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 microonda 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 probabile età cretacea.

ABSTRACT

Five Somali sepiolites were studied using a variety of analytical techniques: chemical, X-ray diffraction (at different tempera-
The aim of the work reported in this paper was to study the mineralogical and chemical features of these Somalian sepiolite deposits.

**EXPERIMENTAL**

**Materials**

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

**Methods**

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

**Experimental**

Using natural aggregates of sepiolite fibres, scanning electron micrographs were made using a Phillips SEM 500. The samples were prepared using standard procedures. Mineral sections were prepared from opportunistically 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 semiquantitative 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 power samples using a Philips diffractometer (Ni filtered CuKα radiation) with a humidity- and a heating-stage attachment. The temperature increments were of about 50°C in the range 20-700°C, SiO₂ and ClH₄O (BRINDLEY, 1981) were used as standards.

The unit cell parameters were obtained by the 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 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 AHLRICHES et al. (1975), FARMER (1974), FARMER and RUSSELL (1964), NAGATA et al. (1974), PHÖST (1973). Only the stretching vibration (at 3470 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.

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

Fig. 2 - Infrared spectra of sepiolites studied.
Thermal analysis

The thermal behaviour of the sample studied (Fig. 3) is very close to that of Ampandrandava sepiolite (RAUTUREAU and MIFFAUD, 1977). In the TG and DTG curves (Fig. 4), two difference 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 MIFFAUD, 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 formula 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 ion exchange or repeated washing in distilled water.

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 1500 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
### Table 2

**Chemical composition of sepiolites studied**

(Left by XRF, right by EDS/EDAX)

<table>
<thead>
<tr>
<th></th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th></th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
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<tr>
<td>SiO₂</td>
<td>52.67</td>
<td>52.80</td>
<td>52.64</td>
<td>51.42</td>
<td>53.60</td>
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<td>TiO₂</td>
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<td>0.01</td>
<td>0.03</td>
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<td>tr</td>
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<tr>
<td>Al₂O₃</td>
<td>0.55</td>
<td>0.77</td>
<td>0.70</td>
<td>0.85</td>
<td>0.70</td>
<td>0.78</td>
<td>0.65</td>
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<tr>
<td>Fe₂O₃</td>
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<td>0.42</td>
<td>0.40</td>
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<td>0.02</td>
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<tr>
<td>MgO</td>
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<td>24.25</td>
<td>23.97</td>
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</tr>
<tr>
<td>K₂O</td>
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<td>0.04</td>
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<td>0.42</td>
<td>tr</td>
<td>0.29</td>
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<td>SO₃</td>
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<td>Cl</td>
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<td>20.60</td>
<td>19.50</td>
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### Table 3

**Structural formulae of sepiolite**

(Left by XRF, right by EDS/EDAX)

<table>
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<tr>
<th></th>
<th>B</th>
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<th>D</th>
<th>E</th>
<th></th>
<th>B</th>
<th>C</th>
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<td>Si</td>
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<td>11.80</td>
<td>11.75</td>
<td>11.74</td>
<td>11.78</td>
<td>11.74</td>
<td>11.81</td>
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<tr>
<td>Al</td>
<td>0.14</td>
<td>0.20</td>
<td>0.18</td>
<td>0.23</td>
<td>0.18</td>
<td>0.20</td>
<td>0.17</td>
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<tr>
<td>Fe³⁺</td>
<td>0.06</td>
<td>0.07</td>
<td>0.03</td>
<td>0.03</td>
<td>0.04</td>
<td>0.06</td>
<td>0.02</td>
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<td>12.00</td>
<td>12.00</td>
<td>12.00</td>
<td>12.00</td>
<td>12.00</td>
<td>12.00</td>
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<td>-0.20</td>
<td>-0.25</td>
<td>-0.26</td>
<td>-0.22</td>
<td>-0.26</td>
<td>-0.19</td>
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<td></td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>0.04</td>
<td>0.07</td>
<td>0.04</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
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</tr>
<tr>
<td>Mg</td>
<td>8.01</td>
<td>7.93</td>
<td>7.98</td>
<td>7.93</td>
<td>8.00</td>
<td>7.97</td>
<td>7.98</td>
<td></td>
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<tr>
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<tr>
<td>Ti</td>
<td>0.04</td>
<td>0.07</td>
<td>0.00</td>
<td>0.04</td>
<td>0.06</td>
<td>0.06</td>
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<tr>
<td>tot.</td>
<td>8.02</td>
<td>8.00</td>
<td>7.99</td>
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<td>8.02</td>
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<td>8.01</td>
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<tr>
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<td>-0.09</td>
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<tr>
<td>Na</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
<td>0.02</td>
<td></td>
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</tr>
<tr>
<td>K</td>
<td>0.04</td>
<td>0.10</td>
<td>0.10</td>
<td>0.12</td>
<td>0.08</td>
<td>0.13</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Ca</td>
<td>0.04</td>
<td>0.05</td>
<td>0.08</td>
<td>0.04</td>
<td>0.03</td>
<td>0.12</td>
<td>0.12</td>
<td></td>
<td></td>
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</table>
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 CaSO₄ 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.

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.

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).

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.

Acknowledgements

Thanks are due to Prof. A. Russo (Istituto di Paleontologia dell'Università di Napoli) for micropaleontological and age determinations; to Dr. W. Mazzucchelli (Istituto di Mineralogia dell'Università di Ferrara) and Dr. P. L. Fabbrini (Centro Strumenti dell'Università di Modena) for help in chemical determinations.

The authors are indebted to the Istituto di Mineralogia dell'Università di Ferrara for the use of X-ray fluorescence and to the

Istituto di Mineralogia e Petrografia dell'Università di Padova for the execution of slices.

This work was supported by the Consiglio Nazionale delle Ricerche, Rome, and the Centro di Calcolo dell'Università di Modena, and Centro Strumenti dell'Università di Modena.

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Fig. 5 - Electron micrographs of El Bur sepiolite 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 significant area of sample C (1250 x). Picture of the surface and distribution maps for the reported elements in the same area.
Morfologia, sedimentologia e dinamica fluviale di due corsi d'acqua effimeri della Somalia settentrionale

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Riassunto
La presente nota riferisce delle ricerche di morfologia e sedimentologia fluviale intraprese in prossimità di Berbera (Somalia settentrionale) su due corsi d'acqua effimeri: il Togga Bijiguare ed il Togga Kalajab. Questi scorrono in direzione sud-nord, dall'Altopiano Somali al Golfo di Aden, e possiedono bacini limitrofi caratterizzati da una morfologia simile.

Nelle zone più a monte, corrispondenti alla scarpa principale, i versanti sono assai ripidi e gli alvei rettilinei. Nelle parti mediane dei bacini, nelle aree più prossime alla base della scarpa, i due corsi d'acqua hanno inciso profondi canyons, mentre più a valle, nonostante la grande abbondanza di sedimenti, scorrono in alvei confinati, delimitati da superfici sommitali spesso corrispondenti a vecchi terrazzamenti. In questi tratti il tracciato dei canali è del tipo intrecciato (braided stream).

Prima di raggiungere la pianura costiera attraversano un rilievo montuoso, nel quale il Bijiguare ha inciso una stretta gola al di là della quale raggiunge poi il mare, mentre il Kalajab ha invece formato un passaggio molto più ampio a valle del quale si sviluppa un'esteso condotto terminale nei cui rami le seque di piena riescono raramente a raggiungere il mare.