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A sepiolite of large crystalline growth from "La Adela" mine province of Río Negro, Argentina

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With 4 figures and 2 tables in the text

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Abstract: A white, fibrous, flexible, and soft mineral found in a dolomitic limestone of the "La Adela" quarry, located in the Department San Antonio Oeste (Province of Río Negro, Argentina) was studied. The mineral occurs in veinlets, placed along bedding planes and joints, showing a remarkable crystalline growth. Fibers are up to 8 cm long. In order to identify the mineral, optical microscopy, XRD, SEM, TEM, TG, DTA, IR, capacity of cationic exchange, and chemical analysis were used. It was concluded that the mineral was a sepiolite. This mineral is associated with subordinate amounts of montmorillonite, talc, phlogopite, kaolinite, and the amphibole minerals tremolite and anthophyllite. The carbonate related with the veinlets is calcite.

Key words: Sepiolite, Argentina, dolomite, veinlet.

Introduction

"La Adela" quarry is located in the Department San Antonio Oeste, some 15 km southeast of the "Gonzalito" mine, at about 75 km WNW of the village of Sierra Grande, Province of Río Negro (Fig. 1).

The studied mineral occurs along veinlets of up to 3 cm thick. It occurs in joints and bedding planes of a crystalline dolomite inserted into pre-Silurian micaceous schists, corresponding to the Valcheta Group (Caminos et al., 1984).

Background

Hayase et al. (1970), refer to the finding of sepiolite in a hydrothermal limestone occurring in Tertiary sediments, some 60 km NW of the currently studied quarry. Deguillén (1977), makes mention of poorly crystallized sepiolite, associated with gypsum, calcite, opal, and chalcedony, within veinlets of up to 1 cm in thickness, ascribing a hydrothermal origin. La Iglesia (1978),

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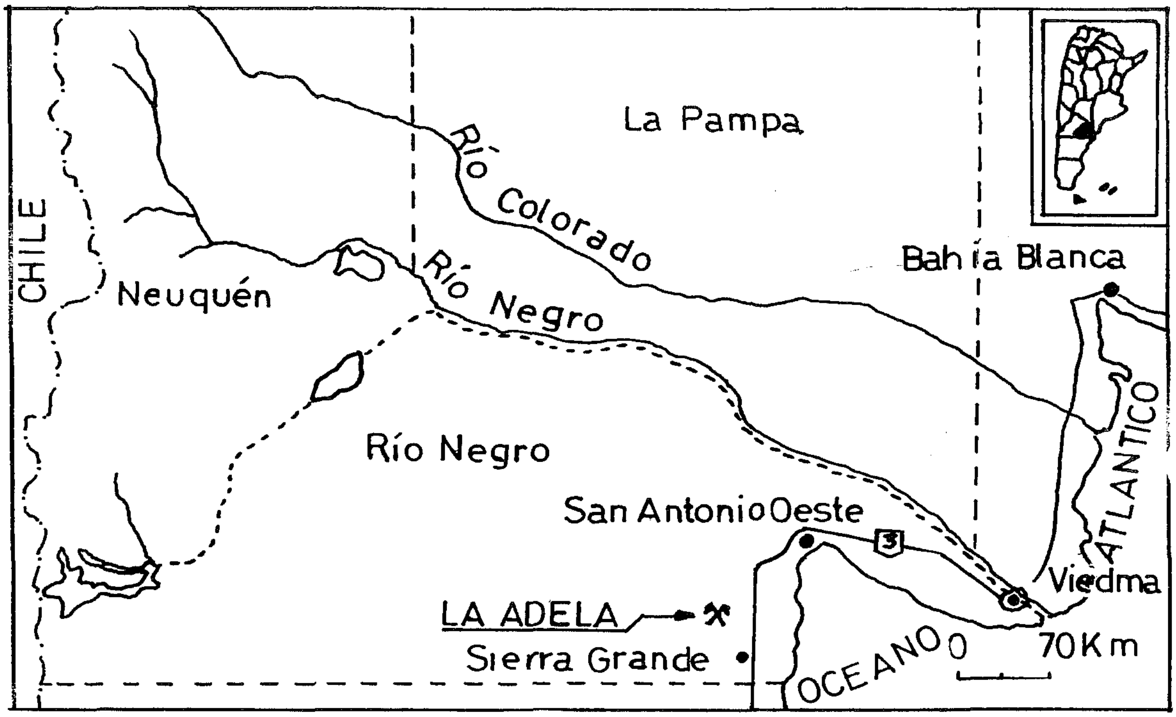

Fig. 1. Location map of the mine "La Adela".

performed a precipitation of sepiolite, at room temperature, from periclase and a silica solution, with the addition, in some cases, of aluminum, within a pH range between 6 and 9. He obtained sepiolite, either with or without aluminum, at pH values greater than 6 whose crystallinity increases with alkalinity.

Methods

Determinations were performed with a petrographic microscope, a Rigaku Denki Geigerflex X-ray diffractometer, computerized D-max IIIC with Cu Kα, a JEOL JSM 35 CF scanning electron microscope, and JEOL JSM-100 CX II transmission electron microscope, a Rigaku simultaneous thermoanalyzer, and a Perkin Elmer 580-B IR spectrometer.

Results

Mineralogical characteristics

A white, fibrous, very flexible and soft mineral, of cylindrical-columnar habit, hardness of 2 to 2.5, with a remarkable crystalline growth, in up to 8 cm long and 0.5 cm wide specimens was found in the joints and bedding planes of the dolomite. Jones et al. (1988) made mention of maximum sizes of a few millimeters long for a sepiolite from Madagascar.

The mineral occurs as bundles of fibers parallel to the fractures in dolomite and, commonly, they are associated to calcite and some other clay minerals. The exogenous processes removed the clays, leaving the surfaces covered with large sepiolite crystals (Fig. 4 a).

Thin sections, under the microscope revealed a colorless to gray, fibrous mineral, at times acicular and of very low relief, refraction indices $n\alpha = 1.512$ and $n\gamma = 1.522$, low birefringence: 0.01, right extinction angle and positive elongation. Fig. 4 b shows the sepiolite associated to carbonates.

X-ray diffractometry

The sepiolite was isolated by manually removing impurities for its XRD analysis. Table 1 gives the values of the obtained reflections and they are com-

Table 1. X-ray reflections sepiolite "La Adela" in comparison with ASTM.

Sepiolite		ASTM 13-595		
d Å	I/I_o	d Å	I/I_o	h k l
12.100	100	12.10	100	1 1 0
7.481	10	7.47	10	1 3 0
6.722	9	6.73	6	0 4 0
5.024	9	5.01	8	1 5 0
4.512	21	4.50	25	0 6 0
4.325	31	4.31	40	1 3 1
3.973	8	4.02	8	3 3 0
3.751	24	3.75	30	2 6 0
3.542	13	3.53	12	2 4 1
3.356	29	3.37	30	0 8 0
3.195	26	3.20	35	3 3 1
3.050	13	3.05	12	2 6 1
2.897	9 (D)	–	–	–
2.826	8	2.825	8	4 1 1
2.690	13	2.691	20	5 1 0
2.620	20	2.617	30	4 4 1
2.590	19	2.586	2b	5 3 0
2.563	31	2.560	55	3 7 1
2.449	15	2.449	25	2 0 2
2.405	13	2.406	16	1 4 2
2.262	16	2.263	30	5 4 1
2.119	7	2.125	8	5 6 1
2.064	11	2.069	20	4 1 2
1.955	6	1.957	4	5 8 1
1.877	7	1.881	8	0 10 2
1.704	8	1.700	10	0 15 1
1.588	9	1.592	10	3 15 1
1.550	10	1.550	16	0 17 1

(D) Dolomite.

pared with those of the ASTM card 13-595. Its structure is orthorhombic, with a_0 = 13.50, b_0 = 26.97, and c_0 = 5.255 Å. The only impurity recognized in the analysed sample is dolomite. The cell fitting was performed with those values. Obtained parameters are: a_0 = 13.515, b_0 = 26.960, c_0 = 5.249 Å.

Chemical analysis

The sample used for the analysis was selected by means of XRD until the specimen had calcite as the only impurity.

Determinations of SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO and H_2O, were performed by gravimetric methods, while those for Na_2O and K_2O were done by flame spectrophotometry. The determined CaO, was ascribed to calcite, th impurity of the sample, and the values for the remaining components were recomputed.

The obtained results are shown in Table 2, where they are compared with chemical analysis data from different sepiolites.

Table 2. Chemical composition of sepiolites.

	(1)	(2)	(3)	(4)	(5)
SiO_2	53.15	52.85	52.50	53.70	55.11
Al_2O_3	1.83	1.08	0.60	1.15	1.88
Fe_2O_3	1.31	0.04	2.99	0.64	0.04
FeO	–	0.01	0.70	0.02	
MgO	24.08	23.74	21.31	23.31	22.82
CaO	–	0.51	0.47	0.03	1.45
Na_2O	0.10	–	–	0.67	–
K_2O	–	–	–	0.61	–
H_2O^+	11.81	9.04	21.27	9.83	8.10
H_2O^-	6.73	12.67	–	9.76	12.90
total	99.01	99.89	99.84	99.72	100.30

(1) Sepiolite, La Adela.
(2) Sepiolite, Kuzuu District, Japan (Jones et al., 1988).
(3) Sepiolite, Ampandrandara, Madagascar (Jones et al., 1988).
(4) Sepiolite, Amboseli, Kenya (Jones et al., 1988).
(5) Sepiolite, Cecchi quarry, Argentina (Hayase et al., 1970).

The computed formula on the basis of $O_{30}(OH)_4(H_2O)_2$ is:

$$(Si_{11.58},Al_{0.42})(Al_{0.06},Fe_{0.14},Mg_{7.8})Na_{0.01}$$

Thermal analysis

Jones & Galan (1988), divide the DTA curve into three regions:

– Low temperature region, lower than 300 °C. Here, the curve shows a strong endothermic reaction at 120 °C, caused by loss of the absorbed and of the zeolitic waters. The weight loss is greater than 10 %. Within this temperature range, no significant structural changes occur.

- Central region, between 300 and 600 °C: In this area, two endothermic peaks appear at 350 °C and between 500 and 550 °C, ascribed to the loss of the first two combined water molecules.
- High temperature region, higher than 600 °C: an endothermic peak is present at 800 °C, immediately followed by an exothermic maximum. The first peak corresponds to the dehydroxilation of the structure, along with entropic changes due to the collapse of the structure. Dehydroxilation is confirmed by the weight loss shown in the TG. The exothermic peak occurs due to the formation of clinoenstatite.

In the sepiolites, total water content is of about 20 wt.%, including 2.4 to 3 % of dehydroxilation water.

Fig. 2 shows the thermograms corresponding to the studied sepiolite. Curve a, corresponds to the TG, where a weight loss of 21.43 % was determined. This

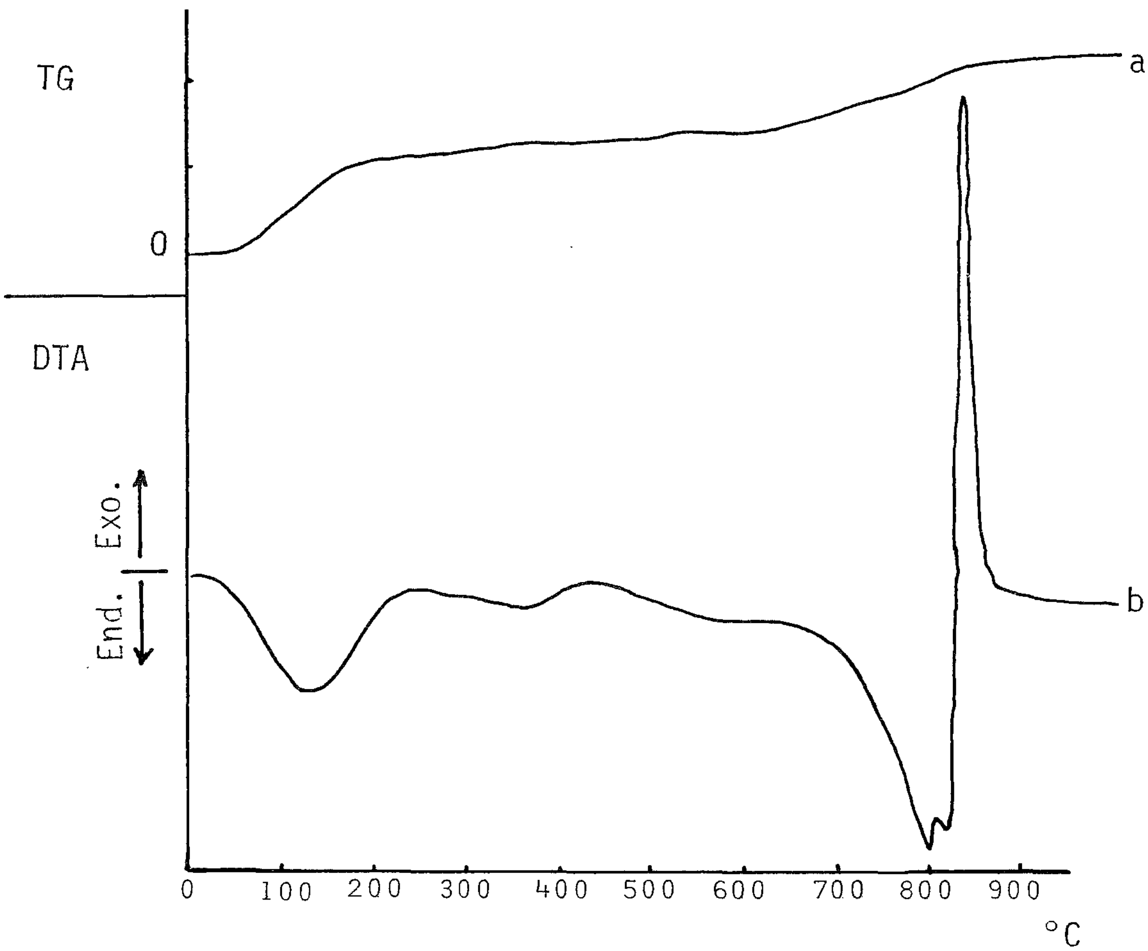

Fig. 2. TG and DTA curve of sepiolite "La Adela".

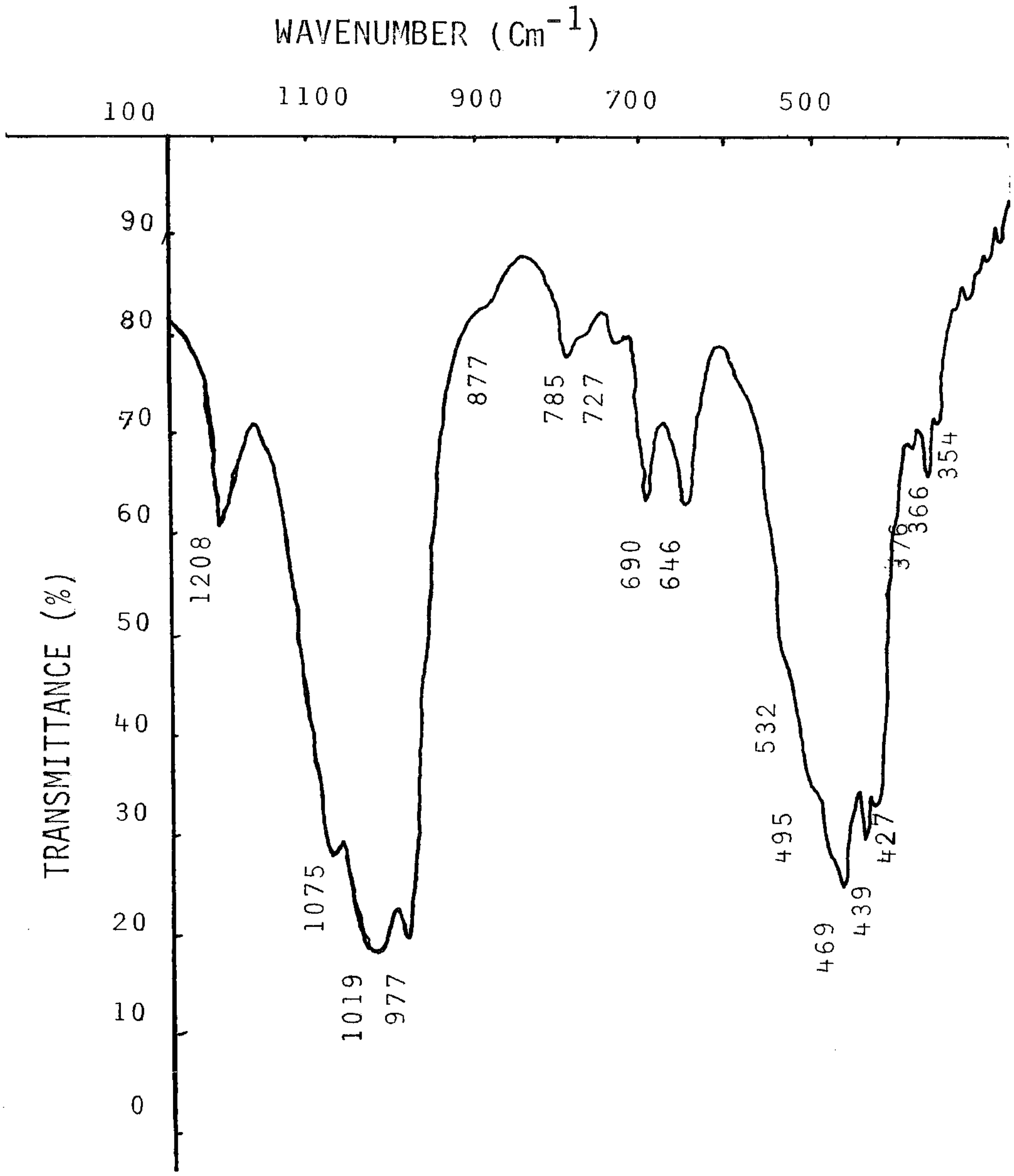

Fig. 3. IR-spectrum of sepiolite "La Adela".

is due to the water release from sepiolite and CO_2 from calcite, that was the impurity of the sample.

Curve b corresponds to the DTA. The first endothermic peak was observed at 128 °C. In the central region, two endothermic peaks occur, one at 360 °C, and the other at 560 °C. In the high temperature region, a very strong endothermic peak was recorded at 805 °C, with a step, probably caused by CO_2 from calcite, and an exothermic peak at 835 °C. The higher temperature values obtained in the studied sepiolite are ascribed to the high degree of crystallinity shown by this mineral.

Electron microscopy

SEM

A bundle of very well developed, fibrous sepiolite crystals is observed (Fig. 4 c) within a mass with carbonate impurities. In Fig. 4 d, the crystals are flexed around isolated carbonate crystals.

TEM

Fig. 4 e shows typical, long and thin, sepiolite crystals, with practically no impurities. Fig. 4 f is a detail of the former.

Infrared

The method of the KBr cake was used in the analysis of the sample. The obtained spectrum (Fig. 3) is similar to those reported by VAN DER MAREL & BEUTELSPACHER (1976) for sepiolites from diverse places of the world, although showing a better definition of its bands.

Cationic exchange capacity

The cationic exchange capacity (c.e.c.) of sepiolite is low. Theoretical values range between 5 and 40 meq/100 g for a sepiolite sample from Vallecas, Spain. The sepiolite from "La Adela" quarry has a c.e.c. of 11.5 meq/100 g.

Considerations and conclusions

The analytical methods allowed to determine that the studied mineral is sepiolite. From the results of the chemical analysis, the following formula was computed on the basis of $O_{30}(OH)_4(H_2O)_2$:

$$(Si_{11.58},Al_{0.42})(Al_{0.06},Fe_{0.14},Mg_{7.8})Na_{0.01}.$$

Precipitation of sepiolite occurred in an alkaline medium. The large size of the fibers and the high degree of crystallinity permit to assume that this mineral crystallized from hydrothermal solutions.

The origin of the studied sepiolite is considered to be a product of the reaction of the magnesium released from dolomite through a dedolomitization process, as a consequence of the action of solutions rich in alkaline elements, mainly sodium. Silica is furnished by the alteration of the clay minerals contained as impurities in limestone.

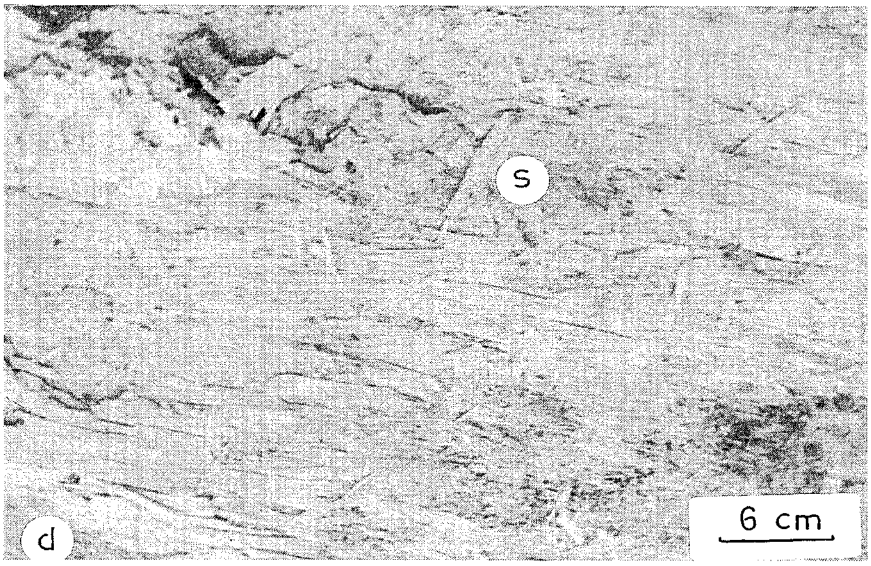

Fig. 4 a. Sepiolite (s) crys developed along a joint plane in dolomite (d).

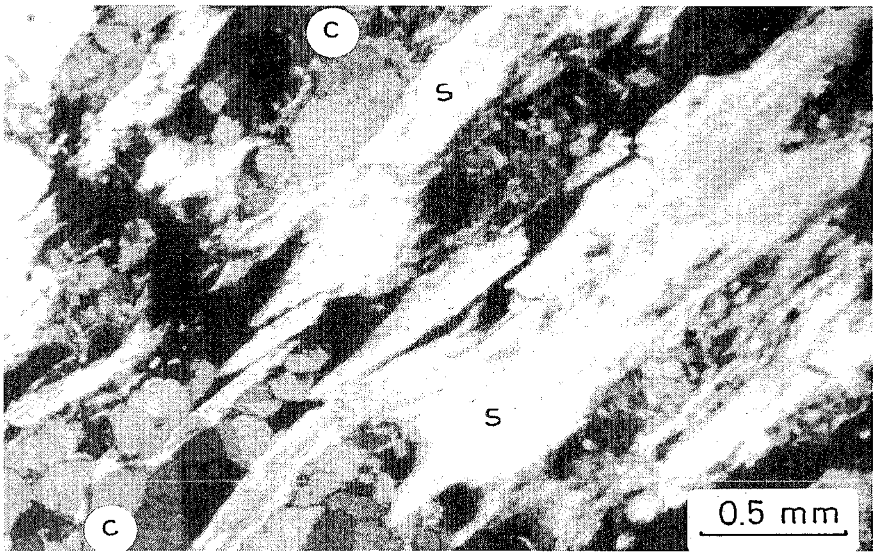

Fig. 4 b. Sepiolite (s), under crossed nicols. Fibrous crystals within a calcite (c) mass.

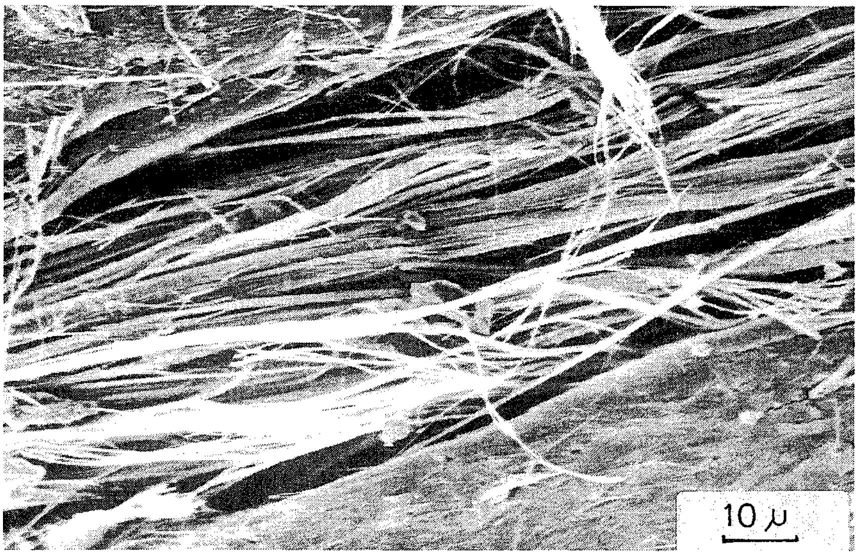

Fig. 4 c. SEM, showing of flexed, long sepiolite fibers.

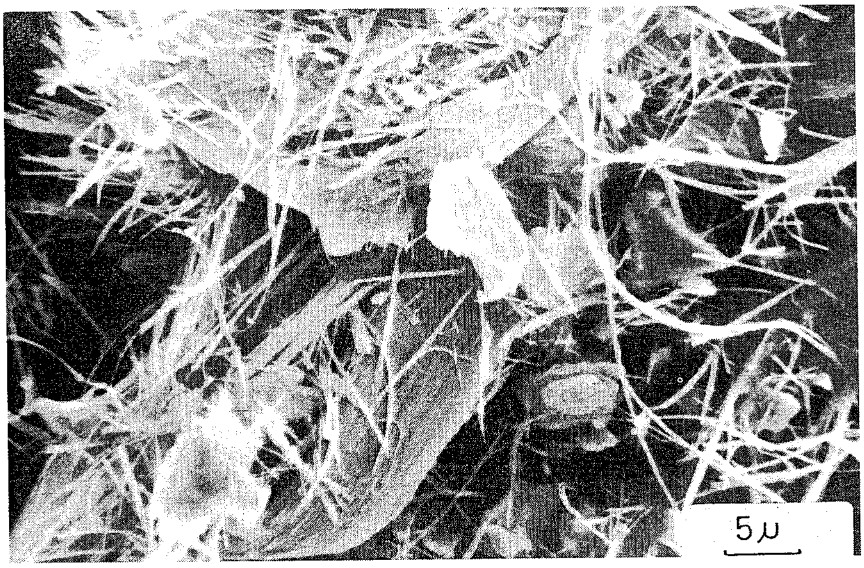

Fig. 4d. SEM of sepiolite crystals.

Fig. 4e. TEM showing characteristic sepiolite fibers (× 14,000).

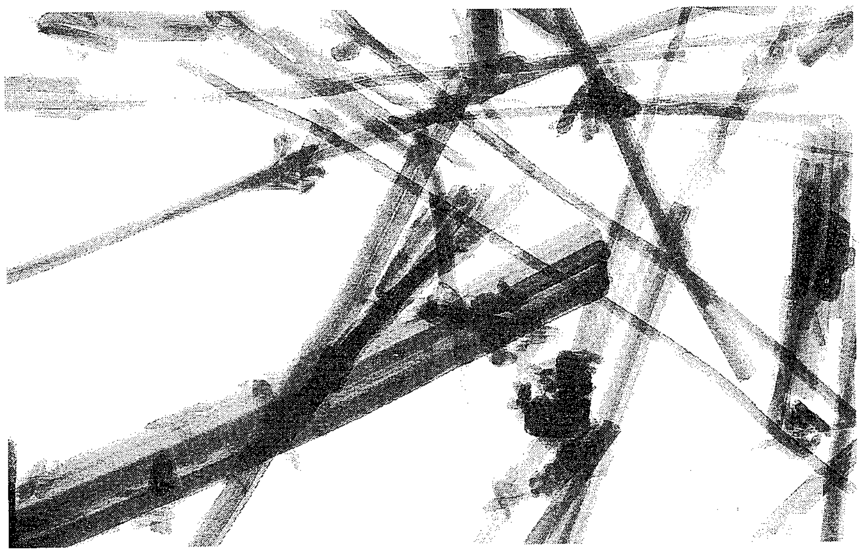

Fig. 4f. Detail of Fig. 4e (× 40,000).

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