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A hydrothermal sepiolite occurrence at Măgureni Hill, Preluca Veche (Maramureş County, Romania)

KOVÁCS-PÁLFFY, Péter[1], KÓNYA, Péter[2], KALMÁR, János[2], FEHÉR, Béla[3]
FÖLDVÁRI, Mária[2]

[1]Bécsi út 62, H–2518 Leányvár, kovacs.palffy.peter@gmail.com
[2]Geological and Geophysical Institute of Hungary, H–1143, Budapest, Stefánia út 14, konya.peter@mfgi.hu, johannkalmar@gmail.com, foldvari56@gmail.com
[3]Department of Mineralogy, Herman Ottó Museum, H–3525 Miskolc, Kossuth L. u. 13, feherbela@upcmail.hu

Măgureni-domb, Preluca Veche (Máramaros megye, Románia), egy hidrotermális szepiolit-lelőhely

Összefoglalás

A Preluca-hegységben (ÉNy-Erdély, Románia), a Măgureni-domb területén proterozoos metamorfizált karbonátos kőzetek (dolomitok és mészkövek) ismertek. A késői, hercíniai regionális metamorfózis alkalmával nagyszámú pegmatittest nyomult be a metamorf összletbe. A pegmatitok képződését diopszid-tremolit-flogopit összetételű szkarn kialakulása, majd hidrotermás folyamatok kísérték. A SiO_2-tartalmú, alkáli, illetve semleges vizes oldatoknak a Mg-dús kőzetekkel való reakciója következtében magnéziumos agyagásvány-társulás képződött. Ezek közül mind ásványtani, mind gazdasági szempontból a szepiolit-előfordulások a legfontosabbak.

A lelőhely szepiolitja vékony teléreket és lencséket képez. Kísérő ásványai a talk, szaponit, klorit, kaolinit, markazit, kalcit és opál. Kémiai, röntgendiffrakciós, termoanalitikai, infravörös spektroszkópiai és elektronmikroszkópos vizsgálatok igazolták a majdnem tiszta Mg-szepiolit jelenlétét, kis mennyiségű alumínium- és vas-oxid beépüléssel. Ugyancsak kimutatható a Mg-ot koordináló és a szabad (zeolitos) víz jelenléte.

Végül bemutatjuk a technológiai kísérletek eredményeit is a szepiolit kitermelése, dúsítása és alkalmazása tekintetében.

Kulcsszavak: Románia, Preluka-hegység, Măgureni Karbonát Formáció, dolomitok, pegmatitok, szepiolit, elemzési adatok

Abstract

In the Măgureni Hill, situated in the Preluca Mts (NW Transylvania, Romania) proterozoic metamorphosed carbonatic rocks (dolomites and limestones) occur. During the latest phase of regional (Hercynian) metamorphism in this area, a great number of "hot" pegmatite bodies were intruded into these rocks. The consolidation of pegmatites was accompanied by the diopside-tremolite-phlogopite skarn formation and was followed by hydrothermal processes. The SiO_2-bearing, alkaline or neutral aqueous solutions reacted with the Mg-rich wall rocks, resulting in the formation of a magnesian clay mineral association. Sepiolite is the most interesting among the constituents of this association, both from a mineralogical and from an economic point of view.

The sepiolite of the Măgureni Hill occurs as thin veinlets and lenses. The accompanying minerals are talc, saponite, chlorite, kaolinite, marcasite, calcite and opal. The chemical, X-ray diffraction, thermoanalytical, IR-spectroscopy and electron microscopic studies reported in this paper proved the presence of nearly pure, magnesian sepiolite, with a very small amount of alumina and iron oxide. Mg-coordinated and free (zeolitic) water were also indicated.

Also presented here are the technological experiences related to the extraction and enrichment of the sepiolite and the possibility of its utilisation.

Keywords: Romania, Preluca Mts, Măgureni Carbonate Formation, dolomite, pegmatite, sepiolite, analytical data

Introduction

Sepiolite, known as a fibrous clay mineral, formed in sedimentary and hydrothermal environments. In a sedimentary environment, sepiolite-bearing residual clays can be formed by alteration of the Mg-rich igneous rocks (i.e. basalts, gabbros, peridotites, and dunites). Magnesium-carbonates and hydrated magnesium-silicates, such as serpentines, chlorites, saponite, vermiculite, talc and sepiolite are formed by hydrodiagenetic-hydrothermal alteration of the above-mentioned igneous rocks, too. Sepiolite, associated with some dolomite, magnesite and magnesium-salts, is a precipitate in hypersaline (bitter) lakes in arid areas (ATKINSON & WAUGH 1979). Sepiolite also occurs in some marine or lacustrine marls and limestones (POWER 1981).

Sepiolite, formerly known as "Meerschaum" (sea froth), is a non-swelling, lightweight, porous clay with a large specific surface area. Unlike common clays, the individual particles of sepiolite have a needle-like morphology.

The high surface area and porosity, as well as the unusual particle shape of this clay account for its outstanding sorption capacity and colloidal properties. Such properties make it a valuable material for a wide range of applications (NEMECZ 1973).

In the studied Măgureni Hill area, a new genetic type was found: this was the vein-like sepiolite formed by the reaction between late pegmatitic solutions and metamorphosed carbonate rocks such as dolomitic and calcitic-dolomitic marbles.

Geological setting

The Măgureni Hill area is situated in the NW part of Transylvania, Romania, near to the city Baia Mare, in the northern and central part of Preluca Mts. The main sepiolite occurrences can be found in the Măgureni, Preluca Veche and Dealul Corbului villages.

The Preluca Mts represents is one of the eight metamorphic "inselbergs" situated between the Apuseni Mts and Eastern Carpathians *(Figure 1)*. More precisely, they are the uplifted basement of the Pannonian Domain, i.e. the north-eastern edge of the Tisza Unit.

Here, according to the Geological Map of Romania (Sc. 1:50 000, L 34-24 C Preluca Sheet 1986), four stratigraphic units (crystalline formations) can be distinguished in the Preluca Mts: the Răzoare Gneiss Formation, the Măgureni Carbonate Formation, the Preluca Nouă Micaschist and Amphibolite Formation *(Figure 2)* and far in the SW corner, the Ţicău Micaschist Formation.

Upper Cretaceous, Palaeogene and Neogene detrital and carbonatic rocks form the sedimentary cover of the metamorphic basement.

The Măgureni Carbonate Formation

The typical succession of the Măgureni Formation can be found between the localities of Măgureni, Preluca Veche and Dealul Corbului villages.

In the upper part of the Răzoare Gneiss Formation, a few white and grey calcitic marble lenses are embedded. The transition between the biotite-almandine-kyanite-An_{35} plagioclase paragneisses and marbles is sharp; however in the

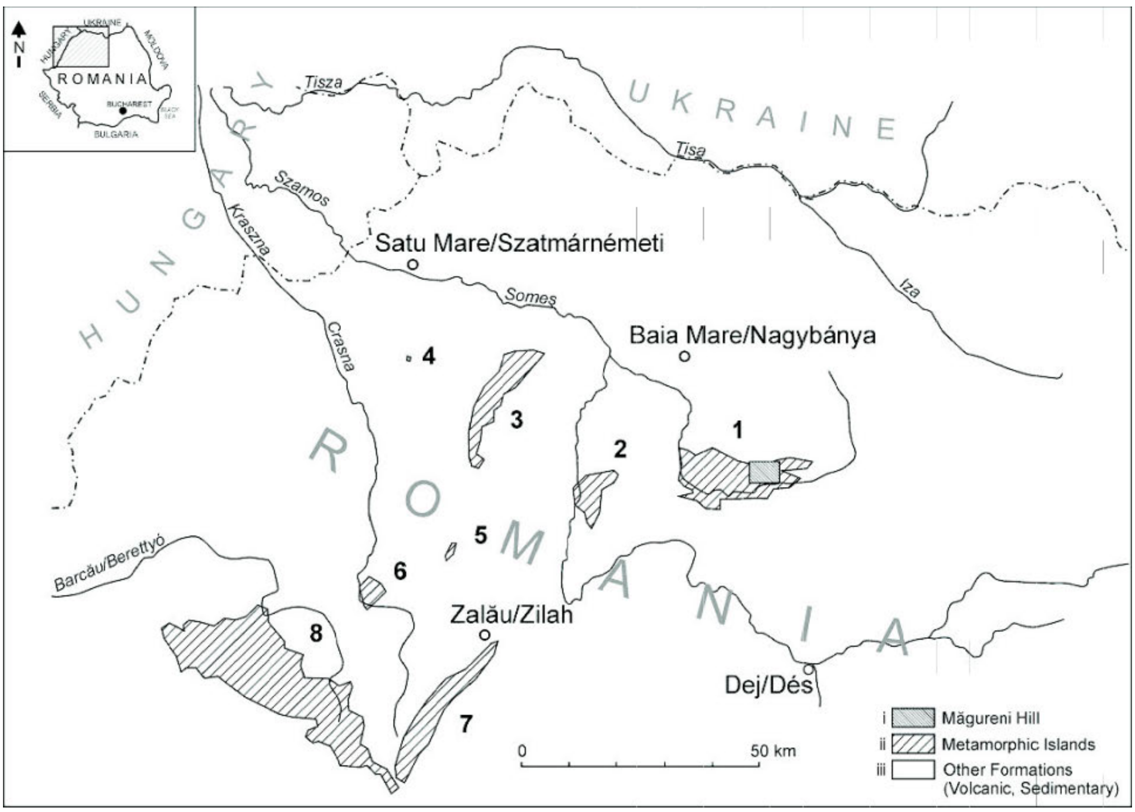

Figure 1. Metamorphic "inselbergs" in NW Romania
1 – Preluca & Ineu, 2 – Ţicău, 3 – Bâc-Codru, 4 – Ardud, 5 – Heghieş, 6 – Măgura Şimleului, 7 – Meseş, 8 – Plopiş (modified after KALMÁR et al. 1997)

1. ábra. *ÉNy-Románia metamorf röghegységei*
1 – Preluca & Ineu (Preluka & Ünő), 2 – Ţicău (Cikó), 3 – Bâc-Codru (Bükk), 4 – Ardud (Erdőd), 5 – Heghieş (Hegyes), 6 – Măgura Şimleului (Somlyói Magura), 7 – Meseş (Meszes), 8 – Plopiş ; Măgureni-domb (i), metamorf röghegységek (ii), egyéb képződmények (vulkáni, üledékes)(iii) (KALMÁR et al. 1997 után módosítva)

lower part of the carbonatic rocks 1–5 m thick paragneiss and micaschist lenses can be observed in continuous layers of 100–300 m length. The Măgureni Carbonate Formation is covered by the Preluca Nouă Micaschist and Amphibolite Formation, and it lies along an important stratigraphic unconformity (KALMÁR 1972a).

The Măgureni Carbonate Formation is built up of five stratigraphic subdivisions, which are as follows: (1) the Lower Calcitic Member; (2) the Lower Dolomitic Member; (3) the Main Tremolitic Level; (4) the Upper Dolomitic Member and (5) the Upper Calcitic Member. Mica-bearing marbles ("cipollino"), tremolitic marbles, as well as rare micaschist and imbedded amphibolites also appear at different stratigraphic levels. These occur together mainly on the southern part, in the Dealul Paltinului, Valea Socilor area (ANGULESCU et al. 1978, 1986), but they cannot be correlated with each other.

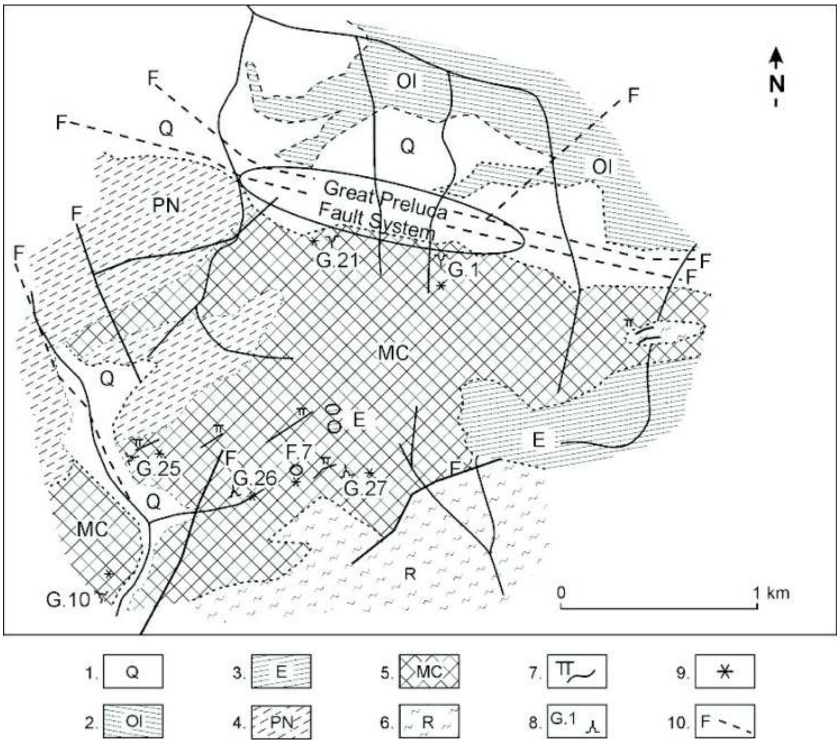

Figure 2. Geological map of the Măgureni Hill, showing the occurrences of sepiolite (modified after KALMÁR et al. 1997)

1 – Quaternary, 2 – Oligocene, 3 – Eocene, 4 – Preluca Nouă Formation, 5 – Măgureni Carbonate Formation, 6 – Răzoare Gneiss Formation, 7 – Pegmatites, 8 – Galleries, 9 – Sepiolite occurrences, 10 – Faults

***2. ábra.** A Măgureni-domb földtani térképe a szepiolit-előfordulásokkal (KALMÁR et al. 1997 után módosítva)*

1 – Kvarter, 2 – Oligocén, 3 – Eocén, 4 – Preluca Nouă Formáció, 5 – Măgureni Karbonát Formáció, 6. Răzoare Gneisz Formáció, 7 – Pegmatitok, 8 – Tárnák, 9 – Szepiolit-előfordulások, 10 – Vetők

The main and rather exclusive mineral of these rocks is the coarse grained, twinned carbonate, dolomite and/or calcite (*Plate I, photo 2*). Beside the carbonate — which represents 95–99% of the rocks — detrital quartz and muscovite, as well small crystals of phlogopite, tremolite and powder-like carbon modification were identified (KALMÁR et al. 1986, 1997).

The MgO content of the carbonatic rocks varies between a few percents in the white calcitic marbles and 18–23w% in the The chemical analyses frequently demonstrate an excess of the MgO, up to a theoretical level of 21.7%.

In the carbonatic rocks tremolite forms white, 0.2–5.0 mm-large, flattened, foliation-oriented, subhedral, twinned prisms. The chemical analysis indicated the presence of small amounts of iron and magnesium.

The metamorphosed carbonatic rocks are massive, banded or, rarely schistose. Near the northern Great Preluca Fault System, these rocks were intensively brecciated, and formed a loose angular autobreccia. The latter is mined in several quarries and is used as a raw material for construction.

The pegmatites and skarn-like contact zones

A great number of pegmatite veinlets and lenses were developed in the paragneisses of the Răzoare Gneiss Formation and in the carbonatic rocks. They form 0.3–2 m-thick, 10–150 m-long, tabular, branched or irregular, frequently zoned bodies. Usually, the zonation is due to the disposition of the quartz- and muscovite-rich levels as well as the tourmaline- and garnet-bearing segregations (KALMÁR 1972b).

The pegmatites consist of quartz, orthoclase, plagioclase (20–30% An), muscovite, tourmaline and almandine. The crystals of these minerals often measure 5–10 cm in size. Aplite and hydrothermal quartz veinlets traverse the main pegmatite bodies.

In the contact zone with the carbonatic rocks, skarn-like, 5–20 cm-thick diopside-magnetite-tremolite-phlogopite lenses have formed. This mineral association is stable at 500–650 °C and 2.0–2.5 kb (HATHWAY & SACHS 1965, WINKLER 1970). The sepiolite-bearing veins occur frequently in the neighbourhood of these reaction zones *(Figure 3).*

The occurrences of sepiolite

The main sepiolite occurrences in the Preluca Mts can be found in the northern slope of the Măgureni Hill (*Figure 2*), and also in its western slope, near to the Valea Arinului hamlet (which is part of the village of Preluca Veche); furthermore , sepiolite is present in the Arinului rivulet (Paltinului Hill), (in a southwards direction from Preluca Veche) and in the prospection trenches of the Socilor Hill (Dealul Corbului village). In the course of the investigations for the present research, sepiolite veins were identified in the dolomitic marbles of the Eastern Preluca Mts (Răzoare,

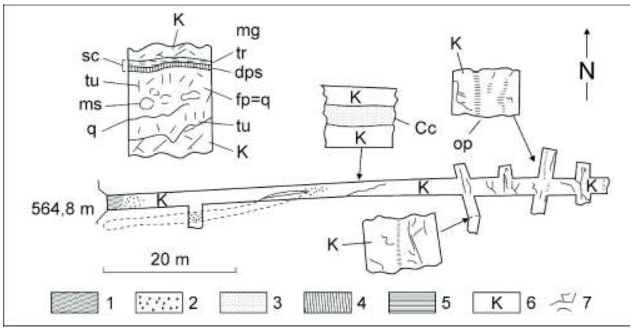

Figure 3. Sketch of Gallery No. 25 (564.8 m)

1 – slope debris, 2 – dolomitic breccia, 3 – dolomite, 4 – skarn-like reaction zone (sc), 5 – sepiolite veins, 6 – dolomitic marble, 7 – thin sepiolite veins, Cc = calcitic-quartzose dolomites, pegmatites, fp = feldspar, ms = muscovite, tu = tourmaline, q = quartz, dps = diopside, mg = magnetite, tr = tremolite, op = opal

3 . ábra. *A 25. sz. táró vázlatos képe (564,8 m)*

1 – lejtőtörmelék, 2 – breccsás dolomit, 3 – dolomit, 4 – szkarnszerű reakció zóna (sc), 5 – szepiolit erek, 6 – dolomitos márvány, 7 – vékony szepiolit erek, Cc = kalcitos-kvarcos dolomitok, pegmatitok, fp = földpát, ms = muszkovit, tu = turmalin, q = kvarc, dps = diopszid, mg = magnetit, tr = tremolit, op = opál

bentonite quarry), in southern Preluca (Aspra) and in the Inău Hill, between the villages Borcut and Inău. Such veins were also evident in the deep boreholes which can be found east of the Preluca Mts (Dămăcuşeni, Suciul de Jos).

Sepiolite veins were first discovered at in the galleries created for sampling the dolomite body from the Măgureni Hill *(Plate I, photo 1)*. These veinlets were traversed in Gallery No. 21 in the northern slope of the Măgureni Hill (POP & ANGELESCU 1981). The strongly-brecciated Upper Dolomitic Member contains disrupted, lenticular veinlets; furthermore, 1–2 cm secondary sepiolite nests were found in dolomitic powder which fills the voids between the breccia elements.

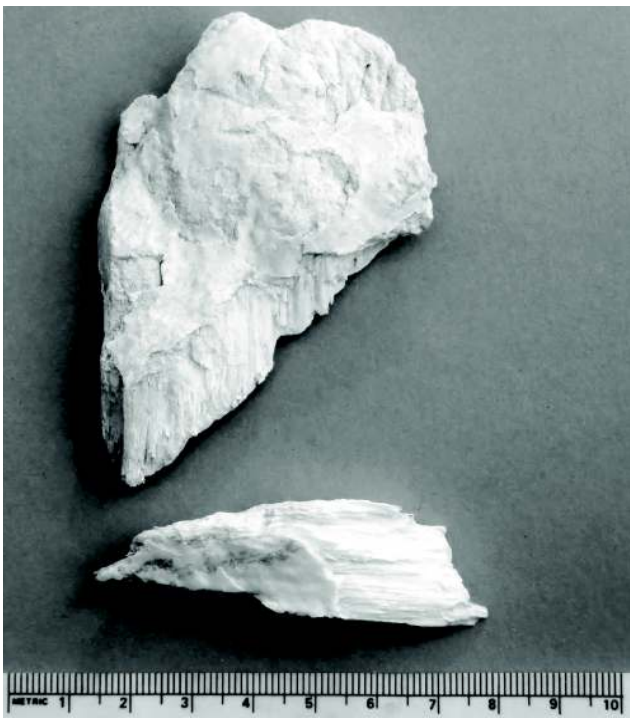

Figure 4. Sepiolite samples from Gallery No. 25

4. ábra. *Szepiolitminták a 25. táróból*

The sepiolite occurs as a compact earthy or fibrous fabric, and is white, yellowish-white, greenish, grey or pink in colour *(Figure 4)*.

A thin vein of sepiolite was found in dolomite gravel. This discovery was the result of the reworking of the basal breccia of the Palaeogene deposits present in a small pit. This pit can be found in the southern slope of Măgureni Hill, near the limit of the Palaeogene sandstones. The most interesting group of sepiolite veins occurs in Gallery No. 25 *(Figure 3)*. Twelve zones of veinlets are traversed here and four of them can be followed directionally. They are developed in carbonate rocks, comprising one is calcitic-graphitic and two are dolomitic marble banks of the Lower Calcitic Member. These rocks are traversed by a pegmatite in the left side of the gallery.

Sepiolite fills a N–S oriented, 1–5 cm-thick discontinuous vein. Here it forms lenticular, felty or nacreous, fibrous aggregates (or felty sheets) in the thinner, millimetre joints of the marbles. The rhombic or polygonal cross-sectioned, 0.5–2 mm-thick sepiolite needles are arranged into parallel or radiating aggregates. They are present with small amounts of

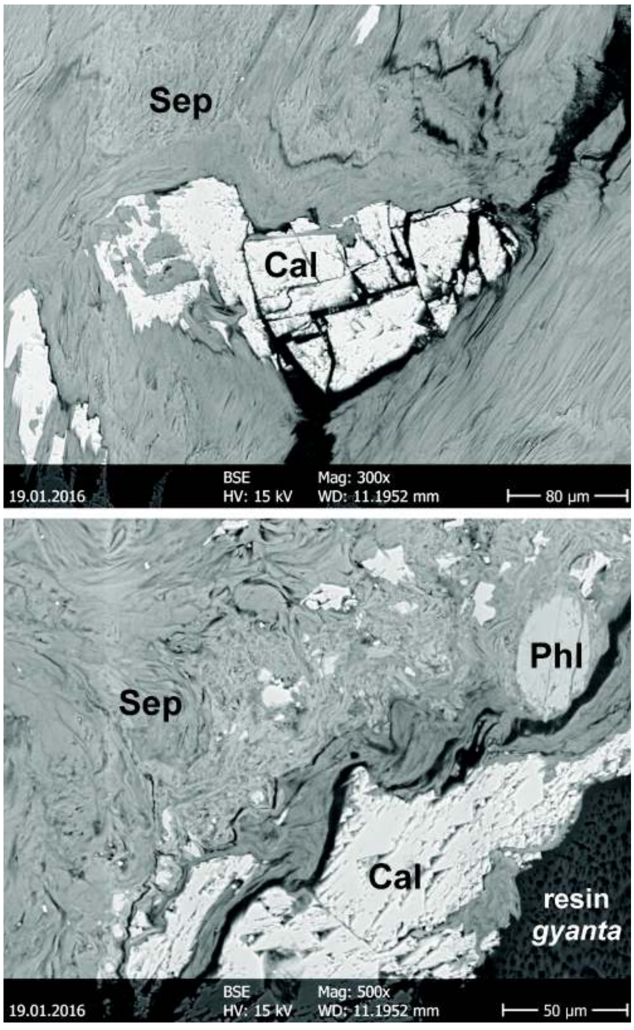

Figure 5. Calcite (Cal) and phlogopite (Phl) in sepiolite (Sep) aggregates. BSE images

5. ábra. *Kalcit (Cal) és flogopit (Phl) szepiolithalmazokban (Sep). Visszaszórt-elektronképek* other clay minerals, secondary carbonates and amorphous silica-drops (KALMÁR et al. 1994a, b).

Alongside the sepiolite there are some other minerals such as talc, nontronite, calcite, phlogopite and opal with a few marcasite impregnations *(Figure 5)*.

The succession of the mineral formation — based on the spatial relationship between the sepiolite-bearing veins and lenses and the homogenization temperature in the two-phase fluid inclusions of the white and limpid calcite crystals (KALMÁR et al. 1997) — is presented in *Table I.*

Table I. Succession of the mineral formation
I. táblázat. *Az ásványok képződési sorrendje*

Minerals	350 °C (?)		212–225 °C		108–132 °C	
Opal						—
Dolomite powdery			-?		—	—
Marcasite					-	-
Calcite II						—
Kaolinite					—	
Sericite			–	—		
Calcite 1				—		
Saponite			–			
Sepiolite			——	–		
Chlorite		—				
Talc	—					

Experimental methods

The *X-ray diffraction analyses* were carried out using a Philips PW 1730 diffractometer under the following conditions: Cu anti-cathode, 40 kV accelerating voltage and 30 mA tube-current, graphite monochromator, and goniometer speed 2 °/min.

The *thermal analyses* were completed with a Derivatograph–PC alongside a simultaneous TG, DTG and DTA set, in a corundum crucible, with a heating speed of 10 °C/minute up to 1000 °C and with Al_2O_3 as inert material.

For *infrared (IR) analysis*, KBr wafers were prepared (1.5%w/w) and scanned from 4000 to 600 cm^{-1} in a Perkin Elmer Fourier Transformation IR spectrometer.

SEM investigations and *EMPA* (Electron Microprobe Analysis) were performed using a Hitachi scanning electron microscope at the University of Debrecen.

Three samples were analysed with the traditional, wet chemical method, where the H_2O and CO_2 contents were determined by *thermogravimetry*.

Electron-microprobe analyses were performed on a sample from Gallery No. 25 using a JEOL JXA-8600 instrument operated in wavelength-dispersive mode; this took place at the Institute of Mineralogy and Geology, University of Miskolc. Operating conditions were: accelerating voltage 15 kV, probe current 20 nA, a final beam diameter of 5 μm, the peak count-times were 10 s and the background count-times were 5 s. The standards employed were: zircon (Si), ilmenite (Ti, Fe), garnet (Al), olivine (Mg), chromium-augite (Ca), MnS_2 (Mn), anorthoclase (Na) and microcline (K). The raw intensity data were corrected using a PAP matrix correction.

Mineralogy of the sepiolite occurrences

In thin section, sepiolite shows a parallel or irregular-radial aggregate of thin, light green or colourless fibres *(Plate I, photo 3).* It has lenticular separations of talc and clay minerals as well as disseminated euhedral carbonate and opaque grains.

In electron-microscopic images sepiolite shows a hair-like aggregate of a few mm long and 0.01–0.02 mm-thick fibres; the latter are composed of 0.05–0.1 mm-thick elementary fibres. Talc, calcite, opal and other minerals occur between the fibres. The biggest m difficulty with respect to the chemical analyses is caused by very small, 0.01-0.02 nm-large opal spherules; these spherules are captured between the elementary sepiolite fibres and are inseparable from them *(Plate I, photo 4, Plate II)*.

The sharp peaks in the X-ray diffractogram *(Figure 6)* revealed the well crystallised character of the studied sample by the set of sharp reflections. The position of the peaks are listed in the *Table II.*

The water molecules in the palygorskite and sepiolite structure can be found in different positions (BRAUNER & PREISINGER 1956, PREISINGER 1961):

— connected to the terminal ion (mainly Mg) of the repeatedly broken octahedral-layer (structural water, bound water, coordination water),

— placed in the channels in the structure (zeolitic or free water), exchangeable with different ions,

— sometimes bound to the external surface (adsorbed water).

Theoretically, the first endothermic peak of sepiolite appears at around 150 °C, representing the release of free water, both from external surfaces and from within the channels. This is followed by two smaller endothermic peaks at 350–450 °C and 500–600 °C, representing the loss of the structurally bound water *(Figure 7)*. According to

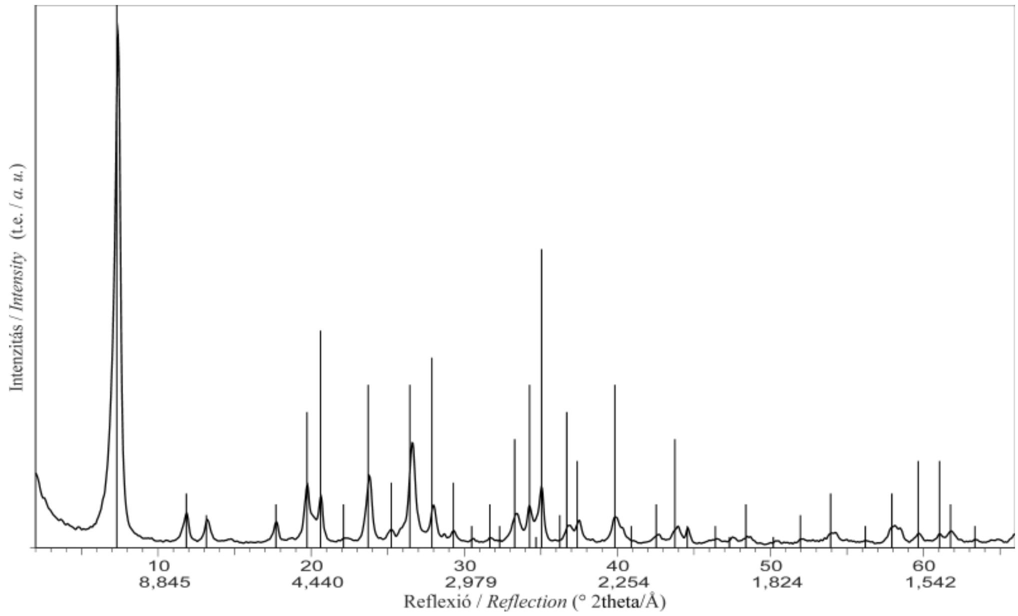

Figure 6. X-ray diffractogram of the Măgureni sepiolite sample (treated with acetic acid), with the reflection of the JCPDS 13-0595 card

6. ábra. *A Măgureni-i szepiolit-minta diffraktogramja (ecetsavazott)a JCPDS 13-0595 kártya reflexióival*

Table II. X-ray powder diffraction data for sepiolite from the Măgureni Hill compared with the corresponding reflections of the JCPDS 13-0595 card

II. táblázat. *A Măgureni-domb szepiolitjának röntgen-pordiffrakciós adatai, összehasonlítva a JCPDS 13-0595 kártya megfelelő reflexióival*

JCPDS		POP & ANGELESCU 1981				Sample 83/a-Gallery 25			
13-0595		SM-1/gal. 21		SM-2/gal. 21		original		fraction < 2μ, treated with acetic acid	
d_{obs}(Å)	I_{rel} (%)	d_{obs}(Å)	I	d_{obs}(Å)	I	d_{obs}(Å)	I_{rel} (%)	d_{obs}(Å)	I_{rel} (%)
12.100	100	12.199	vs	12.099	vs	11.970	100	11.756	100
7.470	10	7.557	w	7.48	w	7.466	6	7.375	7
6.730	6	6.752	w	6.66	vw	6.717	5	6.608	5
5.010	8							4.972	5
4.500	25	4.525	m	4.525	m	4.497	14	4.546	3
								4.466	13
4.310	40	4.337	m	4.295	m	4.306	11		
4.020	8					3.969	1		
3.750	30	3.757	m	3.754	m	3.740	16	3.720	14
3.530	12	3.54	vw			3.539	3	3.501	3
3.370	30	3.373	s	3.351	s	3.351	23		
3.200	35	3.211	m	3.186	m	3.189	9	3.178	8
				3.123	w	3.113	2	3.169	8
3.050	12	3.068	w			3.050	3	3.038	3
2.691	20	2.696	m	2.701	w	2.683	7	2.677	7
						2.674	7		
2.617	30	2.621	m	2.625	m	2.613	9	2.610	8
2.560	55	2.571	m	2.564	m	2.559	14	2.552	12
2.449	25	2.452	w	2.45	w	2.443	4		
						2.433	4	2.437	5
2.406	16	2.409	w	2.406	w	2.396	5	2.394	5
						2.345	1	2.337	2
2.263	30	2.268	m	2.265	m	2.265	6		
2.125	8	2.129	vw	2.126	vw	2.117	2		
2.069	20	2.061	w	2.064	w	2.069	3		
1.921	2					1.912	2		
1.881	8					1.876	2		
1.818	2					1.812	1		

d_{obs} (Å): position of reflection in Å, I_{rel} (%): relative peak intensity (%), m: medium, s: strong, vs: very strong, vw: very weak, w: weak.

d_{obs} (Å): a reflexiók helye Å-ben, I_{rel} (%): relatív csúcsintenzitás (%), m: közepes, s: erős, vs: nagyon erős, vw: nagyon gyenge, w: gyenge.

KIYOHIRO & OTSUKA (1989) the two-step dehydration of bound water is caused by the following two factors: (1) the difference in the activation energy of the dehydration between the water in the unfolded open channel and that in the folded one, and (2) the change in the rate determining process from the water separation process to the water diffusion one.

A further endothermic peak appears at 750–800 °C and this represents the release of OH and the total destruction of the lattice. This peak is immediately followed one of over 800 °C. The latter is an exothermal peak representing the heat released at the formation of a new crystal phase (enstatite).

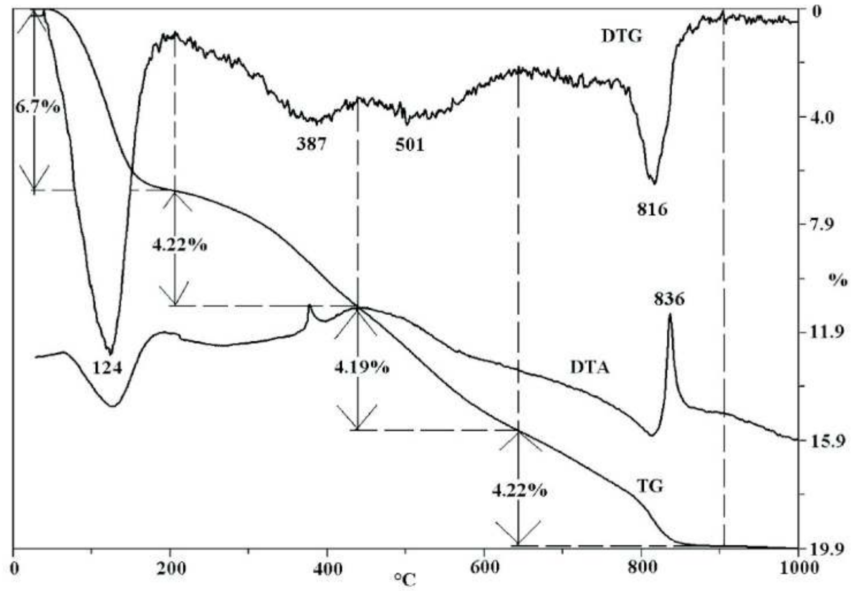

Figure 7. Thermoanalytical curves of the investigated sepiolite
7. ábra. *A vizsgált szepiolit termoanalitikai görbéi*

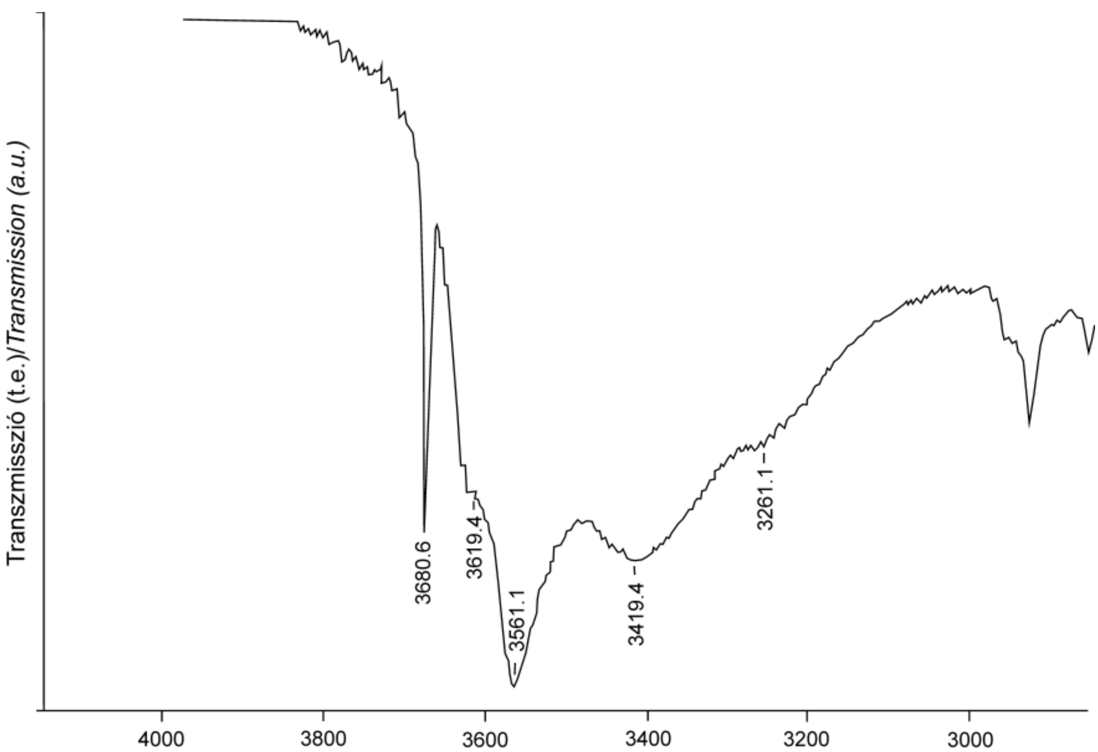

Figure 8. IR adsorption spectra of sepiolite from the Măgureni hills
8. ábra. *A măgureni szepiolit IR spektruma*

However, with respect to the above, different authors posit different proportions to the steps of the mass loss. According to the theoretical calculations, the total water found in sepiolite, with the water which originated from the OH groups, is 19.5 %; the somewhat higher measure of 19.9%, which is occasionally given, is due to the absorbed water.

The bands on the IR spectrum of the samples *(Figure 8, Table III)* are similar to those observed by HAYASHI et al. (1969) and VAN DER MAREL & BEUTELSPACHER (1976).

Table III. Characteristic IR adsorption bands of sepiolite from the Măgureni Hill
III. táblázat. *A Măgureni-domb szepiolitjának IR adszorpciós sávjai*

HAYASHI et al. 1969	VAN DER MAREL & BEUTELSPACHER 1976	Măgureni KALMÁR et al. 1997	Assignation
cm^{-1}			
3678.6	3685	3680.6	stretching of the OH-valence coordinated to octahedral layers *az oktaéderes rétegben lévő OH csoportok vegyértékrezgése*
3622.8	3620	3619.4	O-H stretching of the Mg (Fe)-coordinated structural water at the end of the octahedral layer *az oktaéderes réteg végén lévő Mg (Fe)-hoz koordinálódó szerkezeti kötött vízek OH vegyértékrezgése*
3560.5	3560	3561.1	O-H stretching of the Mg (Fe)-coordinated structural water and of the free (zeolitic) water at the end of the octahedral layer *az oktaéderes réteg végén lévő Mg (Fe)-hoz koordinálódó szerkezeti kötött víz és szabad (zeolitos) víz OH vegyértékrezgése*
3350	3410–3380	3419.4	O-H stretching of the Mg (Fe)-coordinated structural water and of the free (zeolitic) water at the end of the octahedral layer *az oktaéderes réteg végén lévő Mg (Fe)-hoz koordinálódó szerkezeti kötött víz és szabad (zeolitos) víz OH vegyértékrezgése*
3200	3245	3261.1	O-H stretching of free (zeolitic) water molecules in the canals and O-H bending of H_2O molecules (overtone) *a csatornákban lévő szabad (zeolitos) víz O-H vegyértékrezgése és a H_2O molekulák deformációs rezgésének felhangja*

Chemistry

Sepiolite is a magnesium-silicate-hydroxide mineral with an ideal formula; $Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$. Most calculated structural formulae for sepiolite indicate a minor amount of Al^{4+} and/or Fe^{3+}; the latter substitute for Si^{4+} in the tetrahedral (*T*) sites. Although the Mg-rich variety is the most common, sepiolite-type minerals present a wide range of substitution. This range is mostly accommodated at the *M* (metal) sites in the octahedral layer (WEAVER & POLLARD 1973).

For the determination of the crystal-chemical properties of sepiolite from Măgureni Hill, several wet chemical and electron-microprobe analyses were prepared.

The formulae, calculated from the wet chemical analyses *(Table IV)* are; $(Mg_{3.02}Al_{0.40}Ca_{0.18}Fe^{3+}_{0.14}Fe^{2+}_{0.11}Na_{0.10}K_{0.03})_{\Sigma=3.98}(Si_{5.66}Al_{0.34})_{\Sigma=6.00}O_{15}(OH)_{2.00} \cdot 4.67H_2O$ and $(Mg_{3.63}Al_{0.16}Fe^{3+}_{0.07}Fe^{2+}_{0.04}Na_{0.04}K_{0.03}Ca_{0.01})_{\Sigma=3.98}(Si_{5.89}Al_{0.11})_{\Sigma=6.00}O_{15}(OH)_{2.00} \cdot 3.45H_2O$ (for the material of Gallery No. 19), and $Mg_{4.01}Si_{5.99}O_{15}(OH)_{2.00} \cdot 6.00H_2O$ (for the material of Gallery No. 25).

The material of Gallery No. 19 has rather a mix of cation occupancy at both the *M* and *T* sites, although the excess of some elements (e.g. Ca, Al) could be attributed to mineral inclusions (e.g. calcite, clay minerals). The rather low water content indicates a partly dehydrated condition of the investigated specimens.

The chemistry of the material from Gallery No. 25 corresponds to an essentially pure end-member sepiolite.

The results of 12 individual electron-microprobe spot analyses, prepared on a sample from Gallery No. 25, as well as the cation numbers for 16 oxygens are shown in *Table V*. The empirical formula calculated from the average values is $(Mg_{4.01}Na_{0.06}Ca_{0.02})_{=4.09}(Si_{5.92}Al_{0.06}Fe_{0.01})_{=5.99}O_{15}(OH)_2 \cdot 6H_2O$; this is in good agreement with the wet chemical results.

Table IV. Wet chemical analyses of sepiolite from Măgureni Hill (wt%)
IV. táblázat. *A Măgureni-domb szepiolitjának nedves kémiai elemzési adatai (tömeg%)*

Gallery No.	19/2	19/4	25
SiO_2	53.30	58.60	55.54
TiO_2	0.00	0.00	0.00
Al_2O_3	5.92	2.30	0.00
Fe_2O_3	1.75	0.86	0.00
FeO	1.19	0.50	0.00
MnO	traces	0.02	0.00
MgO	19.09	24.20	24.89
CaO	1.55	0.09	0.00
Na_2O	0.48	0.18	0.00
K_2O	0.24	0.26	0.00
H_2O^+	16.00	13.22	19.44
CO_2	traces	0.00	0.00
P_2O_5	0.25	0.00	0.00
Total/ Összesen	**99.77**	**100.23**	**99.78**
Cation numbers based on 16 oxygens *Kationszámok 16 oxigénre*			
Si	5.66	5.89	5.99
Ti	0.00	0.00	0.00
^{IV}Al	0.34	0.11	0.00
$^{IV}Fe^{3+}$	0.00	0.00	0.00
Σ*T*	**6.00**	**6.00**	**5.99**
^{VI}Al	0.40	0.16	0.00
$^{VI}Fe^{3+}$	0.14	0.07	0.00
Fe^{2+}	0.11	0.04	0.00
Mn	0.00	0.00	0.00
Mg	3.02	3.63	4.01
Ca	0.18	0.01	0.00
Na	0.10	0.04	0.00
K	0.03	0.03	0.00
Σ*M*	**3.98**	**3.98**	**4.01**

Table V. Electron-microprobe analyses of sepiolite from Gallery No. 25, Măgureni Hill (wt%)
V. táblázat. *A 25. táró (Măgureni-domb) szepiolitjának elektron-mikroszondás elemzései tömegszázalékban*

Anal. No.	1	2	3	4	5	6	7	8	9	10	11	12	Average/ *Átlag*
SiO_2	54.47	54.62	54.71	54.64	54.75	55.55	54.90	55.20	54.93	54.87	54.83	54.84	54.86
TiO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00
Al_2O_3	0.55	0.51	0.52	0.49	0.51	0.42	0.48	0.39	0.50	0.44	0.46	0.41	0.47
Fe_2O_3*	0.15	0.07	0.13	0.05	0.14	0.13	0.11	0.14	0.14	0.07	0.09	0.09	0.11
MgO	25.28	25.21	25.08	25.27	24.93	24.21	24.92	24.53	24.71	24.97	24.98	25.05	24.93
CaO	0.14	0.14	0.15	0.09	0.15	0.06	0.11	0.20	0.19	0.10	0.09	0.10	0.13
MnO	0.00	0.03	0.00	0.04	0.05	0.06	0.03	0.00	0.04	0.04	0.00	0.04	0.03
Na_2O	0.37	0.31	0.27	0.30	0.33	0.17	0.26	0.23	0.27	0.31	0.33	0.27	0.28
K_2O	0.02	0.02	0.00	0.02	0.00	0.00	0.00	0.03	0.00	0.00	0.02	0.00	0.01
H_2O	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**19.45
Total/ Összesen	**80.97**	**80.92**	**80.87**	**80.89**	**80.86**	**80.59**	**80.82**	**80.71**	**80.77**	**80.80**	**80.81**	**80.84**	**100.27**
Cation numbers based on 16 oxygens *Kationszámok 16 oxigénre*													
Si	5.88	5.89	5.90	5.89	5.91	5.99	5.92	5.96	5.93	5.92	5.92	5.92	5.92
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	0.07	0.06	0.07	0.06	0.06	0.05	0.06	0.05	0.06	0.06	0.06	0.05	0.06
Fe	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
ΣT	**5.96**	**5.96**	**5.98**	**5.95**	**5.98**	**6.05**	**5.99**	**6.02**	**6.00**	**5.99**	**5.99**	**5.98**	**5.99**
Mg	4.07	4.05	4.03	4.06	4.01	3.89	4.01	3.95	3.98	4.02	4.02	4.03	4.01
Ca	0.02	0.02	0.02	0.01	0.02	0.01	0.01	0.02	0.02	0.01	0.01	0.01	0.02
Mn	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.08	0.06	0.06	0.06	0.07	0.04	0.05	0.05	0.06	0.06	0.07	0.06	0.06
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ΣM	**4.17**	**4.13**	**4.11**	**4.13**	**4.10**	**3.95**	**4.07**	**4.02**	**4.06**	**4.09**	**4.10**	**4.10**	**4.09**

n.d. = not determined / *nincs meghatározva.*
* Total Fe was regarded as Fe_2O_3. / *Az összes vasat Fe_2O_3-ként vettük figyelembe.*
** Calculated from stoichiometry. / *A sztöchiometrikus összetételből számolva.*

Conditions of formation

Our observations show a close association between the carbonatic host rocks, the pegmatitic lenses, and the sepiolite veins.

In a later phase of the metamorphic recrystallisation of the siliciclastic rocks of the Preluca Mts, Si-, Al- and Fe-bearing hot fluids from the deeper zone penetrated the carbonate rocks, along the lithological discontinuities and fractures. Due to their reaction with the carbonatic host rocks, thin skarn-like rims formed around the pegmatitic lenses.

The crystallisation of minerals from pegmatitic fluids was a long process occuring with a progressively decreasing temperature. The whole process started with the formation of garnet, black tourmaline, oligoclase, microcline and smoky quartz, then came the formation of biotite, muscovite, albite and milky quartz and, finally, secondary orthoclase and translucent, limpid (euhedral) quartz crystallisation. In a later phase, the newly-formed pegmatitic body was broken and the resulting cracks were filled, either by quartz-albite-orthoclase aplite, or by milky quartz. However, despite the crystallisation of main pegmatitic minerals, the energy of deep sources was not exhausted. Thus the ascension of the aqueous fluids continued: they ascended into the fractures of the carbonatic rocks and reacted with them, forming a hydrothermal association. The latter was consisting of three mineral assemblages: (i) the high temperature association (talc, chlorite), (ii) the medium temperature minerals (sepiolite, saponite, white calcite, sericite) and (iii) the "colder" association: kaolinite, limpid calcite, marcasite and opal.

The thermal conditions of the last two phases were determined by palaeothermometry. Thus, the biphasic inclusion in the white calcite crystals homogenised at 212–225 °C, and in "colder" limpid calcite, at 108–132 °C.

Chemical analyses confirm the pure, iron-free character of sepiolite taken from Gallery No. 25.

The sepiolite samples investigated earlier, taken from the northern slope of the Măgureni Hill (Galleries No. 1, 21, 22) presented 0.1–0.3 iron ions per formula unit in the octahedral site (POP & ANGELESCU 1981). Therefore, it can be suggested, that the Mg/Fe ratio of sepiolite depends on the MgO content of the host rock. This is proved by our observations in accordance with the earlier published data (WOLLAST et al. 1968). The crucial condition of the sepiolite formation is the pH range, i.e. between 8.0–9.2 assured by the presence of buffering Ca^{2+} ions.

Potential utilisation of sepiolite

The sepiolite accumulations from the Măgureni Hill are studied, between 1978–1986, by repeated experiences for establish the suitable method for the extraction and enrichment of useful sepiolitic concentrate. The optimal results were obtained in the laboratories of the Research and Project Institute for Ceramics and Building Materials (ICPMC) at Cluj-Napoca in Romania (CHELBEA et al. 1978).

The concentration of sepiolite was based in 3.5 m^3 of rock samples, extracted from Gallery No. 25. The sepiolitic raw material was milled in a ball and tube mill and classed in a helicoidally class or linked in circuit with a hydrocyclon (Ø>300 mm). The slime was flocculed with polyacrilamide and treated with HCl 1:10.The neutralised, filtered and dried sepiolite concentrate contains 80% sepiolite, 15% other clay minerals, 3% quartz and 2% HCl-insoluble carbonates. In this way, were obtained 18–20 kg/m^3 of sepiolitic concentrate.

The iron free sepiolitic concentrate from the Măgureni Hill is an ideal filling material for (i) the preparation of pesticides and insecticides, (ii) fillings in thermo-resistant plastic materials, (iii) pharmaceutical industry, and (iv) for molecular filters.

Conclusions

Sepiolite and accompanying clay and non-clay minerals were formed through the reaction of residual, neutral or alkaline, SiO_2-bearing aqueous solutions with carbonatic, Mg-rich wall-rocks, related to the formation of the pegmatitic bodies. Thus, they mark one of the last steps of mineral formation; this step closed the metamorphic processes long before the deposition of the Mesozoic and Cenozoic sedimentary cover.

The sepiolite of these occurrences shows a well-ordered lattice, having the chemical composition close to the theoretical formula of iron free sepiolite.

Therefore, these clay minerals are can be put to highly productive use in the chemical and pharmaceutical industries.

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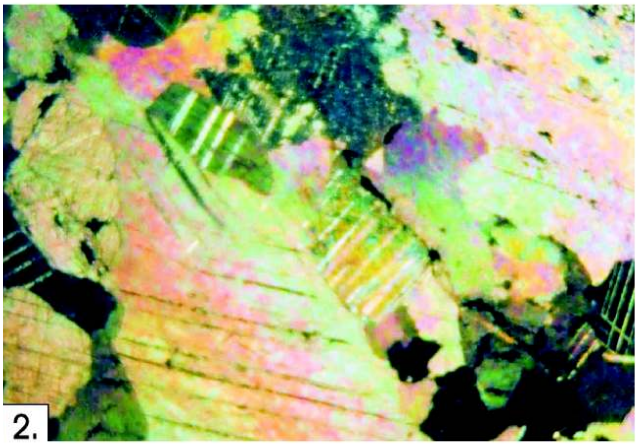
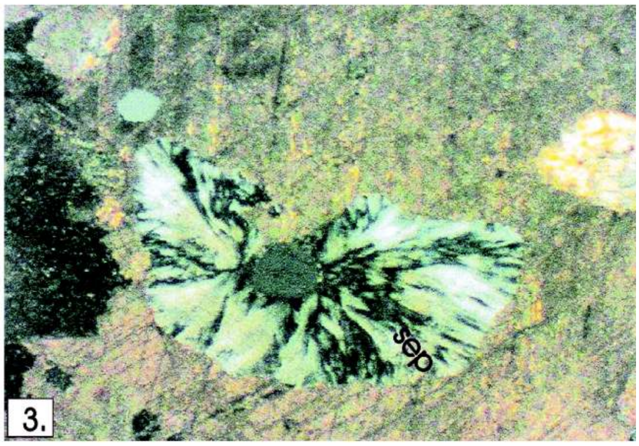
Kézirat beérkezett: 2016. 05. 12.

Plate I — I. tábla





1. Preluca Veche: old pits, with the Măgureni Hill in the background
2. Coarse grained calcitic-dolomitic crystalline limestone, Gallery No. 2, 86 m, northern slope of the Măgureni Hill. Thin section, + nicols, Width of the picture 1 cm
3. Sepiolite rosette in calcitic-dolomitic crystalline limestones. Gallery No. 25, Valea Arinului, 11 m. Thin section, + nicols, Width of the picture 5 mm
4. Sepiolite (sep), oriented fibres and isolated elementary fibres. Talc (st), opal spherules (op), calcite (cc). Gallery No. 25, Valea Arinului, 16 m, third vein group

1. Preluca Veche: régi bányák, háttérben a Măgureni-dombbal

2. Durvaszemcsés, kalcitos-dolomitos kristályos mészkő, 2. táró, 86 m, a Măgureni-domb északi lejtője. Vékonycsiszolat, keresztezett nikolok, képszélesség 1 cm

3. Szepiolit rozetta a kalcitos-dolomitos kristályos mészkőben. 25. táró, Valea Arinului, 11 m. Vékonycsiszolat, keresztezett nikolok, képszélesség 5 mm

4. Szepiolit (sep), orientált szálak és elszigetelt rostok. Talk (st), opálgömbök (op) kalcit (cc). 25. táró, Valea Arinului, 16 m, a harmadik telércsoport

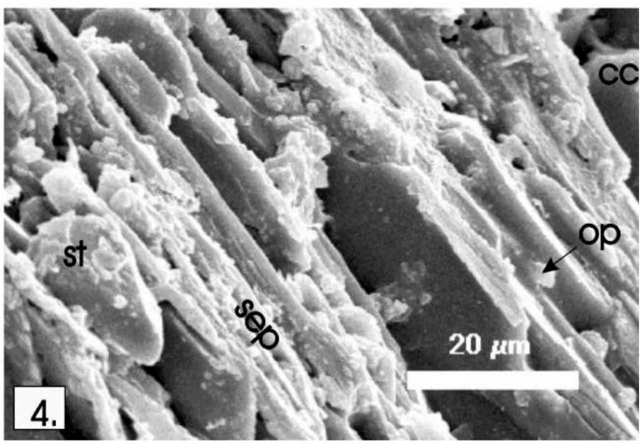
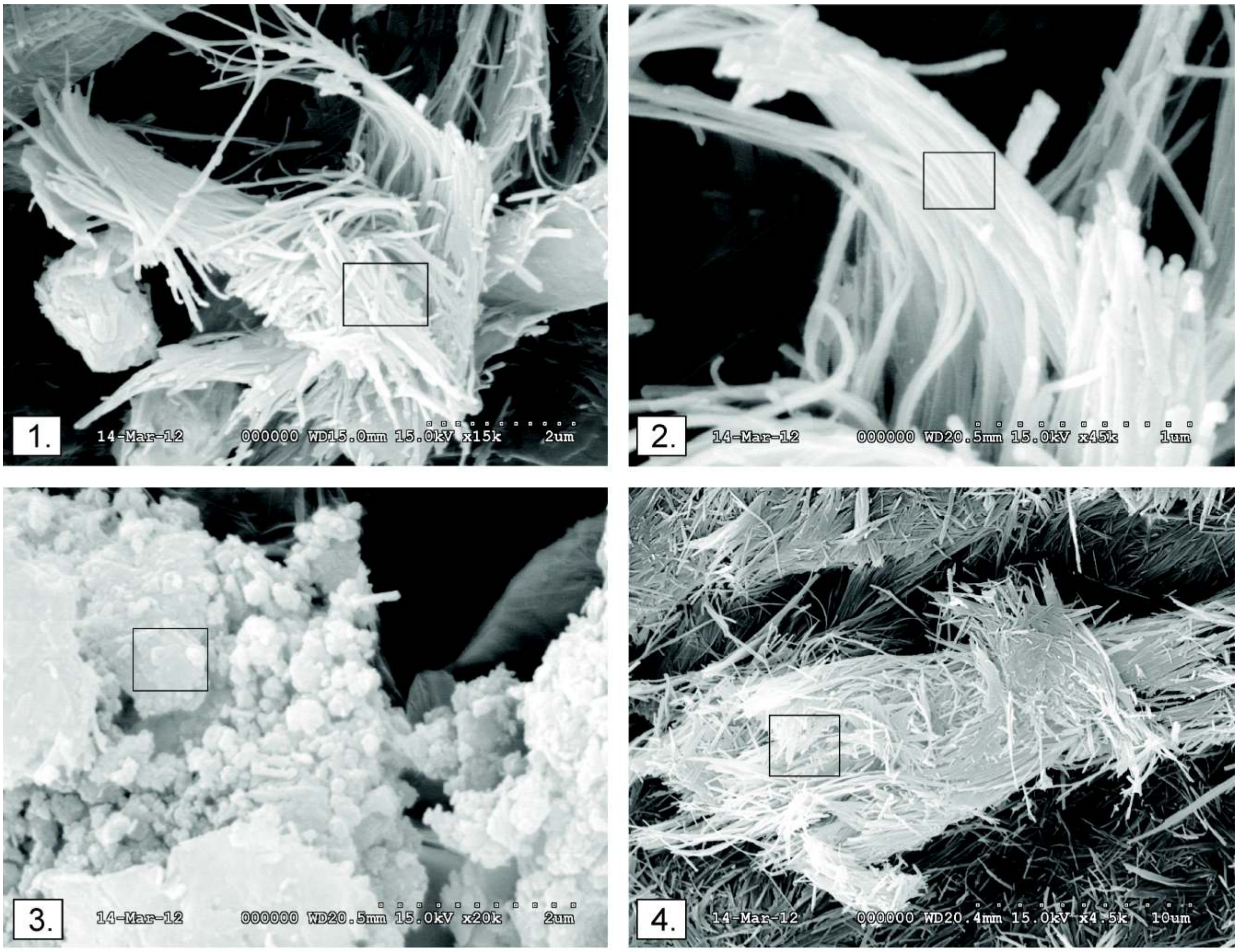


Plate II — II. tábla



1-4. Morphology of sepiolite from the thin veinlets (Gallery No. 25). SEM image

1-4. A szepiolit megjelenése a vékony telérekben (25. tárό). Pásztázó elektronmikroszkópos kép