90	L	

SCL: Sandy Clay Loam, SC: Sandy Clay, SiL: Silty Loam, SL: Sandy Loam and L: Loam,

Table (2) shows that the soils are alkaline to strongly alkaline except in the deepest layer of profile 4 which is mildly alkaline. The soils are non-saline to slightly saline and the cationic composition of the soil saturation extract is dominated with Ca^{++} and / or Na^+ followed by Mg^{++} and K^+ while the anionic composition is dominated with either SO_4^- or Cl^- followed by HCO_3^- and CO_3^- is entirely absent. Therefore, salinization is of the sulphate- chloride type. CaCO_3 content varies widely between 2.98 % and 50.21%, the lowest content characterizes the top surface layers of profiles 2 and 3 whereas the highest content is found in the 60-90 cm. layer of profile 5. The CaCO_3 content appeared in a diffused powdery pattern, sometimes in the form of nodules and concretions, rarely in surface crust. These forms agree with those described by Peter and Matthew (2005). Nevertheless, the pedogenic calcic horizon cannot be distinguished and carbonate content has a tendency to increase downward in some profiles while being irregularly distributed in some others. Similar findings were recorded by Stephen *et al.*, (2007) in the soils of terrace sequence of Sicily, Italy.

Table: (2) Some Chemical characteristics of the studied soils.

Location and profile No.	Depth, (cm.)	CaCO ₃ %	pH (1:2.5)	EC dS/m	Cations me/l				Anions me/l			
					Ca ⁺⁺	Mg ⁺⁺	K ⁺	Na ⁺	CO ₃ ⁻	HCO ₃ ⁻	Cl ⁻	SO ₄ ⁻
1	0-30	21.28	8.78	0.10	0.40	0.20	0.01	0.39	0.00	0.20	0.40	0.40
	30-60	22.98	8.62	0.27	0.60	0.30	0.07	1.73	0.00	0.40	0.80	1.50
	60-90	19.99	8.78	0.48	0.80	0.60	0.10	3.30	0.00	0.60	1.00	3.20
	90-120	23.40	9.37	0.46	0.70	0.50	0.99	2.50	0.00	0.50	0.90	3.20
2	0-30	2.98	8.32	1.23	5.00	2.50	0.32	4.48	0.00	1.80	8.06	2.44
	30-60	15.74	8.42	0.51	2.00	1.00	0.23	1.87	0.00	0.90	2.20	2.00
	60-90	22.98	8.57	0.66	2.30	1.40	0.24	2.66	0.00	1.10	3.40	2.10
	90-120	14.47	8.28	1.18	4.60	2.40	0.40	4.40	0.00	1.70	7.10	3.00
El-Arish	0-30	2.98	8.67	0.23	0.50	0.20	0.06	1.54	0.00	0.30	0.60	1.40
	30-60	8.34	8.75	0.22	0.40	0.10	0.04	1.66	0.00	0.20	0.50	1.50
	60-90	14.72	8.88	0.15	0.30	0.20	0.05	0.95	0.00	0.10	0.40	1.00
	90-120	16.17	8.74	0.18	0.40	0.30	0.06	1.04	0.00	0.10	0.50	1.20
3	0-30	4.08	8.51	0.21	0.40	0.30	0.07	1.33	0.00	0.20	0.50	1.40
	30-60	19.49	8.46	0.49	0.90	0.70	0.20	3.10	0.00	0.70	1.20	3.00
	60-90	28.76	8.43	0.29	0.70	0.40	0.09	1.71	0.00	0.50	0.90	1.50
	90-120	28.51	7.71	0.48	0.80	0.60	0.10	3.30	0.00	0.60	1.10	3.10
4	0-30	12.68	8.41	1.86	7.00	5.00	1.30	5.30	0.00	2.40	10.80	5.40
	30-60	48.51	8.48	2.34	10.60	6.90	1.80	4.10	0.00	4.90	14.40	4.10
	60-90	50.21	8.31	2.67	12.90	7.40	1.90	4.50	0.00	5.50	16.60	4.60
	90-120	35.74	8.46	1.28	6.40	2.80	0.70	2.90	0.00	1.90	9.60	1.30
5	0-25	38.81	8.24	2.91	14.40	8.80	2.30	3.60	0.00	6.70	18.80	3.60
	25-50	42.55	8.51	0.58	1.00	0.30	0.30	4.00	0.00	0.80	1.40	3.60
	50-70	46.63	8.47	0.82	3.20	1.90	0.40	2.70	0.00	1.40	4.30	2.30
	70-100	52.59	8.67	0.37	0.80	0.40	0.10	2.40	0.00	0.60	2.20	0.90
6	0-30	48.51	8.26	2.20	9.90	7.10	2.10	2.90	0.00	3.90	14.40	3.70
	30-70	32.49	8.33	1.05	4.20	2.10	0.60	3.60	0.00	2.10	5.40	3.00
	70-90	53.87	8.35	0.86	3.80	2.00	0.70	2.10	0.06	1.70	4.90	2.00
	90-110	38.48	8.05	8.50	30.00	20.00	2.10	32.90	0.00	18.80	40.90	25.30
7 Ras Sudr	0-40	53.01	8.11	1.16	4.10	3.20	0.30	4.00	0.00	1.60	6.10	3.90
	40-70	48.74	8.23	1.00	3.90	2.20	0.20	3.70	0.00	1.10	5.40	3.50
	70-80	53.01	8.00	2.16	9.10	6.80	2.40	3.30	0.00	3.00	12.20	6.40
	80-100	52.16	8.02	8.71	40.00	25.00	3.40	18.70	0.00	20.20	50.90	16.00
8	100-125	48.74	8.11	4.17	18.90	9.00	2.00	11.80	0.00	12.12	25.50	4.08
	125-140	37.62	8.03	3.08	15.10	7.50	1.80	6.40	0.00	7.00	20.50	3.30
	0-20	47.03	7.81	1.97	8.70	6.60	1.90	2.50	0.00	2.20	10.20	7.30
	20-40	49.59	7.97	1.28	6.30	2.90	0.80	2.80	0.00	1.80	9.70	1.30
9	40-80	51.30	8.06	1.00	3.80	2.30	0.40	3.50	0.00	1.10	5.40	3.50
	80-100	59.85	8.26	0.93	3.00	2.00	0.30	4.00	0.00	0.90	5.50	2.90

2- Ras Sudr soils.

These soils are represented by four profiles (Nos.6-9) related to the taxonomic subgroup Typic Torriorthents with non distinguishable calcic horizon or any other diagnostic horizon. Tables 1 and 2 present the major characteristics of these soils. Soil texture is loam to sandy clay loam with a dominance of sandy loam textured layers. In general, particle size distribution and soil texture confirmed the discontinuity and stratification within each soil profile. Soil reaction is mildly alkaline to alkaline. The soils are generally saline to slightly saline; however pronounced increase of salinity is quite obvious in the deepest layer of profile 7 and the deeper layer of profile 8. The chemical composition of the saturation extract is commonly dominated with Ca^{++} and /or Na^+ followed by Mg^{++} and K^+ while anions are mostly in the descending order: $\text{Cl}^- > \text{SO}_4^{--} > \text{HCO}_3^-$ and CO_3^{--} is entirely absent. CaCO_3 is found as thin films or coatings around sand grains, diffused powdery, nodules and concretions, rarely as thin surface soil crust. Carbonate content is considerably high, being in the range of 32.49-59.85 % and its distribution in the soil profiles follows two patterns characterized by a tendency of increase downward soil profiles (Nos. 6 and 9) and irregular distribution (profiles Nos. 7 and 8) with no distinctive formation of calcic horizon.

Carbonate forms and mineralogy.

Carbonate-enriched sediments referred to as calcareous soils irrespective of their ages, contain appreciable amounts of limestone which is formed mainly of calcium carbonate (CaCO_3) and dolostone, formed mainly of magnesium-calcium carbonate [$\text{Ca Mg}(\text{CO}_3)_2$] as the main rock types. Despite their chemical simplicity, they commonly underwent complex chemical transformation during diagenesis and soil formation processes, (Joel 2007).

In calcareous soils, some of these carbonates are geogenic and some others are pedogenic depending on the depositional environments and magnitude of soil development which involves concurrent interaction of biological, chemical and physical processes in soil profiles.

As already mentioned, the carbonate forms identified in the studied soil profiles are mainly crust, diffused or powdery carbonates, films and coatings around soil particles, concretions and nodules. Due to the importance of soil carbonates to plant nutrition and their effect on soil physical, chemical and biological properties, it was convenient to throw light on soil carbonates mineralogy.

X-ray diffraction patterns, in the range of 29° - 60° 2 theta presented in (Figs. 2 to 5) and interpreted as frequency distribution of carbonate minerals (Table 3) reveal the presence of 14 carbonate minerals, out of which only 6 and 5 carbonate minerals are shown to be the most predominant in El-Arish and Ras Sudr soils, respectively.

Following the criteria established by Stuart *et al.*, (2009), the identified carbonate minerals are categorized under their divisions as follows:

i) Anhydrous carbonates.

Calcite group (trigonal) that includes:

- Calcite (CaCO_3).
- Gaspette (Ni, Mg, Fe^{2+}) CO_3 .

- Magnesite (MgCO_3).

ii) Aragonite group (orthorhombic) that includes:

- Aragonite (CaCO_3).

iii) Anhydrous carbonates with confound formulas.

- Dolomite group (trigonal) which includes ankerite [$\text{Ca Fe} (\text{CO}_3)_2$], dolomite [$\text{Ca Mg} (\text{CO}_3)_2$], huntite [$\text{Mg}_3\text{Ca} (\text{CO}_3)_4$], minrecordite [$\text{Ca Zn} (\text{CO}_3)_2$].

iv) Carbonates with hydroxyl or halogen.

- Carbonate with hydroxide (monoclinic) which includes azurite [$\text{Cu}_3 (\text{CO}_3)_2 (\text{OH})_2$].

v) Hydrated carbonates which includes hydromagnesite.

[$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$], lansfordite [$\text{MgCO}_3 \cdot 5(\text{H}_2\text{O})$], monohydrocalcite ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$) and natrun [$\text{Na}_2\text{CO}_3 \cdot 10(\text{H}_2\text{O})$]. An account on the mineralogical constitution of soil carbonates in the studied soils is given hereafter.

Calcite is the predominant carbonate mineral, it constitutes 11.29-62.00 % and 39.49-66.42 % of soil carbonates of Wadi El-Arish and Ras Sudr soils, respectively except in the top surface layer of profiles 2-5 of El-Arish where it forms only 3.89 % of soil % carbonate. In most cases, calcite in the top surface of El-Arish profiles displayed low percent. This could be rendered to its migration to the subsurface layers under agricultural practices. This situation is not evidenced in Ras Sudr soils which are recently reclaimed.

Ankerite content varies widely from 0.61 to 54.95 % and 1.73 to 12.31 % of soil carbonates in El-Arish and Ras Sudr soils respectively with entire absence in the 30-60 Cm. layer of profile 2 of El-Arish. The relatively high content of ankerite especially in El-Arish soil carbonate is mainly ascribed to the metastable nature of this carbonate mineral, this may be confirmed by the pronounced accumulation of this carbonate mineral in the uppermost surface layer of most profiles. The great difference between ankerite content in El-Arish and Ras Sudr soils is essentially rendered to the parent materials contribution as well the sedimentation regime during soil formation in each locality.

Monohydrocalcite is detected in all layers of the studied soil profiles where it constitutes 0.66 to 25.74 % and 8.56 to 21.57 % of soil carbonates in El-Arish and Ras Sudr soils respectively. Its presence in high content mostly characterizes the top layers of El-Arish (profiles 1 and 2) and most soil profiles of Ras Sudr. This is expected due to the effect of prevailing soil moisture especially in top layer, as well as irrigation and agricultural practices which enhance its formation particularly in the presence of calcite as a predominant mineral.

Gaspeite is detected in all soil profiles regardless of location or depth. Its content ranges from 0.34 to 7.17 and 0.35 to 8.79 % in El-Arish and Ras Sudr soil profiles respectively.

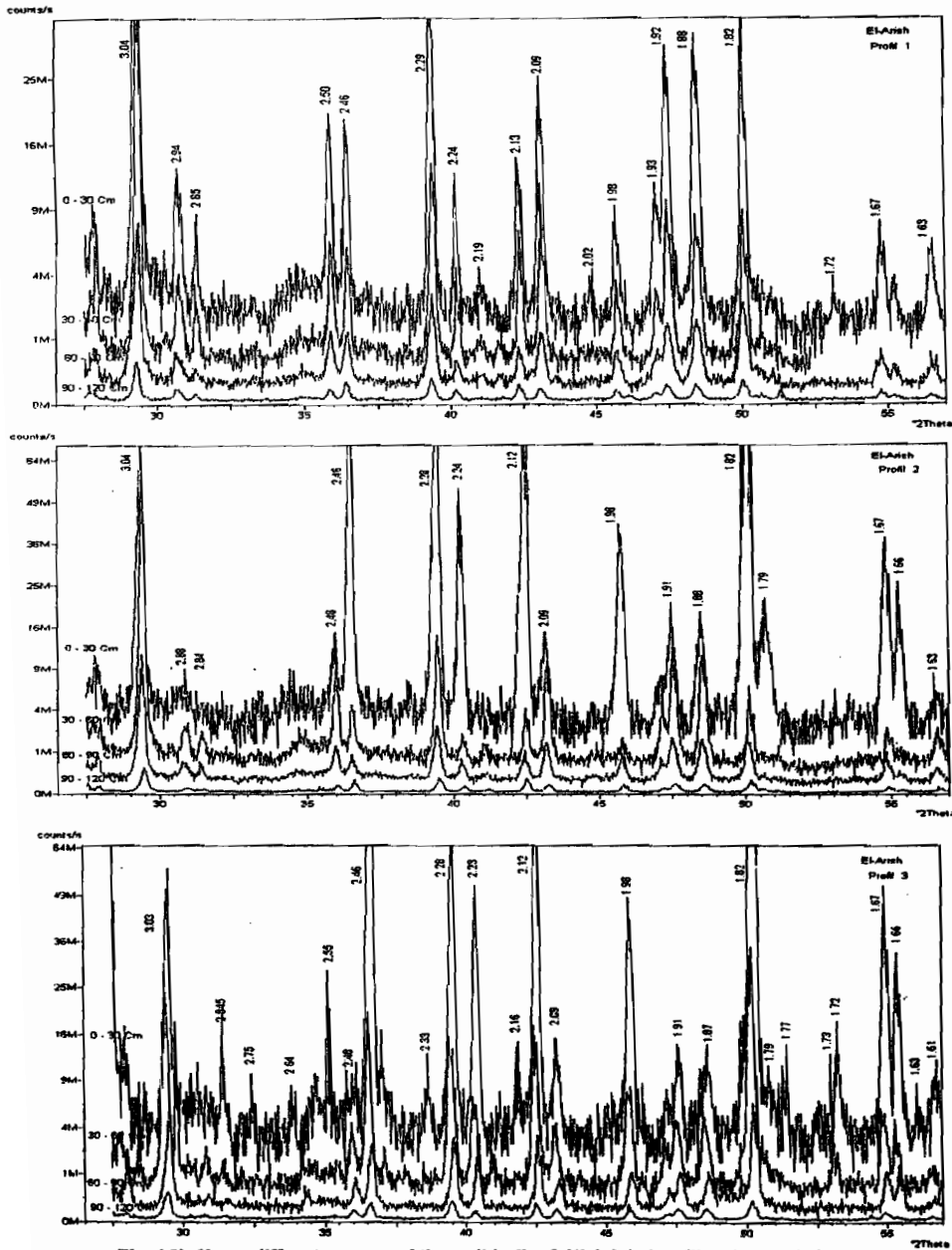


Fig. (2): X-ray diffractograms of the soil bulk of El-Arish (profiles 1, 2 and 3)

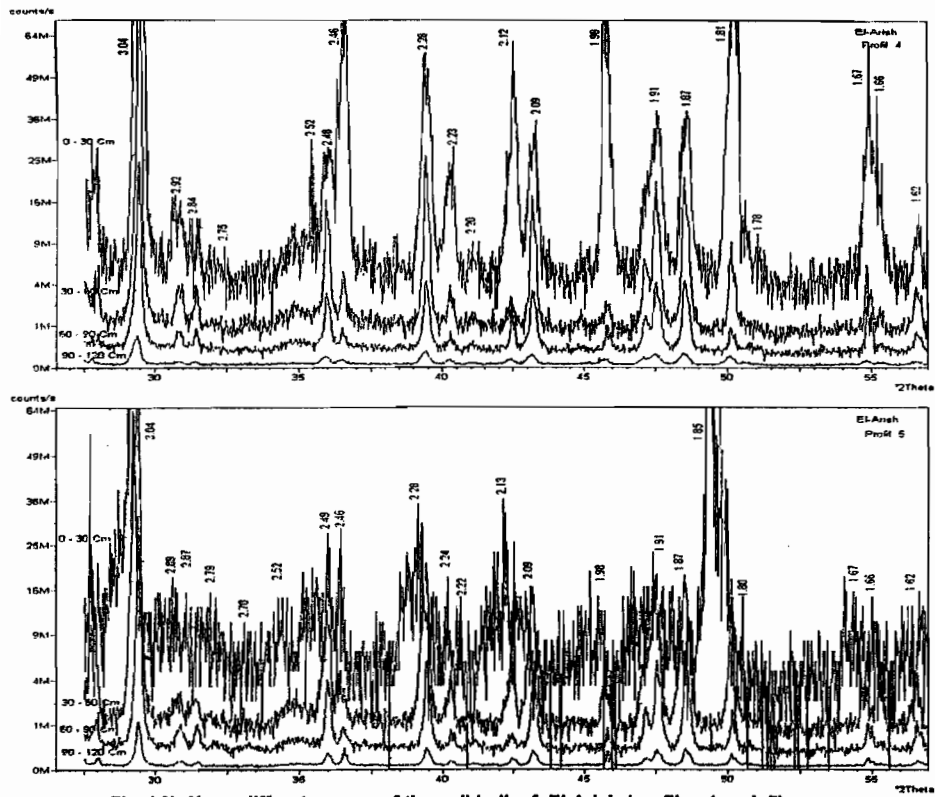


Fig. (3): X-ray diffractograms of the soil bulk of El-Arish (profiles 4 and 5).

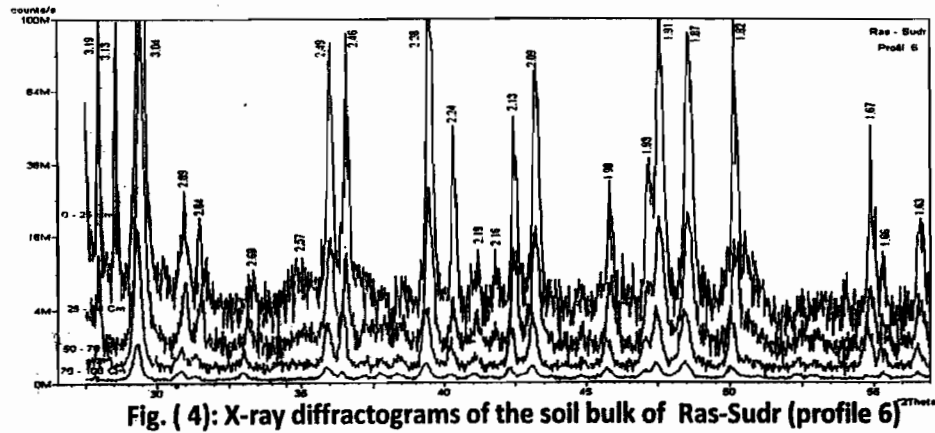


Fig. (4): X-ray diffractograms of the soil bulk of Ras-Sudr (profile 6)

Table: (3): Percentage distribution of carbonate minerals in the studied soil samples of El-Arish & Ras-Sudr profiles.

Location and profile No.	Depth, Cm.	Total CaCO ₃ %	Cal.	Ank.	Mon.	Gas.	Mag.	Arag.	Dolo.	Hunite	Min.	Azurite	Natron	Gla.	Northupite	Gaud.		
El-Arish	1	0-30	21.28	49.95	13.82	17.00	1.81	1.46	1.38	0.35	2.98	0.00	1.91	0.00	0.45	5.84	3.06	
		30-60	22.98	53.78	9.31	13.96	1.64	2.30	2.49	2.96	1.60	0.00	3.16	0.00	0.08	4.80	3.93	
		60-90	19.99	47.39	18.71	12.19	3.05	0.79	2.35	0.66	0.00	0.13	1.37	0.00	0.32	4.46	8.60	
		90-120	23.4	37.56	13.52	14.34	3.61	8.47	0.26	1.84	5.14	1.80	2.50	0.33	3.61	0.42	6.61	
	2	0-30	2.98	22.94	18.83	12.83	6.01	0.38	4.35	8.00	0.44	0.08	9.18	0.38	0.00	1.41	15.18	
		30-60	15.74	58.36	0.00	8.57	2.16	1.59	3.49	2.55	2.55	8.32	2.89	0.00	2.80	6.73	0.00	
		60-90	22.98	53.15	0.91	8.89	3.13	0.31	1.29	10.06	7.53	6.00	2.22	0.00	0.00	4.63	1.87	
		90-120	14.47	43.00	4.60	5.67	2.82	3.81	2.94	10.00	2.94	4.61	2.53	2.47	2.74	3.22	8.65	
	3	0-30	2.98	11.29	12.70	3.98	4.98	2.67	1.28	0.43	2.90	30.72	5.60	1.69	1.75	0.43	19.59	
		30-60	8.34	27.10	14.50	3.35	3.68	7.58	0.37	1.90	4.71	15.59	2.38	8.25	0.37	1.54	8.70	
		60-90	14.72	28.90	0.61	22.89	7.14	6.66	4.92	1.17	0.43	0.91	8.00	3.07	2.70	3.07	9.72	
		90-120	16.17	35.17	16.46	10.13	3.52	8.69	10.53	0.67	0.57	1.33	2.68	0.00	0.00	3.18	7.06	
	4	0-30	4.08	17.38	16.25	5.74	5.36	5.53	7.56	5.83	6.44	6.44	1.70	11.93	1.14	1.84	6.89	
		30-60	19.49	62.00	5.02	9.92	4.33	3.89	2.64	1.29	1.20	2.42	1.08	3.69	0.47	0.47	1.58	
		60-90	28.76	55.60	1.71	17.98	7.17	2.39	1.55	1.29	0.98	1.29	0.84	2.64	0.52	5.06	0.98	
		90-120	28.51	38.74	3.75	15.29	1.58	2.58	4.24	1.15	0.86	0.00	1.36	25.36	0.00	3.45	1.65	
	5	0-30	12.68	3.89	54.95	0.66	0.34	1.22	0.39	34.18	0.61	0.00	0.00	0.00	1.01	1.43	1.32	
		30-60	48.51	52.93	10.42	15.97	5.88	0.00	1.66	1.48	0.62	1.19	1.81	1.52	0.48	5.06	1.08	
		60-90	50.21	57.63	2.38	25.74	2.22	0.48	0.79	1.44	1.04	0.31	0.87	0.00	0.57	5.49	1.04	
		90-120	35.74	47.81	5.56	16.27	1.96	0.00	9.01	1.16	0.83	0.68	0.98	1.03	0.29	4.33	10.09	
	Ras-Sudr	6	0-25	38.81	53.46	6.44	15.06	3.03	0.67	1.46	1.66	0.90	1.12	2.58	1.34	0.30	4.48	7.51
			25-50	42.55	52.90	5.37	16.48	1.90	0.66	2.01	3.87	1.81	0.93	1.78	1.46	0.38	5.72	4.72
			50-70	46.63	42.33	6.48	14.22	8.79	3.50	2.27	2.15	1.87	1.93	2.41	1.69	8.34	4.02	0.00
			70-100	52.59	50.06	2.68	17.32	1.64	6.68	3.61	1.99	1.48	7.45	1.07	0.51	2.92	0.00	2.59
7		0-30	48.51	56.08	3.92	21.22	1.31	1.75	2.61	2.11	2.21	0.00	1.31	0.00	0.00	4.39	3.11	
		30-70	32.49	52.14	10.01	11.78	3.09	5.48	2.95	1.53	0.56	0.00	2.53	0.00	3.09	3.15	3.69	
		70-90	53.87	49.44	13.27	13.62	2.84	2.60	3.87	2.36	0.80	0.00	2.32	0.00	0.44	3.57	4.87	
		90-110	38.48	50.70	11.63	8.91	1.30	4.67	2.63	9.35	1.08	0.27	0.54	2.17	0.32	3.37	3.06	
8		0-40	53.01	48.68	7.53	21.57	1.62	3.59	2.83	1.50	2.67	0.00	1.39	0.00	0.36	5.56	2.70	
		40-70	48.74	42.05	4.46	17.92	0.81	7.27	1.13	0.00	1.08	9.72	1.08	1.62	0.00	3.19	9.67	
		70-80	53.01	56.04	7.40	15.12	1.60	2.06	0.67	4.39	1.39	0.37	1.22	0.00	0.30	7.27	2.15	
		80-100	52.16	66.42	1.73	17.03	0.35	1.12	0.75	0.25	1.25	0.10	0.00	1.25	1.21	6.40	2.14	
9		100-128	48.74	57.36	3.40	13.14	0.84	7.90	0.67	1.95	1.85	0.40	1.76	0.57	0.92	7.18	2.05	
		125-140	37.62	39.49	5.86	9.94	1.31	1.26	1.64	1.88	1.77	1.36	4.19	9.31	3.47	16.22	2.30	
		0-20	47.03	54.82	4.52	19.17	6.97	0.34	2.10	0.48	0.99	1.09	1.44	0.12	0.63	5.34	1.98	
		20-40	49.59	48.64	12.31	13.59	2.06	0.22	1.30	1.81	0.96	0.17	1.12	0.00	0.41	4.38	13.02	
		40-60	51.3	42.19	3.21	8.56	5.51	0.47	1.52	0.21	0.54	0.31	0.19	31.13	0.33	3.44	2.40	
		60-100	59.85	50.38	3.07	18.18	7.56	0.34	0.22	2.09	7.45	1.01	1.42	0.00	0.00	5.59	2.69	

Cal: Calcite, Gas.: Gaspeite, Mag. Magnesite, Arag. Aragonite, Ank.: Ankerite, Dolo: Dolomite, Min.: Minrecordite, Mon.: Monohydrocalcite, Gla.: Glaukosphaerite and Gaud.: Gaudfroyite

Likewise, **magnesite** is found in all profiles layers except the subsurface and deepest layers of profile 5 (El -Arish). Its content ranges from 0.0 to 8.69 % and 0.22 to 7.90 % of total carbonates. Also, **aragonite** is detected in all profiles layers of both locations, in percentages not exceeding 5 % of soil carbonates, except in the deepest layer of profile 3 and the uppermost surface of profile 4 where its percent rises up to 10.53 and 7.56 %, respectively. **Dolomite** constitutes traceable amount not exceeding 5.83 and 4.39 % of soil carbonate minerals in most profile layers except for some layers such as the top and deepest layers of profile 2 (El-Arish) and the uppermost surface of profile 5 (El-Arish) where its content reaches about 8.0 – 10.0 and about 34.0 % respectively also, in the deepest layer of profile 7 (Ras Sudr) where its percent rises up to about 9.0 % of soil carbonates in contrast to its entire absence in the 40-70 Cm. layer of profile 8 (Ras Sudr).

Huntite is identified in traceable amounts , not exceeding 3 % of total carbonate except in the deepest layers or closer in profiles 1 and 2 (El-Arish) and profile 9 (Ras Sudr) as well as the top surface of profile 4 (El-Arish). **Minrecordite** is also present in traceable amounts below 2 % or even absent in many layers of the studied soil profiles in both areas but its content is considerably high in the top surface layer of profile 3 and the surface or subsurface layers of profiles 2 and 4 (El-Arish) and profile 8 (Ras Sudr). **Azurite** constitutes traceable amounts of soil carbonate minerals where its percent is normally below 3 % and entirely absent in the top surface of profile 5 (El-Arish) and in the 100-125 Cm. layer of profile 8 (Ras Sudr). However, its percent is relatively higher in some profile layers such as the top surface of profile 2 , the top and deeper layers of profile 3 (El-Arish) and also in the deepest layer of profile 8 (Ras Sudr) where its percent reaches 4.19-9.18 % of soil carbonates.

Natron is identified in low percent in most profiles layers and even absent in some layers, however its content is exceptionally high in the deepest layer of profile 4, in the surface or subsurface layers of profiles 3 and 4 (El-Arish) as well as the deeper layer of profile 9 (Ras Sudr).

Glaukosphaerite is also detected in very low amount, not exceeding 3.6 % of soil carbonate in both studied localities and normally lower than 1 % or even absent, however its content in the 50-70 Cm. layer of profile 8 (Ras Sudr) is exceptional as it reaches 8.34 % of soil carbonates.

Northupite is identified in all layers of the studied profiles in both localities except the deepest layer of profile 6 (Ras Sudr). Its content varies within the ranges of 0.42 to 6.73 % and 0.0 to 7.18 % of soil carbonates in both El-Arish and Ras Sudr profiles, respectively. An exceptional case is found in the deepest layer of profile 8 (Ras Sudr) where northupite content rises up to 16.22 % of soil carbonate.

Gaudefroyite content varies considerably within and between soil profiles of both El-Arish and Ras Sudr soils. Its content ranges from 0.0 to 19.59 % and 0.0 -13.02 % in profiles representing those soils, respectively with slightly higher values in El-Arish soil carbonates.

In a trial to correlate crystalline carbonate minerals with soil variables, statistical analysis is performed and the obtained significant correlations are summed up as follows:

- i) Calcite and monohydrocalcite are positively corrected with silt, ($r = 0.600^{**}$ and 0.494^*) and total soil carbonates, $r = 0.693^{**}$ and 0.679^{**}) while being negatively correlated with coarse sand $r = -0.733^{**}$ and -0.513^{**}).
- ii) Ankerite and azurite are positively correlated with coarse sand ($r = 0.445^*$ and 0.421^*) while being negatively correlated with total soil carbonate by Holzer and Stumpf (1980). ($r = -0.404^*$ and -0.513^*).
- iii) Azurite and gaufroyite are negatively correlated with silt ($r = -0.462^*$ and -0.446^*).
- iv) Northupite and gaufroyite are positively correlated with clay, by Pabst, *et al.* (1963) ($r = 0.483^*$ and 0.504^*).
- v) All the dominant crystalline carbonate minerals in both soils are positively correlated with soluble Ca^{++} , Mg^{++} and HCO_3^- ions.

For further investigation of the data of X-ray diffraction which were used to detect carbonate crystalline minerals in all the studied soil samples, one should first mention that the contents of carbonate varies considerably within and between profiles representing both soils under study. Computation of the weighted mean of soil carbonates in each profile (table 4) reveals that the mean total carbonate ranges from 10.55 to 36.79 and from 41.84 to 56.09 % in the soils of El-Arish and Ras Sudr, respectively with a total average of 20.70 % and 49.49 % of all profiles in those locations. In other words, the whole average of carbonates in Ras Sudr soils is 2.5 times that in El-Arish soils.

Table (4): Weighted mean of total carbonate and crystalline carbonate minerals as percent of total carbonate in the studied soils.

Location	Profile No.	Total CaCO ₃ %	Calcite	Ankerite.	Mon.	Gaspeite	Mag.	Arag.	Dolo.	Huntite	Minre.	Azurite	Natron	Glauk.	Northupite	Gaud.
El-Arish	1	21.91	47.17	13.84	14.37	2.53	3.25	1.62	1.45	2.43	0.48	2.23	0.08	1.11	3.88	5.55
	2	14.04	44.36	6.08	8.99	3.53	1.52	3.02	7.65	3.36	4.75	4.20	0.71	1.39	4.00	6.42
	3	10.55	25.61	11.07	10.04	4.83	6.40	4.27	1.04	2.15	12.14	4.66	3.25	1.21	2.06	11.27
	4	20.21	43.42	6.68	12.23	4.61	3.60	4.00	2.39	2.37	2.54	1.25	10.90	0.53	2.71	2.78
	5	36.79	40.57	18.33	14.66	2.60	0.42	2.94	9.56	0.77	0.55	0.92	0.64	0.59	4.08	3.38
Whole mean		20.70	40.23	11.20	12.06	3.62	3.04	3.17	4.42	2.22	4.09	2.65	3.12	0.97	3.34	5.88
Ras-Sudr	6	45.44	50.07	5.06	15.93	3.48	3.04	2.40	2.41	1.50	3.13	1.89	1.19	2.71	3.35	3.83
	7	41.84	52.46	9.24	14.17	2.23	3.79	2.97	3.26	1.15	0.05	1.80	0.40	1.26	3.61	3.63
	8	54.60	56.76	5.60	18.98	1.84	4.47	1.73	1.38	1.90	2.46	1.63	1.64	0.90	7.30	4.13
	9	56.09	48.59	5.87	11.77	4.58	0.33	1.28	2.76	3.48	0.79	4.54	6.23	0.15	4.94	4.71
Whole mean		49.49	51.97	6.44	15.21	3.03	2.91	2.09	2.45	2.01	1.61	2.46	2.36	1.26	4.80	4.08

Mon.: Monohydrocalcite, Mag. Magnesite, Arag. Aragonite, Dolo: Dolomite, Minre. : Minrecordite, Glauk. : Glaukosphaerite and Gaud. : Gaudefroyite

Weighted means of X-ray results indicate that the crystalline calcite is present in high content and ranged from 25.61 to 47.17 % and 48.59 to 56.76 % with the whole means of 40.23 and 51.97 % from the total carbonate minerals content of El-Arish and Ras Sudr soils, respectively .

The crystalline monohydrocalcite is the second predominant soil carbonate mineral where its weight mean varies from 8.99 to 14.66 and 11.97 to 18.98 % of total carbonate minerals of El-Arish and Ras Sudr soils, respectively with the whole means of 12.06 and 15.21 % in those soils.

Ankerite is the third predominant crystalline carbonate mineral where its weighted mean ranges from 6.08 to 18.33 % and 5.06 to 9.24 % of the total carbonate minerals of El-Arish and Ras Sudr soils, respectively with a whole mean of 11.20 and 6.44 % in those soils.

The crystalline Gaufroyite, dolomite and minrecordite are also detected in few amounts, not exceeding a weighted mean of 6 % from the total soil carbonate minerals content in El-Arish while northupite and gaufroyite constitute less than 5 % of soil carbonate minerals in Ras Sudr soils. In addition, the studied soil samples also contained other carbonate minerals in various traceable amounts integrated in weighted means of 0.97-3.62 % and 1.26-3.03 % from the total soil carbonate minerals of those localities, respectively.

These weighted means dictate that calcite formation in geochemical environment is more rapid than other associated crystalline carbonate minerals that are detected at lower levels and sometimes absent in profiles layers. These data are fairly demonstrated in Figs. (6 -14) which show the distribution of dominant carbonate minerals in the subsequent layers and the depthwise distribution of such minerals (Figs. 15 &16) in each representative profile.

Commenting on the obtained results, it is well known that the studied soils of El-Arish and Ras Sudr are formed from the limestone- enriched rocks of El-Tih and Egma plateau, respectively and transported during late Pleistocene as limestone alluvium parent material that deposited along the low-lying plains to form the calcareous sediments in both regions. Therefore, the soils develop in calcareous parent material under the prevailing aridity. Since these soils are recent from the pedological view point, and displayed less development, most of their carbonates are mechanically inherited from the parent materials that have been termed primary, geogenic or lithogenic (Drees and Wilding 1987) and Doner and Lynn 1989). However, some carbonates are expected to form in soil profiles due to weathering and soil formation processes, these are termed; secondary, authigenic or pedogenic, (Gile *et al.*, 1965) and Pal *et al.*, 2000).The latter carbonates are distinguished from field evidence of carbonate morphology such as concretions, nodules, sand grain

coatings, diffused carbonate such as concretions, nodules, sand grain coatings, diffused carbonate, laminar caps and irregular distribution patterns with depth Fig.(6-14). In this connection chemical evaluation of solutions extracted from the studied soils reveals that Na^+ , Ca^{++} and probably Mg^{++} , K^+ , Cl^- , SO_4^- and, to a less extent HCO_3^- are major ionic components.

Many possible minerals could be formed from soil solutions containing these ions upon evaporation, of which carbonate minerals are of major concern.

In this regard, concretions and /or nodules typify some profiles layers in depth, in terms of soil texture. CaCO_3 contents of weighted means 20.70 to 49.49 % irregularly distributed over the whole profiles depth with considerable increase in deeper or deepest layers give rise to soft concretions often with a central core and isolated or composite nodules. However, calcite horizon is not distinguishable and the soil texture differs from sandy loam to sandy clay with an obvious stratification of grain size distribution (lithogenic) at depth and the carbonate content is variable across the soil profile or shows relative increase or decrease in some layers. The relative increase of soil carbonate and its forms in both soils under study are closely connected to their formation and the forms depends as much on carbonate content together with soil texture as well as specific soil characteristics.

According to Monger and Gallegos (2000) and Monger (2002), links between biotic and abiotic CaCO_3 involve concurrent interaction of biological, chemical and physical processes in the soil profile. Biotic processes include CO_2 input into soil via respiration, Ca^{++} extraction by roots and direct precipitation by organisms. These depend on and contribute to abiotic processes which include chemical weathering, dissolution of pre-existing CaCO_3 and precipitation of carbonate resulting from temperature and moisture changes in soil. These interactions through time make pedogenic CaCO_3 a good example of a biogeochemical mineral. In other words, pedogenic carbonate is the result of the C-evolution of biotic and abiotic processes of the ecosystem.

The previously described interaction take place in the studied soils, but in relatively slow and weak processes due to the prevailing aridity which minimizes weathering rates and soil formation processes. This is clearly manifested in the hardly distinguished calcic horizon that is almost unformed and the less appearance of secondary, authigenic or pedogenic carbonates as clarified from field evidence. It is also expected that carbonate forms identified are most probably geogenic rather than pedogenic. In this respect, limestone of the main parent rock of the studied soils forms mainly of CaCO_3 , despite the chemical simplicity of limestone, its rocks commonly undergone complex chemical transformation during diagenesis. The sediment –rock transition and /or modification of existing lithified rock is controlled largely by wet climatic conditions prevailed during late Pleistocene where wet climate generates certain terrains with dissolution, and precipitation being common. Limestone is prone to diagenesis, e.g., alteration which is especially given the susceptibility of calcite and aragonite to chemical alteration. This diagenesis is typically triggered by temporal changes in the environmental setting of limestone involves dissolution, recrystallization (changes in rock texture but no change in mineralogy), replacement (change of mineralogy) and cementation (precipitation of mineral). These processes are ultimately controlled by micro environmental condition in the rock.

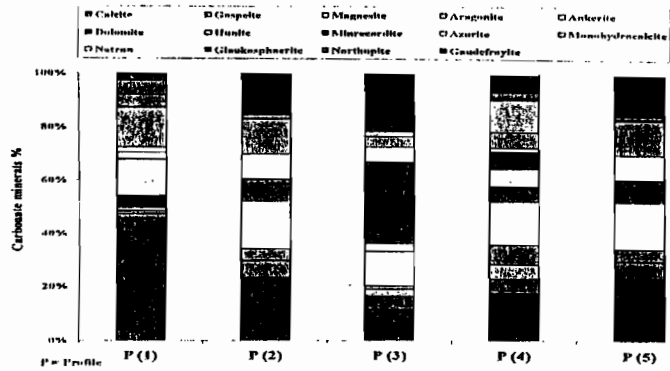


Fig.(6) : Carbonate minerals distribution in the surface layer of El - Arish profiles.

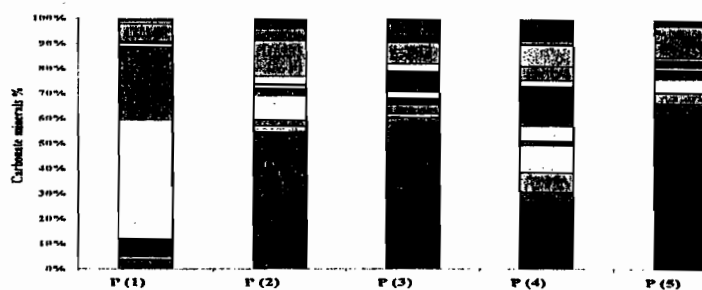


Fig.(7) : Carbonate minerals distribution in the subsurface layer of El - Arish profiles .

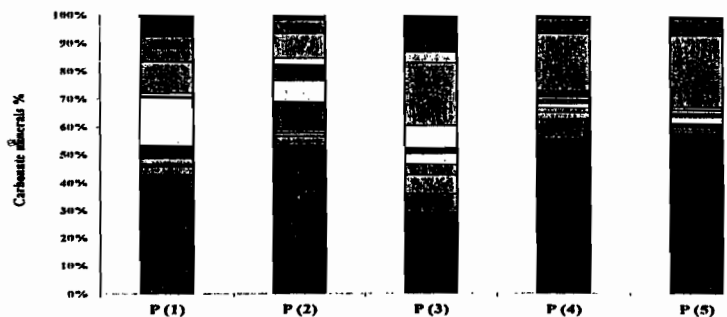


Fig.(8) : Carbonate minerals distribution in the middle layer of El - Arish profiles.

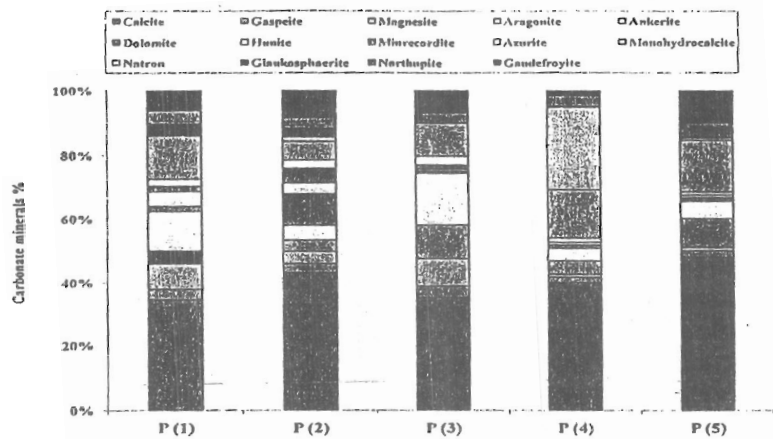


Fig.(9) Carbonate minerals distribution in the deepest layer of El- Arish profiles.

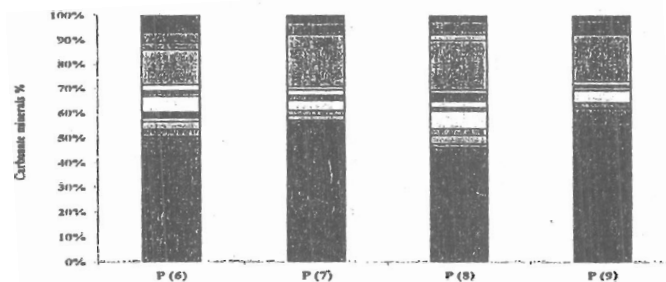


Fig.(10) : Carbonate minerals distribution in the surface layer of Ras Sudr profile.

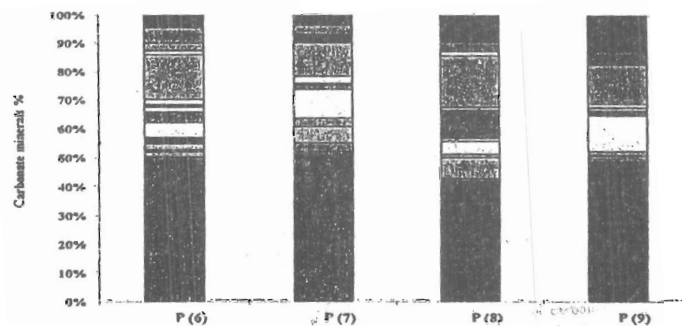


Fig.(11) Carbonate minerals distribution of sub surface layer of Ras Sudr profiles.

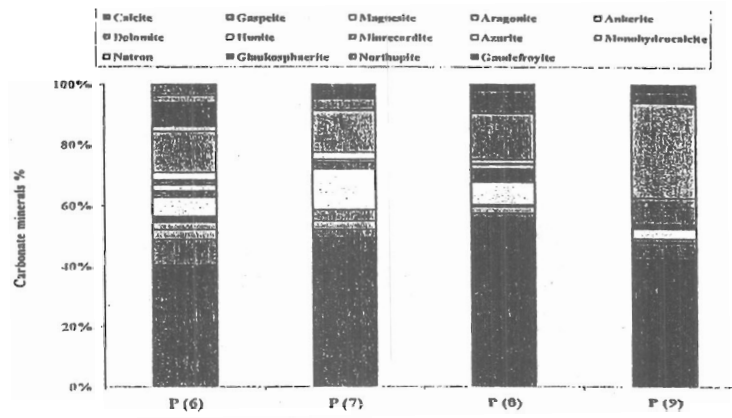


Fig.(12) : Carbonate minerals distribution in the middle layer of Ras Sudr profiles.

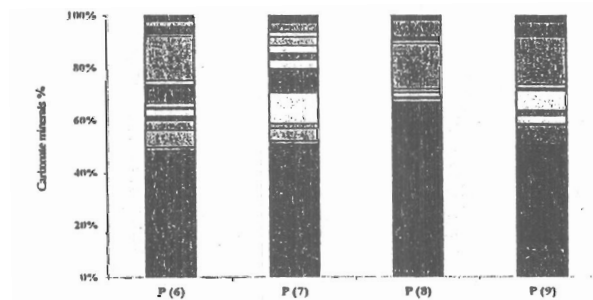


Fig.(13) : Carbonate minerals distribution in the deeper layer of Ras Sudr profiles.

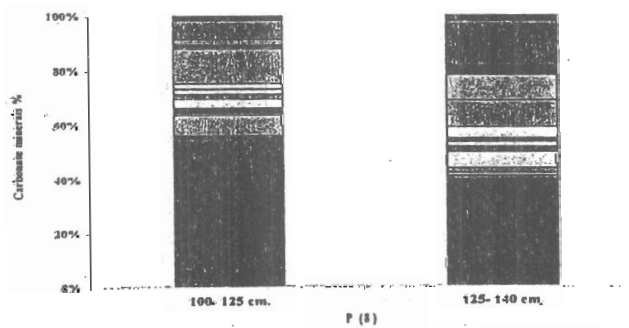


Fig.(14) : Carbonate minerals distribution in the deepest layer of Ras Sudr profile.

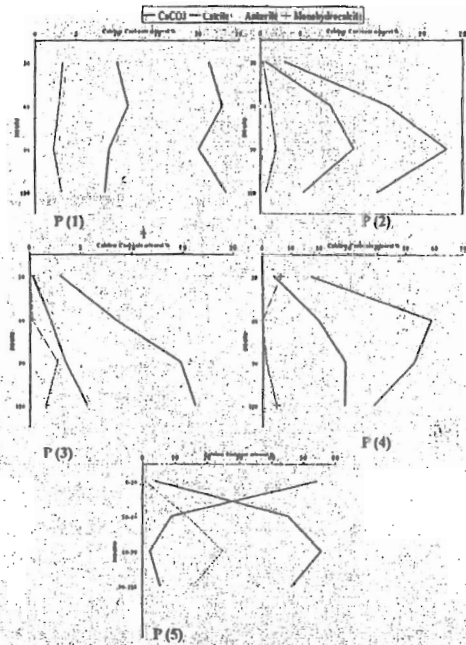


Fig. (15) Depthwise distribution of carbonate minerals and total calcium carbonate in Esh-Arish soils profiles .

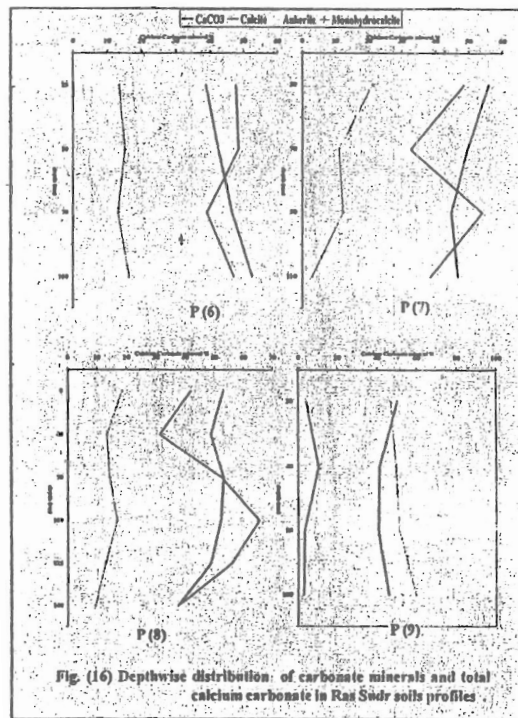


Fig. (16) Depthwise distribution of carbonate minerals and total calcium carbonate in Ras Sidr soils profiles .

In brief, the obtained mineralogy of soil carbonates agrees to a great extent, with Lippmann (1973), who reported that calcite is the most abundant in sedimentary rocks followed by siderite and ankerite (iron-bearing dolomite). The occurrence of Fe-bearing dolomite appears to be related to dolomite source and is detrital whereas calcite may be primarily reprecipitated (secondary), although most calcite may be of detrital nature, e.g. calcite limestone drift. Align with this, Doner and Lynn (1989) showed that calcite, Mg-calcite and dolomite constitute most of carbonate minerals in alkaline soils. Magnesite is also found in sedimentary deposits and has a tendency to form hydrous minerals in contrast to CaCO_3 minerals, (Lippmann 1973).

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دراسة صور الكربونات في بعض الأراضي الجيرية شمال وجنوب سيناء مصر.

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قسم كيمياء وطبيعة الأراضي - مركز بحوث الصحراء - المطرية - القاهرة

تم جمع ثمانية عشر عينة من الطبقات المتعاقبة لتسع قطاعات أرضية تمثل الأراضي الجيرية بالعريش ورأس سدر. وقد أظهرت البيانات الحقلية للصور المختلفة لكربونات التربة وهي: القشرة الأرضية (Crust) والتجمعات (Concretions) والندب (Nodules) والصور الناعمة (Soft) المنتشرة. وقد أجرى تحليل العينات لتقدير صفاتها الطبيعية والكيميائية ثم تم تحليلها بالأشعة السينية لتقدير معادن الكربونات المتبلورة.

وقد أظهرت النتائج أن محتوى الكربونات الكلي بالتربة يختلف بدرجة كبيرة من ٢.٩٨ إلى ٥٠.٢١ و من ٣٢.٤٩ إلى ٥٩.٨٥ % في منطقتي العريش ورأس سدر على التوالي. وأظهر التوزيع الرأسي للكربونات صورتين يميزا باتجاه الزيادة وتوزيع غير متجانس بعمق قطاعات التربة مع عدم وجود أفق تراكم الكالسيوم بيولوجيا.

وأوضح التركيب المنرالوجي للكربونات سيادة معادن الكالسيت والأنكرايت والكالسيت أحادي التأدرت في كلا النوعين من الأراضي مع وجود أقل لإحدى عشر معدن متبلور من معادن الكربونات منها (Gaudefroyite) الذي تم التعرف عليه في كلا الأرضين بنسبة حوالي ٤ - ٦ % من معادن الكربونات كما تم التعرف على معادن Dolomite و Minrecordite و Northupite في كميات بسيطة تتراوح من ٤.٠٩ إلى ٨.٨ % من كربونات التربة بينما شكلت المعادن الأخرى متوسط وزني لا يزيد عن ٤ % من الكربونات لكل معدن.

وقد نوقشت النتائج المتحصل عليها من التحليل المعدني للكربونات في ضوء أصل ومنشأ وتكوين الأراضي التي أظهرت أن معظم معادن الكربونات مشتقة من مادة الأصل (Geogenic) أو (Litheogenic) أو من الصخور الغنية بالحجر الجيري في هضبتي التربة (El-Tih) والعجمة (Egma) لكن هذا لا ينفي الأصل البيولوجي لبعض الكربونات نتيجة التجوية والترسيب الكيميائي الذي يساعده زيادة تركيز أيونات الكالسيوم والماغنسيوم والبيكربونات بالإضافة إلى ثاني أكسيد الكربون ذو الأصل البيولوجي والرابطة بين العوامل الحيوية (Biotic) وغير الحيوية (Abiotic) في تكوين الكربونات والذي نوقش تداخلها في البحث وبالرغم من ذلك فإن التداخلات البيوكيميائية يبدو أنها بطيئة وضعيفة وتحتاج إلى فترة زمنية أطول لتكوين أفق تراكم الكربونات (Calcic horizon) تحت الظروف البيئية السائدة.

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