MINERALOGIA POLONICA
Vol. 7, No 2 — 1976

Grażyna CICHOŃ *

SEPIOLITE FROM RUDNO

UKD 549.623.83(438.312)

Abstract. The paper presents the results of microscopic and X-ray examinations, as well as of thermal, infrared spectroscopic and chemical analyses of sepiolite which occurs as a secondary mineral in the melaphyres of Rudno near Krzeszowice. Sepiolite from Rudno is a very fine-crystalline variety exhibiting fibrous habit. Its structural formula is: $(Si_{11.73}Al_{0.27})(Mg_{7.67}Fe^{3+}{}_{0.15}Al_{0.16})O_{30}[OH]_4[OH_2]_{3.70}Ca_{0.12}K_{00.4}Na_{0.10} \cdot nH_2O$. In the samples studied sepiolite is often accompanied by saponite and frequently also by quartz and calcite.

The igneous rocks in the vicinity of Kraków abound in secondary minerals, a part of which are rare. Some of them were mentioned or described in a general way by Kreutz (1869), Zuber (1886) and Rozen (1909, 1914). A more comprehensive study was devoted to the amethyst and heulandite from Rudno (Gaweł 1947; Piekarska, Gaweł 1954).

Sepiolite under its former name of pilolite was mentioned by Rozen (1909, 1914), who reported the results of its chemical analysis. Yet, since X-ray data were not available then, it is impossible to say whether the sample analysed by Rozen was pure sepiolite or contained admixtures of other minerals, *e.g.* saponite.

Chemical analysis of almost pure sepiolite from Rudno and Alwernia was published by Żabiński (1960), whereas Stoch (1974) presented the DTA curve of sepiolite from Alwernia. It is evident then that the information on sepiolite from Rudno has been so far only fragmentary.

This paper presents more complete data on sepiolite. This mineral can be found in exhausted melaphyre quarries, specifically in the weathered parts of these rocks. The specimens subjected to examinations were partly collected by the author during field investigations and partly derived from the collections of the Department of Mineralogy and Geochemistry of the Academy of Mining and Metallurgy in Kraków.

---

* Silesian University, Institute of Geology, Sosnowiec (Poland), ul. Mielczarskiego.

MACRO- AND MICROSCOPIC CHARACTERISTICS OF SEPIOLITE

Sepiolite concentrations occur in melaphyre fissures in the form of white or light-beige plates up to 3 mm thick, the area of which amounts to a dozen or so square centimetres. The fibrous habit of sepiolite is usually conspicuous. There are also cases when one surface of the *plate* is made up of large scales scapy to the touch (it is most likely saponite) whereas the other surface consists of fibres up to some mm in length. The fibres resemble wood splinters, readily splitting off the platy surface on which they rest. In places they have green, red or black colour.

Sepiolite fibres are not always parallel to one another; in thin section they sometimes display wavy, fanlike or random orientation. They have green-yellowish or orange interference colours and show almost straight extinction. The light, however, is not extinguished simultaneously in the whole fibres, which implies that the fibres are made up of still smaller elements, invisible at microscope magnifications. Due to such structure, the determination of some optical properties of sepiolite presents considerable difficulties. The sign of fibre elongation is positive. The extreme refractive indices determined by immersion method are 1.50—1.52. Those features are typical of sepiolite investigated by e.g. Nagy and Bradley (1955) and Chambers (1959).

In thin section, areas of sepiolite coloured red, brown and green are visible. In the red-brown parts, pigment of iron oxides or hydroxides is discernible whereas the green part is presumably coloured by minerals of the seladonite type.

X-RAY AND ELECTRON MICROSCOPE INVESTIGATIONS

X-ray examinations were carried out in a Rigaku-Denki diffractometer using Cu-K_{α} radiation. The results are presented in Figure 1 and Table 1 and compared with the diffraction patterns of sepiolites from Eski-Shir (Turkey) and Little Cottonwood (USA). In most samples of sepiolite from

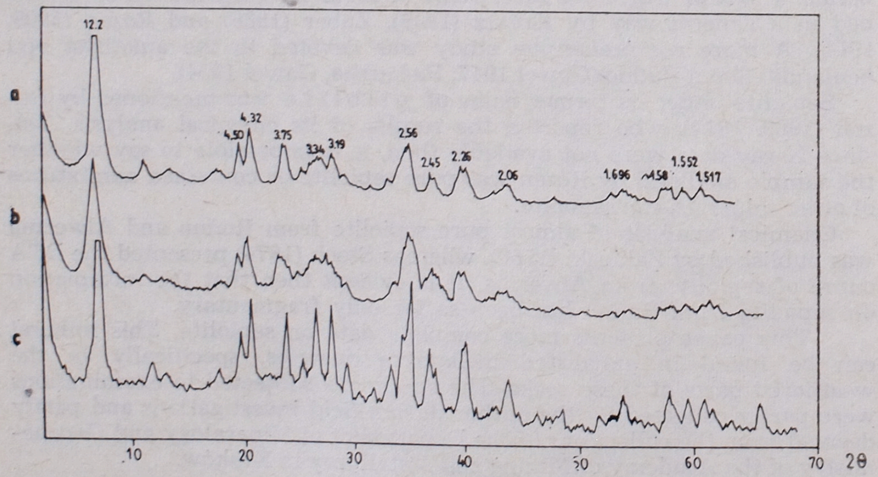


Fig. 1. X-ray powder diffraction patterns of sepiolites
a) Rudno, *b)* Eski-Shir — Turkey, *c)* Little Cottonwood — USA (after Brindley 1959)

Table 1

X-ray powder diffraction data for sepiolites

Rudno		Eski-Shir		Little Cottonwood (after Caillère, Hénin 1961)	
d (Å)	I	d (Å)	I	d (Å)	I
12.2	vs	12.3	vs	12.05	100
7.60	w	7.6	w	7.47	10
6.70	vwbr	6.7	vwbr	6.73	5
5.04	wbr	5.03	vwbr	5.01	7
4.50	m	4.52	m	4.498	25
4.32	s	4.30	s	4.306	40
				4.022	7
3.75	m	3.76	m	3.750	30
3.50	vw			3.533	12
3.34	mbr	3.33	mvbr	3.366	30
3.19	m	3.19	m	3.196	35
3.05	wbr	3.06	vwbr	3.050	12
				2.932	4
2.82	vw			2.825	7
				2.771	4
2.69	vw	2.68	vw	2.691	20
2.612	m	2.610	m	2.617	30
2.583	s	2.58	s	2.586	br
2.568	s			2.560	55
				2.479	5
2.453 }	mbr	2.44 }	mbr	2.449	25
2.402 }		2.40 }		2.406	15
2.260	m	2.266	m	2.263	30
				2.206	3
2.111	vwbr	2.139	vw	2.125	7
		2.087 }	wbr		
2.065	w	2.065 }		2.069	20
				2.033	4
		1.943	vwbr	1.957	4
				1.921	2
1.875	vw	1.890	vw	1.881	7
				1.760	6
1.726	vw	1.723 }	vwbr		
1.696	w	1.690 }		1.700	10
1.598 }	mbr	1.601 }	wbr	1.637	3
1.578 }		1.573 }		1.592	10
1.552	m	1.547	w	1.550	15
1.517	m	1.517	w	1.518	15
1.502	wbr	1.504	w	1.502	8

Rudno an admixture of saponite were detected. Identification of saponite admixture was aided by glycol treatment. As a result of this procedure, the basal saponite reflection was displaced from 15.4 Å to about 17.3Å, while the reflection 12.4 Å corresponding to sepiolite did not change its position.

Electron micrographs made by B. Kwiecińska on Jeol 100 C transmission microscope have revealed a very fine-crystalline character of sepiolite. It appears in the form of tangled fibrous crystals that sometimes form fanlike aggregates (Phots. 1, 2). Even at high magnifications (× 80 000—120 000) sepiolite fibres overlap, producing diffused image and making diffraction on single crystals difficult.

THERMAL ANALYSES

A sepiolite sample subjected to thermal analysis in a F. Paulik, J. Paulik, L. Erdey derivatograph gave the following peaks on the DTA curve (Fig. 2): endothermic peaks at 160° and 805°C, corresponding to dehydration of the sample, and an exothermic peak at 830°C, with is regarded (Kulbicki 1959) as the beginning of enstatite formation. The diffraction pattern of sepiolite from Rudno heated at 850°C showed two, yet not very intesive, reflections (about 2.90 and 3.20 Å) corresponding to enstatite. Distinct enstatite and quartz reflections appeared only on the diffraction pattern of sepiolite sample heated at 1000°C.

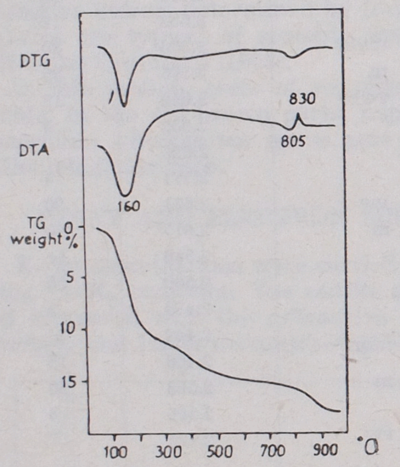


Fig. 2. Thermal curves of sepiolite from Rudno

The respective temperature peaks and the general shape of the DTA curve of sepiolite from Rudno are similar to those of sepiolites from Eski-Shir and Vallecas, particularly to the latter mineral (Langier-Kuźniarowa 1967).

From the TG curve weight-losses of the sample corresponding to three kinds of water in the structure were calculated. The results are presented in Table 2 and compared with those given by other authors.

Table 2

Weight loss of (%) determined by thermogravimetric method

Water type	Rudno	Ampandrandawa	Vallecas	Eski-Shir
Zeolitic water < 250°C	11.2	11.4	11.5	13.6
Coordination water 250° — 600°	5.8	5.8	5.8	5.6
Constitutional water > 600°C	2.3	2.4	2.4	2.4

INFRARED SPECTROSCOPIC INVESTIGATIONS

The infrared absorption spectrum of sepiolite from Rudno (Fig. 3) was recorded on UR-10 (Zeiss) apparatus using KBr disks. It was compared with the spectrum of sepiolite from Eski-Shir. Characteristic of the mineral studied are: intensive absorption bands about 1020 and 470 cm^{-1},

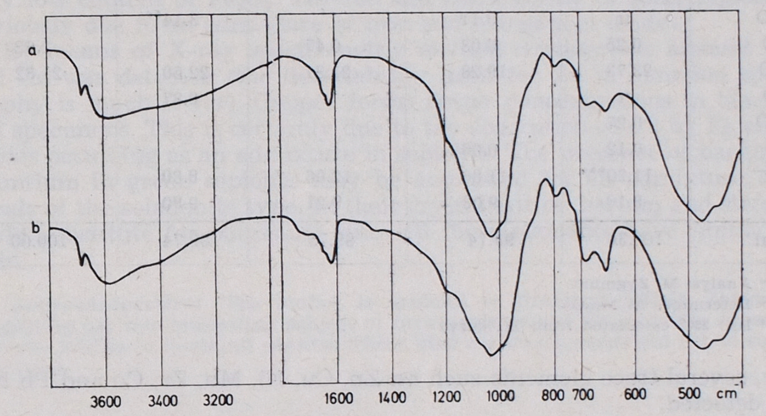


Fig. 3. Infrared absorption spectra of sepiolites
a) Rudno, *b)* Eski-Shir — Turkey

corresponding to Si-O stretching and bending vibrations, respectively; a strong band 660 cm^{-1} produced by OH libration in Mg_3OH units; a composite band 1620—1640 cm^{-1} due to bending vibrations of various types of H_2O molecules; a broad band 3400—3600 cm^{-1} originating from water stretching vibrations; and a weak but sharp band 3680 cm^{-1} produced by OH stretching vibrations in Mg_3OH groupings.

CHEMICAL AND X-RAY SPECTROMETRIC INVESTIGATIONS

Table 3 shows the results of chemical analysis of sepiolite from Rudno, the results of analysis of sepiolite from Rudno presented by Żabiński (1960), and the data for sepiolites from Ampandrandawa, Little Cottonwood and Vallecas published in the literature.

Structural formula on the basis of $O_{30}(OH)_4(OH_2)_4$ (Serna *et al.* 1975) is as follows: $(Si_{11.73}Al_{0.27})(Mg_{7.67}Fe^{3+}_{0.15}Al_{0.16})O_{30}[OH]_4[OH_2]_{3.70}Ca_{0.12}K_{0.04}Na_{0.10}\cdot nH_2O$.

X-ray spectrometric analysis carried out on a Rigaku-Denki apparatus has confirmed the presence of the components listed in Table 3. Additio-

Table 3

Sepiolite analyses (weight %)

Component	Rudno *	Rudno (Żabiński 1960)	Ampandrandawa (Caillère 1936b fide Caillère, Hénin 1961)	Little Cottonwood (Nagy, Bradley 1955)	Vallecas (Martin, *et al.* fide Kulbicki 1959)
SiO_2	54.09	53.86	52.50	52.97	70.57
Al_2O_3	1.70	1.54	0.60	0.86	2.79
Fe_2O_3	0.90	3.86	2.90	0.70	2.20
FeO			0.70		
MnO	tr	0.17		3.14**	
CaO	0.25	0.03	0.47		2.62
MgO	23.73	19.28	21.31	22.50	21.82
CuO	tr			0.87	
Na_2O	0.27				
K_2O	0.12	0.06			
H_2O^-	11.20***	11.86	12.06	8.80	
H_2O^+	8.10	9.08	9.21	9.90	
Total	100.36	99.74	99.75	99.74	100.00

* Analyst M. Zygmunt
** Determines as Mn_2O_3
*** H_2O 250° calculated from TG curve

nally, several trace elements such as: Zn, Cu, Ni, Mn, Zr, Co and Pb have been detected.

Sepiolite samples of green, red and black colour were also analysed for some trace elements, using a PGS-2 spectrograph. The results are given in Table 4.

Table 4

Minor elements in sepiolites from Rudno (emission spectrographic analysis)

Chemical element	Green variety	Black variety	Red variety
Zn	—	—	—
Pb	tr	tr	tr
Ni	+	+	+
Mn	+	++	+
Cu	+	++	++
Co	—	+	—
Ba	++	tr	—
Sr	++	+	+
V	+	+	+
Cr	—	—	—
Ti	+	+	+

Explanation: (−) — non-detected, tr — spectral traces, (+) — contents just above the limits of detectability, (++) — larger concentrations.

DISCUSSION

The secondary minerals noted in the melaphyres in the vicinity of Kraków formed under specific hydrothermal and weathering conditions. This is evidenced by the mode of occurrence of those minerals, as well as by the concentrations of some trace elements.

Sepiolite from Rudno represents a very fine-fibrous variety and may be compared with sepiolite from Vallecas (Brindley 1959; Kulbicki 1959; Serna *et al.* 1975; Caillère, Hénin 1961). Taking into consideration the chemical composition, Caillère and Hénin (1961) have distinguished some varieties of sepiolite: aluminium, iron and iron-nickel. Sepiolite from Rudno is characteristic by a rather low Al_2O_3 content and, in some specimens, very low content of Fe_2O_3. The red and black colour of some sepiolites is obviously due to an admixture of iron and manganese oxides.

By means of X-ray spectrometric method considerable amount of Zn and Cu was detected (the detectability limit for Zn in emission spectrography is much lower). Copper forms larger concentrations in black and red specimens. This is certainly due to the absorption of Cu by Fe and Mn oxides occurring as an admixture in sepiolite. The presence of barium and strontium in green sepiolite may be accounted for an admixture of minerals of the seladonite type. In their crystal lattice, barium and strontium could substitute for potassium since all these elements have similar ionic radii.

Acknowledgements. The author is grateful to Professor Witold Żabiński for suggesting her this interesting subject of investigations and for scientific supervision. She also wishes to thank all persons whose kind assistance permitted her to complete this work.

REFERENCES

BRINDLEY G. W., 1959 — X-ray and electron diffraction data for sepiolite. *Amer. Min.* 44.

CAILLÈRE S., HÉNIN S., 1961 — Sepiolite. The X-ray identification and crystal structures of clay minerals, Brown G.-ed. *Miner. Soc.*

CHAMBERS G. P., 1959 — Some industrial application of the clay mineral sepiolite. *Silicates Industr.* 24, 4.

GAWEŁ A., 1947 — Geologiczne warunki występowania soli niebieskiej, ametystu i fiołkowego fluorytu. *Rocznik PTG* 17.

KREUTZ S., 1869 — Skały plutoniczne w okolicy Krzeszowic. *Rocznik Tow. Nauk. Krakowskiego.*

KULBICKI G., 1959 — High temperature phases in sepiolite, attapulgite and saponite. *Amer. Min.* 44.

LANGIER-KUŹNIAROWA A., 1967 — Termogramy minerałów ilastych. Wyd. Geolog. Warszawa.

NAGY B., BRADLEY W. F., 1955 — The structural scheme of sepiolite. *Amer. Min.* 40.

PIEKARSKA E., GAWEŁ A., 1954 — Heulandyt z Rudna koło Krzeszowic. *Rocznik PTG* 22.

ROZEN Z., 1909 — Dawne lawy W. Ks. Krakowskiego. *Rozpr. Wydz. Matem.-Przyr. Akad. Umiej. w Krakowie* 49.

ROZEN Z., 1914 — Pilolit z Miękini. *Rozpr. Wydz. Matem.-Przyr. Akad. Umiej. w Krakowie* 54.

SERNA C., RAUTUREAU M., PROST R., TCHOUBAR C., SERRATOSA J. M., 1975— Étude de la sépiolite a l'aide des données de la microscopie électronique, de l'analyse thermopondérale et de la spectroscopie infrarouge. *Bull. Groupe Franc. Argiles* 26.

STOCH L., 1974 — Minerały ilaste. Wyd. Geolog. Warszawa.
ZUBER R., 1886 — Skały wybuchowe z okolic Krzeszowic. *Rozpr. Wydz. Matem.-Przyr. Akad. Umiej. w Krakowie* 15.
ŻABIŃSKI W., 1960 — Z badań krzemianowo-magnezowych produktów przeobrażenia melafirów krakowskich. *Spraw. z Pos. Kom. Nauk. Oddz. PAN Kraków.*

Grażyna CICHOŃ

SEPIOLIT Z RUDNA

Streszczenie

Przedstawiono wyniki badań sepiolitu występującego jako minerał wtórny wśród melafirów Rudna koło Krzeszowic. Podano charakterystykę mikroskopową, rentgenowską, termiczną i spektroskopową w podczerwieni badanego minerału oraz wyniki jego analizy chemicznej.

Sepiolit z Rudna należy do odmiany bardzo drobnokrystalicznej o formie włóknistej. W próbkach często towarzyszy mu saponit, a niekiedy także kwarc i kalcyt.

OBJAŚNIENIA FIGUR

Fig. 1. Dyfraktogramy rentgenowskie sepiolitów
a — Rudno, *b* — Eski-Shir (Turcja), *c* — Little Cottonwood (USA, według Brindleya 1959)

Fig. 2. Krzywe termiczne sepiolitu z Rudna
Fig. 3. Widma absorpcyjne sepiolitów z:
a — Rudna, *b* — Eski-Shir (Turcja)

OBJAŚNIENIA FOTOGRAFII

Fot. 1. Obraz elektronowy sepiolitu z Rudna. Pow. × 80 000
Fot. 2. Obraz elektronowy sepiolitu z Rudna. Pow. × 120 000

Гражина ЦИХОНЬ

СЕПИОЛИТ ИЗ РУДНА

Резюме

Представлены результаты исследования сепиолита, вторичного минерала выступаемого в мелафирах Рудна близ Кшешовиц. Дается микроскопическая, рентгеновская, термическая и инфракрасно-спектроскопическая характеристика изучаемого минерала и результаты его химического анализа.

Сепиолит из Рудна принадлежит к очень мелкозернистой разновидности волокнистой формы. В изучаемых образцах обыкновенным спутником является сапонит, а часто также кварц и кальцит.

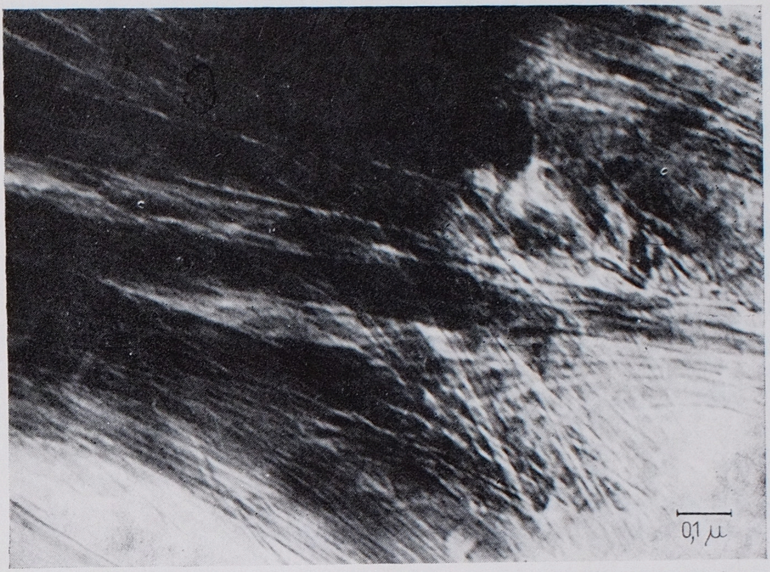
ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Рентгенограммы сепиолитов
а — Рудно, *b* — Эскишехир (Турция), *c* — Литл Коттонвуд — США (по Бриндли, 1959),

Фиг. 2. Термические кривые сепиолита из Рудна
Фиг. 3. ИК-спектры сепиолитов
а — Рудно, *b* — Эскишехир (Турция)

ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

Фот. 1. Электронное изображение сепиолита из Рудна. × 80 000
Фот. 2. Электронное изображение сепиолита из Рудна. × 120 000



Phot. 1. Electron micrograph of sepiolite from Rudno. × 80 000

Phot. 2. Electron micrograph of sepiolite from Rudno. × 120 000

Grażyna CICHOŃ — Sepiolite from Rudno