

SEPIOLITE DEPOSITS OF THE EL-BUR, GALGUDUND AREA, CENTRAL SOMALIA

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RIASSUNTO. — Cinque sepioliti somale sono state studiate con diversi metodi analitici: analisi chimica, raggi X a diverse temperature, analisi termica, spettroscopia infrarossa, microscopia elettronica. La distribuzione areale di ogni elemento è stata messa in evidenza anche mediante microsonda EDS/EDAX.

Questi minerali sono caratterizzati da un alto contenuto in Mg e i parametri della cella elementare sono lievemente diversi da campione a campione. Le mappe ai Raggi X individuano una distribuzione uniforme degli elementi per la maggior parte delle zone esaminate. In tutti i campioni, oltre agli elementi caratteristici contenuti nelle sepioliti, sono presenti Cl e S.

In base a dati micropaleontologici, queste sepioliti possono essere messe in relazione, dal punto di vista genetico, ad un ambiente lagunare di età wealdiana (Cretaceo inferiore).

ABSTRACT. — Five somalian sepiolites were studied using a variety of analytical techniques: chemical, X-ray diffraction (at different temperatures) and thermal analysis as well as IR spectroscopy and electron microscopy. Distribution maps for each element also were made.

The minerals were characterized as high Mg-sepiolites; the cell parameters showed slight differences from sample to sample. The X-ray maps and microprobe analyses indicated a generally uniform distribution of the elements. The presence of Cl and S was observed in all samples.

On the basis of micropaleontological data, the genesis of these minerals can be linked to an alkaline lagoonal environment of Wealdian age (lower Cretaceous).

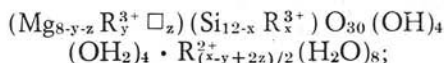
Introduction

The El-Bur locality lies in a region called Galgudund at about 385 km northeast of Mogadishu, in Central Somalia. In this mainly flat, plateau area sepiolite occurs in beds under the limestone. Two levels were

distinguished: the upper one is made up of sepiolite associated with carbonates and the lower one of sepiolite alone. These levels, whose thicknesses vary between 0.30-0.50 m, are very well marked because the sedimentation occurred in a « calm » environment.

The micropaleontological fauna of the upper level consists of *Delerocypris* (GREKOFF, 1957) and *Cypridea diminuta* (VANDERPOOL, 1928, in GREKOFF, 1957). These species were found by GREKOFF (1957) in the Wealdian (Lower Cretaceous) in a test core drilled in Samba (Congo). This fauna is of typical lacustrine or lagoonal origin. It is possible to deduce from these observations that the age of the sepiolite is Wealdian, Lower Cretaceous (RUSSO, private communication).

Sepiolite is designated as a 2:1 Mg-phyllosilicate, with only a minor Al component (BAILEY et al., 1971). This mineral has a structure intermediate between dioctahedral and trioctahedral (MARTIN-VIVALDI and CANO-RUIZ, 1956), which may be the reason for its fibrous morphology (MILLOT, 1970). The ideal structural formula for sepiolite is:



the space group: *Pncn*; the cell parameters: $a \cong 5.28 \text{ \AA}$, $b \cong 26.95 \text{ \AA}$, $c \cong 13.37 \text{ \AA}$, $\beta = 90^\circ$ (BRAUNER and PREISINGER, 1956; PREISINGER, 1959; RAUTUREAU and TCHOUBAR, 1976; RAUTUREAU, 1974).

The aim of the work reported in this paper was to study the mineralogical and

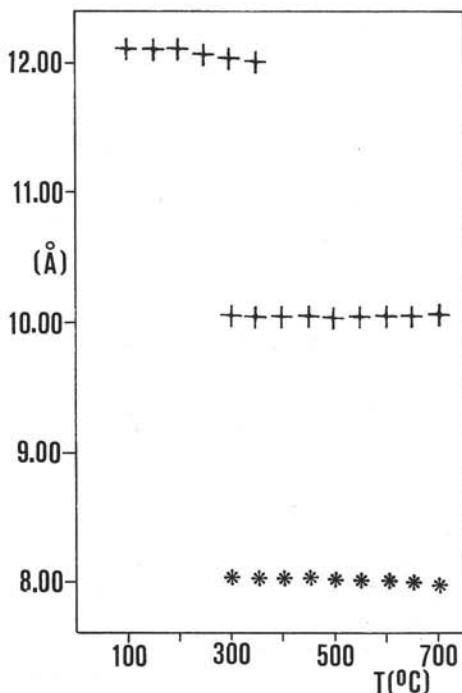


Fig. 1. — Values of d_{110} (+) and d_{120} (*) for sepiolite D as a function of temperature.

chemical features of these somalian sepiolite deposits.

Experimental

Materials

Sepiolite samples were selected on the basis of their purity from five different sites of El-Bur sepiolite deposits.

Methods

X-ray diffraction, thermal and chemical studies were carried out on the 2-0.1 μm fraction obtained by normal sedimentation methods from samples ultrasonically-dispersed in double distilled water.

Using natural aggregates of sepiolite fibres, scanning electron micrographs were made using a Philips SEM 500. The samples were prepared using standard procedures. Mineral sections were prepared from opportunely cemented samples and polished with diamond paste. These sections were studied with an electron microprobe technique based on energy-dispersive electron induced XRF

(EDS/EDAX 9100) which was used to prepare distribution maps of each element. The EDAX equipment was fitted with a minicomputer which allows the semi-quantitative evaluation of detectable elements ($Z = 9$) with a sensitivity of 0.1%. The EDAX analyzer allows the determination of the elemental distribution maps for a chosen element in the sample. The maps are the pictures of a selected area of the sample recorded on a SEM image where the point density, in each position, is proportional to the concentration of the selected element.

X-ray diffraction analyses were carried out on oriented films and loosely packed powder samples using a Philips diffractometer (Ni filtered CuK_α radiation) with a humidity- and a heating-stage attachment. The temperature increments were of about 50° C in the range 20-700° C. SiO_2 and $\text{C}_{14}\text{H}_{29}\text{OH}$ (BRINDLEY, 1981) were used as standards.

The unit cell parameters were obtained by method of least squares on the basis of the structural data proposed by BRAUNER and PREISINGER (1956), PREISINGER (1959), RAUTUREAU and TCHOUBAR (1976).

Thermal studies were made using Du Pont 990 equipment with controlled gas flow and a 20° C/min. heating rate.

Chemical analyses were made using the XRF technique (Philips 1400); oxide percentages were calculated using the method proposed by FRANZINI et al. (1971); LEONI et al. (in press). Na and Mg were determined also by atomic absorption spectrophotometry (Perkin Elmer 603). The weight loss was determined by thermogravimetry. Atomic absorption spectrophotometry was used for quantitative determinations of the exchangeable cations extracted by 1N ammonium acetate solutions.

The structural formulae were calculated according to the structural model proposed by PREISINGER (1959).

The infrared spectra were made with a Perkin Elmer model 180 spectrophotometer; the KBr disc technique was used in the range 4000-300 cm^{-1} .

Results and discussion

X-ray powder diffraction analysis

X-ray diffraction data and the unit cell

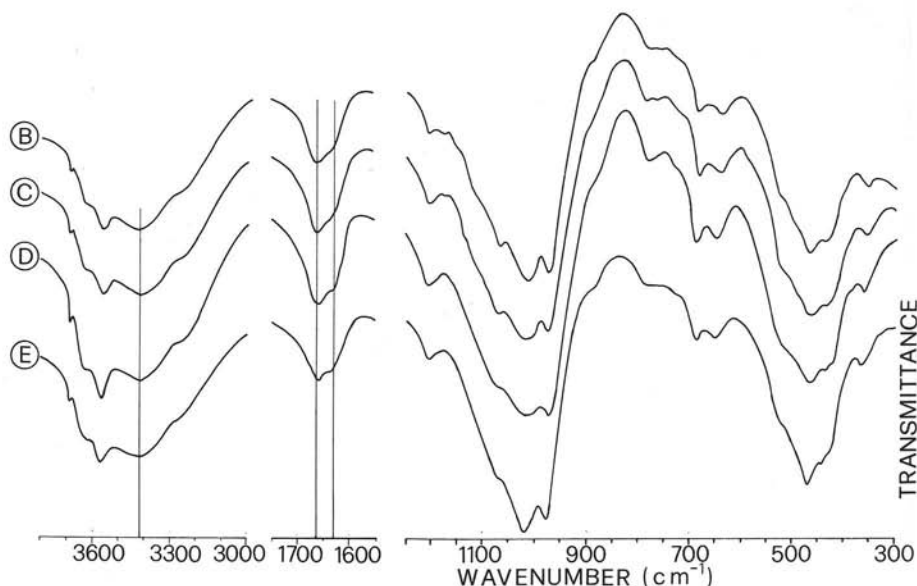


Fig. 2. — Infrared spectra of sepiolites studied.

parameters of the samples studied are given in Table 1. Samples B, C, D, and E appear to be pure, while sample A is a mixture of carbonates and sepiolite; thus, for this sample, only the morphological study is reported. The cell parameters show slight variations from sample to sample, the greatest differences being in the *a* and *b* parameters. The X-ray diffraction data for the heated samples (Fig. 1) is very close to that described by NAGATA et al. (1974).

IR analysis

The IR spectra (Fig. 2) are comparable to those described by AHLRICHS et al. (1975), FARMER (1974), FARMER and RUSSELL (1964), NAGATA et al. (1974), PROST (1973). Only the stretching vibration (at 3420 cm^{-1}) and the bending vibration (at 1670 cm^{-1}) of the water molecules bonded with hydrogen bonds show small differences from the data reported in the previously mentioned literature.

Thermal analysis

The thermal behaviour of the samples studied (Fig. 3) is very close to that of Ampandrandava sepiolite (RAUTUREAU and MIFSUD, 1977). In the TG and DTG curves (Fig. 4), two different effects can be seen in the first step of water loss. The first one

disappears when the material is kept at a relative pressure near zero (at room temperature) in argon gas flow or in vacuum. The second one is related to temperature increase and is found at 120°C . The effects at about 325°C , 540°C and 865°C are very similar to those reported in the literature (RAUTUREAU and MIFSUD, 1977). The last effect is broad only in sepiolite E and occurs at lower temperatures than those reported in the literature.

Electron microscopy

The fibrous nature of sepiolite is apparent in the microphotographs (Fig. 5).

Chemical analysis

The chemical analyses and the structural formulae are reported in Tables 2 and 3.

All the minerals are Mg-rich; Al and Fe (always less than 1%) are in tetrahedral sites and Na, K, and Ca are present as exchangeable cations. The chemical features of the sepiolites studied are very close to those reported in the literature (WEAVER and POLLARD, 1973), but in this case, the presence of Cl and S is reported for the first time. It should be emphasized that these two elements cannot be removed either by ionic exchange or repeated washing in distilled water.

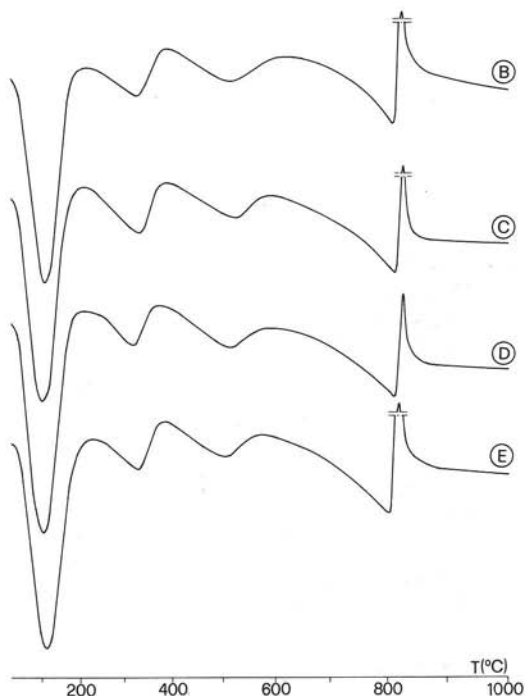


Fig. 3. — DTA curves of samples *B*, *C*, *D*, and *E*.

Chemical analyses and structural formulae of the compounds analyzed in pre-selected areas using the EDS/EDAX analyzer together with a Philips SEM are reported in Tables 2 and 3. In our case, a magnification of 1250 x was used. This map analysis was done only on samples *C*, *D* and *E*. Reported in Figs. 6, 7, and 8 are the maps of some of the most significant elements present in a single zone.

For sample *D* (Fig. 6), the distribution map for Si shows a quite uniform distribution with a strong density for this element. The Ca map shows well defined areas of Ca density; in the S map, the same areas are occupied by S. This may well indicate the presence of small islands of CaSO_4 not observed in the IR and X-ray diffraction patterns. The Mg map shows the presence of Mg with a well distributed density throughout the entire area examined. Also in this map are some poorly populated areas which correspond to the positions of Ca and S thickening. Uniform distribution was found for Cl.

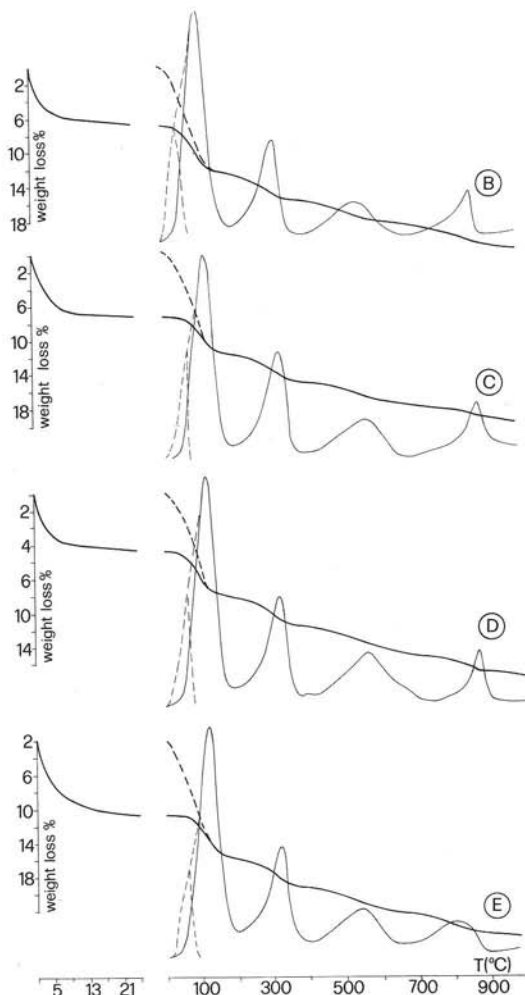


Fig. 4. — TG and DTG tracings of samples *B*, *C*, *D* and *E*: as a function of time (left), as a function of temperature (right). Solid lines: TG and DTG in argon gas flow; dashed lines TG and DTG in air.

In samples *C* and *E* (Figs. 7 and 8) all the distribution maps show a quite uniform distribution for each element as well as the abundance of Si and Mg, the scarcity of Al and the presence of S and Cl. In particular, the uniform distribution of S (as compared to the well defined areas of density for this element found in sample *D*) is evidence that, in these samples, S is present as anions linked to the mineral structure.

TABLE 1
X-ray powder diffraction data for sepiolites B, C, D, E: spacing in Å (top)

h k l	SEPIOLITE B			SEPIOLITE C			SEPIOLITE D			SEPIOLITE E		
	d _(obs.)	d _(calc)	I/I ₀	d _(obs.)	d _(calc)	I/I ₀	d _(obs.)	d _(calc)	I/I ₀	d _(obs.)	d _(calc)	I/I ₀
1 1 0*	12.00	11.99	100	12.07	12.07	100	12.10	12.09	100	12.07	12.05	100
1 3 0*	7.45	7.45	20	7.49	7.49	20	7.49	7.50	20	7.48	7.48	30
1 5 0*	4.984	4.987	20	5.021	5.019	20	5.018	5.018	20	5.007	5.007	20
0 6 0*	4.476	4.477	30	4.507	4.506	30	4.502	4.503	30	4.494	4.494	20
1 3 1*	4.291	4.290	50	4.291	4.292	60	4.298	4.298	60	4.291	4.293	50
2 6 0*	3.723	3.723	40	3.746	3.747	40	3.748	3.748	50	3.739	3.739	40
2 4 1*	3.520	3.520	15	3.528	3.528	20	3.531	3.532	30	3.526	3.526	20
0 8 0		3.358			3.379			3.377			3.371	
4 0 0*	3.351	3.352	40	3.373	3.373	30	3.379	3.380	30	3.367	3.368	30
3 3 1*	3.179	3.181	40	3.191	3.191	30	3.195	3.196	30	3.190	3.189	30
2 6 1		3.037			3.047			3.049			3.044	
3 4 1*	3.035	3.035	20	3.046	3.046	20	3.049	3.050	20	3.044	3.043	20
2 8 1		2.606			2.617			2.618			2.613	
4 4 1*	2.605	2.604	40	2.614	2.615	30	2.620	2.619	40	2.612	2.612	30
1 0 2*	2.576	2.576	40	2.570	2.570	30	2.574	2.575	40	2.574	2.573	30
1 9 1*	2.547	2.547	50	2.558	2.558	60	2.559	2.558	50	2.554	2.554	60
3 7 1		2.566			2.557			2.559			2.554	
0 4 2		2.444			2.442			2.445			2.443	
2 0 2*	2.443	2.444	30	2.442	2.441	30	2.446	2.445	30	2.443	2.443	30
0 6 2		2.264			2.264			2.266			2.264	
3 0 2*	2.263	2.263	30	2.263	2.263	30	2.267	2.267	30	2.264	2.264	30
3 1 2*	2.255	2.255	20	2.255	2.255	20	2.259	2.259	30	2.255	2.256	20
a	13.407(2)			13.491(2)			13.519(2)			13.471(2)		
b	26.860(4)			27.035(3)			27.018(3)			26.966(4)		
c	5.249(1)			5.237(1)			5.245(1)			5.243(1)		
V	1890			1910			1916			1905		

Only the reflections marked with a (*) have been used for the refinement of the unit cell dimensions (bottom).

TABLE 2
Chemical composition of sepiolites studied
(left by XRF, right by EDS/EDAX)

	B	C	D	E	C	D	E
SiO ₂	52.67	53.80	52.64	51.42	53.60	52.57	51.80
TiO ₂	0.02	0.01	0.03	0.05		tr	tr
Al ₂ O ₃	0.55	0.77	0.70	0.85	0.70	0.78	0.65
Fe ₂ O ₃	0.41	0.42	0.40	0.40	0.40	0.35	0.30
MnO	0.02	0.02	tr	0.04			tr
MgO	23.98	24.25	23.97	23.30	24.45	23.95	23.50
CaO	0.16	0.17	0.35	0.17	0.30	0.52	tr
Na ₂ O	tr	tr	tr	0.05	tr		
K ₂ O	0.21	0.04	0.35	0.42	tr	0.29	0.45
SO ₃	0.75	0.32	1.10	0.80	0.41	1.18	0.72
Cl	1.23	0.70	0.86	1.90	0.64	0.76	1.98
H ₂ O	20.00	19.50	19.60	20.60	19.50	19.60	20.60

TABLE 3
Structural formulae of sepiolite
(left by XRF, right by EDS/EDAX)

	B	C	D	E	C	D	E
Si	11.80	11.80	11.75	11.74	11.78	11.74	11.81
Al	0.14	0.20	0.18	0.23	0.18	0.20	0.17
Fe ³⁺	0.06		0.07	0.03	0.04	0.06	0.02
tot.	12.00	12.00	12.00	12.00	12.00	12.00	12.00
charge unbal.	-0.20	-0.20	-0.25	-0.26	-0.22	-0.26	-0.19
Al							
Fe ³⁺	0.01	0.07		0.04	0.02		0.03
Mg	8.01	7.93	7.98	7.93	8.00	7.97	7.98
Mn				0.01			
Ti			0.01	0.01			
tot.	8.02	8.00	7.99	7.99	8.02	7.97	8.01
charge unbal.	+0.05	+0.07	0.00	+0.04	+0.06	-0.06	+0.05
tot.	-0.15	-0.13	-0.25	-0.22	-0.16	-0.32	-0.14
Na				0.02			
K	0.06	0.01	0.10	0.12		0.08	0.13
Ca	0.04	0.05	0.08	0.04	0.07	0.12	

Concluding remarks

The sepiolite from Central Somalia is chemically similar to other sepiolites of arid areas (WEAVER and POLLARD, 1973).

The association with carbonates of both organic and inorganic origin appears only

in the upper level of the deposit, leading to the conclusion that the sepiolite was formed in an evaporitic environment very rich in Si and Mg but with a scarcity of other cations. Ca is present only at the end of sedimentation (sample A).

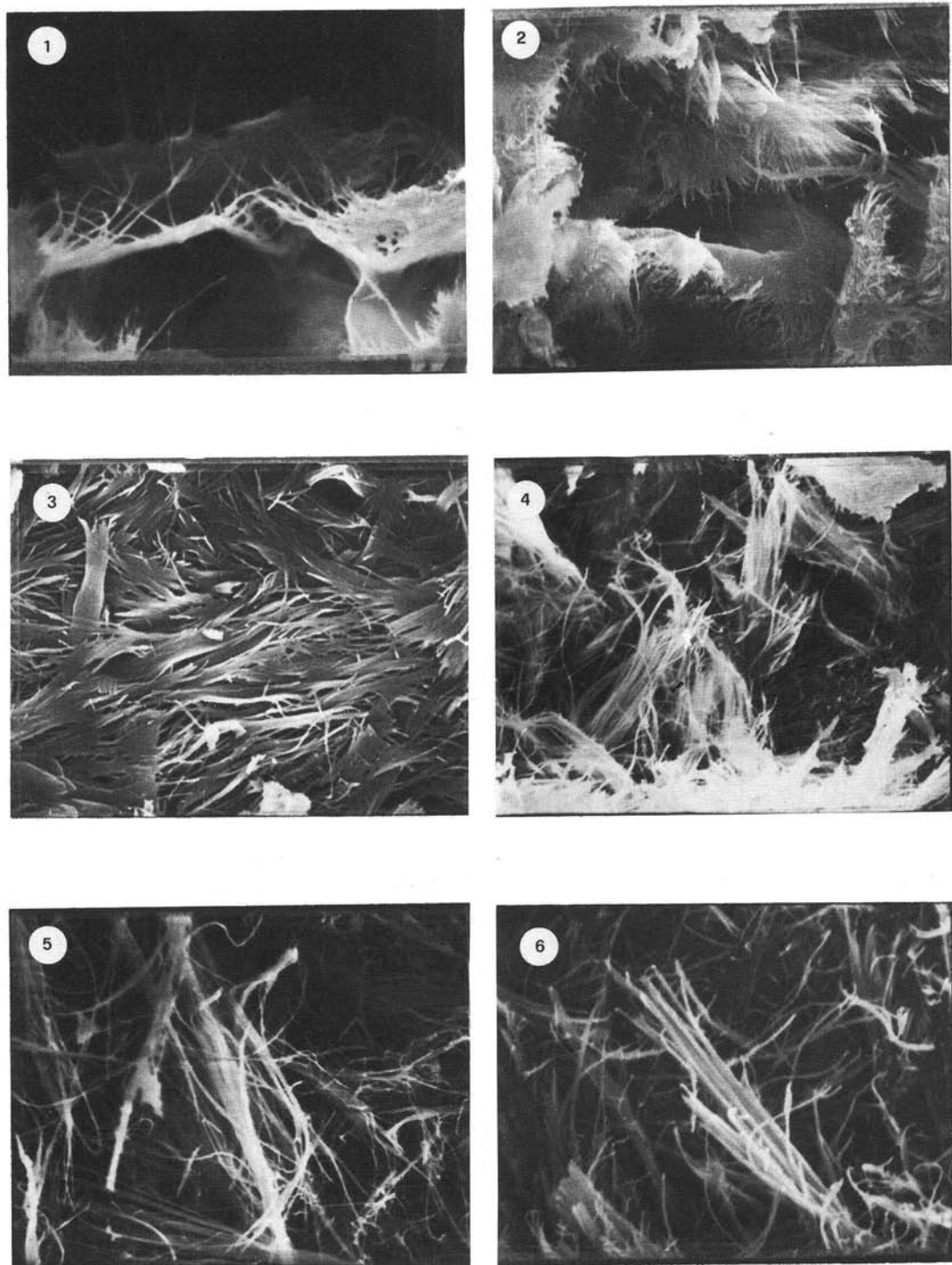


Fig. 5. — Electron micrographs of El Bur sepiolites with different morphology. (1) sample *A* (5000 x); (2) sample *B* (2500 x); (3) sample *D* (5000 x); (4) sample *D* (2500 x); (5) sample *E* (5000 x); (6) sample *E* (10.000 x).

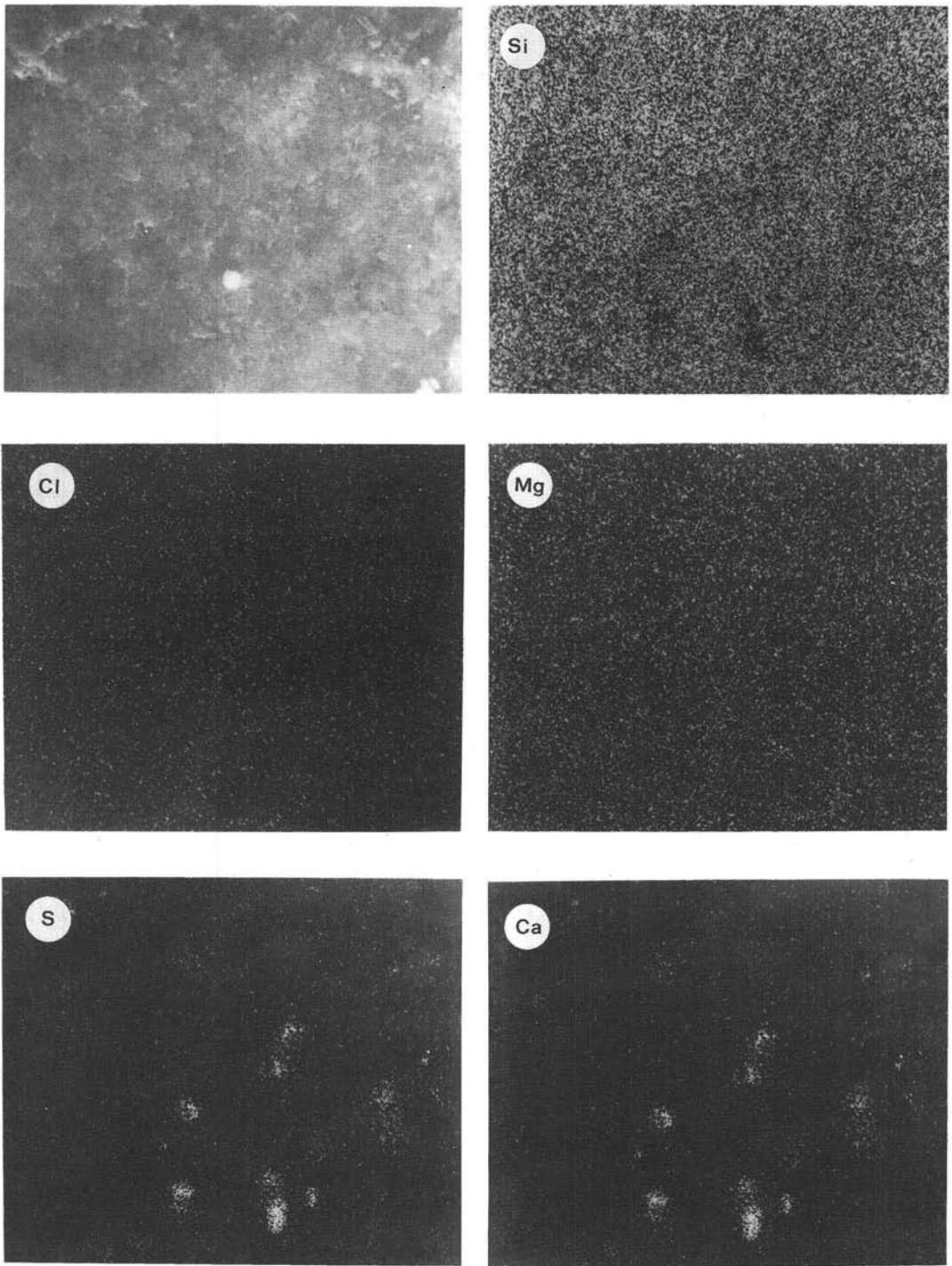


Fig. 6. — Distribution map of elements in a significant area of sample *D* (1250 x). Picture of the surface and distribution maps for the reported elements in the same area.

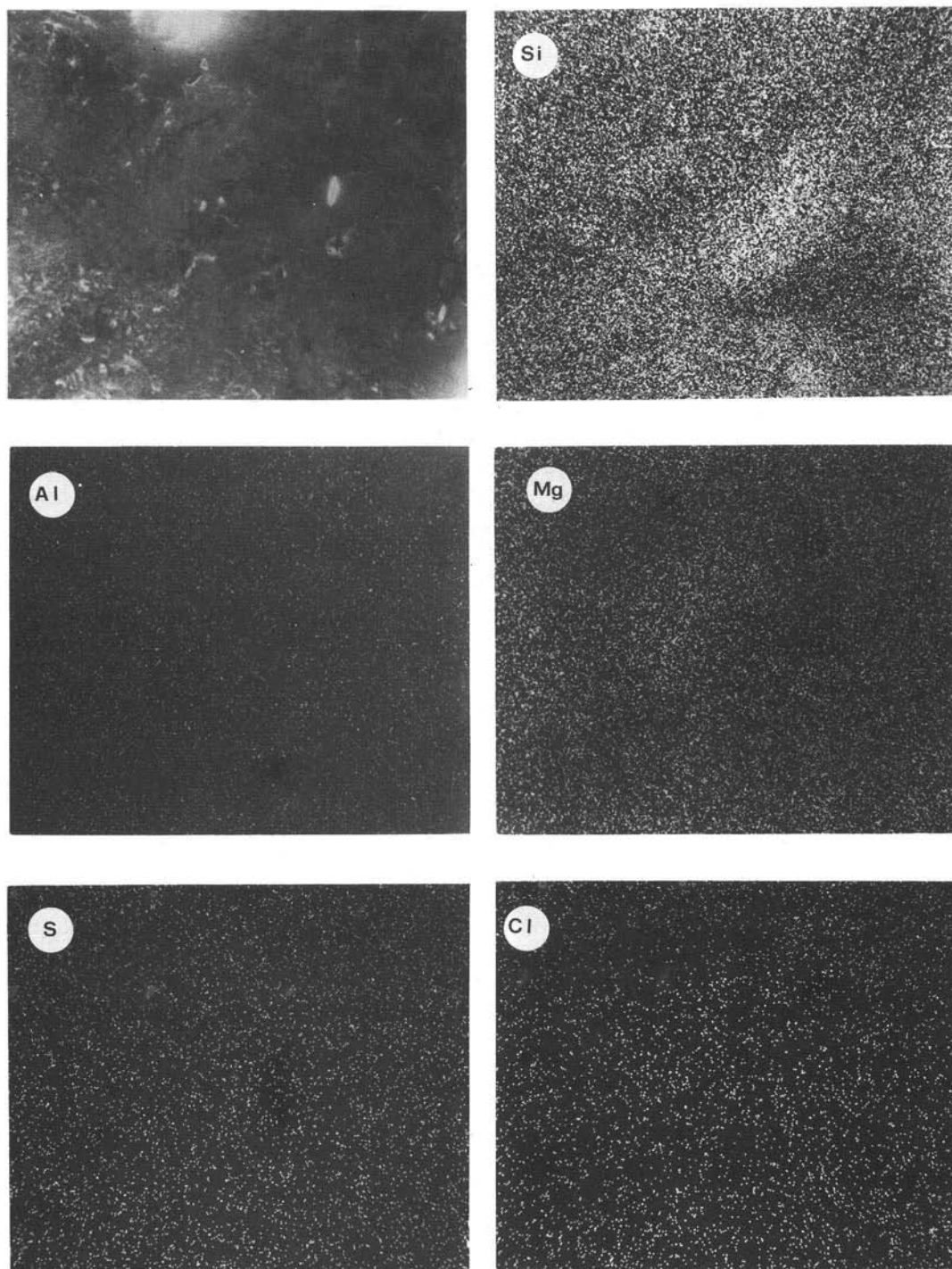


Fig. 7. — Distribution map of elements in a significative area of sample C (1250 x). Picture of the surface and distribution maps for the reported elements in the same area.

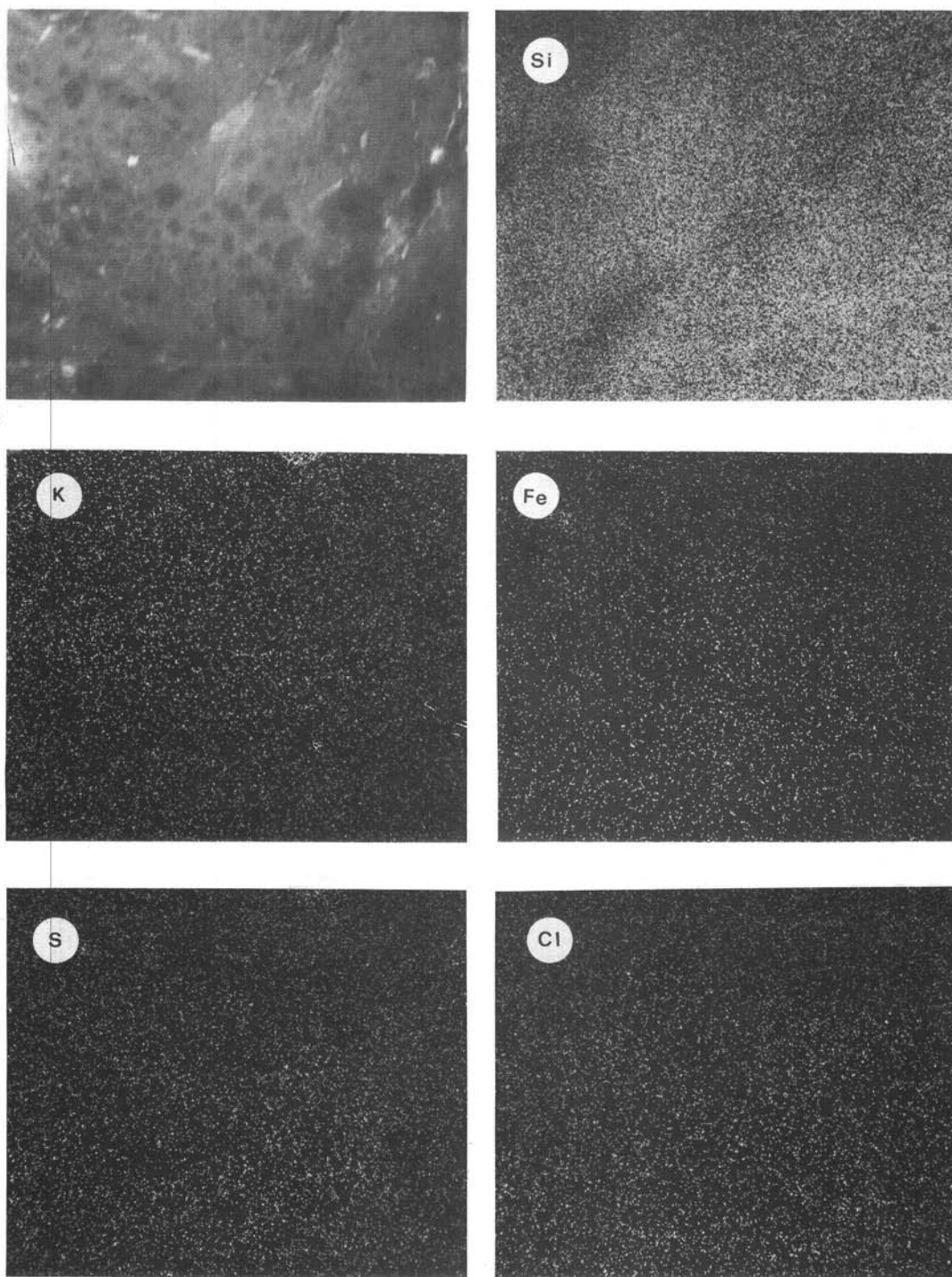


Fig. 8. — Distribution map of elements in a significant area of sample *E* (1250 x). Picture of the surface and distribution maps for the reported elements in the same area.

The presence of the anions Cl and S, definitely entrapped in the structure of the mineral (as is shown by the difficulty of their removal) is indication of the lagoonal marine origin of the minerals.

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