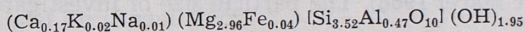


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SAPONITE FROM RUDNO NEAR CRACOW

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Abstract. Saponite occurring in vesicles and larger voids in melaphyre in Rudno near Cracow is described. The results of optical, electron microscopic, X-ray, thermal, IR spectroscopic and chemical investigations of this mineral are presented. Its structural formula is as follows:



It is worthy to note a high Mg content in octahedral sheet, close to the theoretical value. Al is coordinated tetrahedrally.

INTRODUCTION

Saponite is a representative of trioctahedral smectites. They are less common in nature than their dioctahedral equivalents and thus belong to comparatively poorly known minerals.

In Poland, saponite occurs e.g. among secondary products in melaphyres in Rudno near Cracow. It was analyzed in 1909 by Rozen who stated that this mineral resembles so called *pilolite* or saponite. Final identification of it was carried out by Żabiński (1960) by means of chemical, X-ray and thermal methods. Because of unusual purity of the mineral in question, the present authors performed its more detailed examinations.

MEGASCOPIC FEATURES

Saponite fills vacuoles and irregular voids in melaphyres in Rudno, forming white or cream-coloured compact masses, showing earthy fracture and soapy appearance. Green saponite, occurring at the walls of vacuoles, is often accompanied by red or yellow crystals of heulandite (Piekarska, Gawęł 1954). The present paper deals with the results of examination of creamy-coloured saponite (samples 1 and 2).

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In thin section saponite from Rudno is colourless and fine-scaly in shape. When examined with crossed nicols, saponite scales show fairly vivid interference colours (medium birefringence). Saponitic fillings of melaphyre vacuoles consist of submicroscopic flakes oriented parallel to vacuole's walls.

Refractive indices of an air dried sample determined by means of immersion method are 1.525—1.53. Taking into account optical orientation of minerals of the smectite group, this values would correspond to n_g , which is characteristic of saponite with low iron content (Ross, Hendricks 1945 — *vide* Deer *et al.* 1962).

ELECTRON MICROSCOPE INVESTIGATIONS OPTICAL PROPERTIES

Electron microscope observations of morphological features of saponite particles were carried out by TEM Jeol 100C. The grids were prepared from the alcohol suspension. In the micrographs platy particles with irregular shape are visible (Phot. 1) accompanied by laths (Phot. 2) assembled in places in fan-like aggregates (Phot. 3). Lath-like saponite particles were already recognized e.g. in a sample of saponite from South Africa (Beutelspacher, van der Marel 1968). The particle size of investigated saponite are up to 1—2 μm .

X-RAY DATA

X-ray powder patterns of saponite were obtained using Rigaku-Denki diffractometer by applying filtered CuK_α radiation.

A fragment of X-ray pattern of saponite from Rudno (sample 1) is presented in Figure 1. The interplanar spacing are in good agreement with

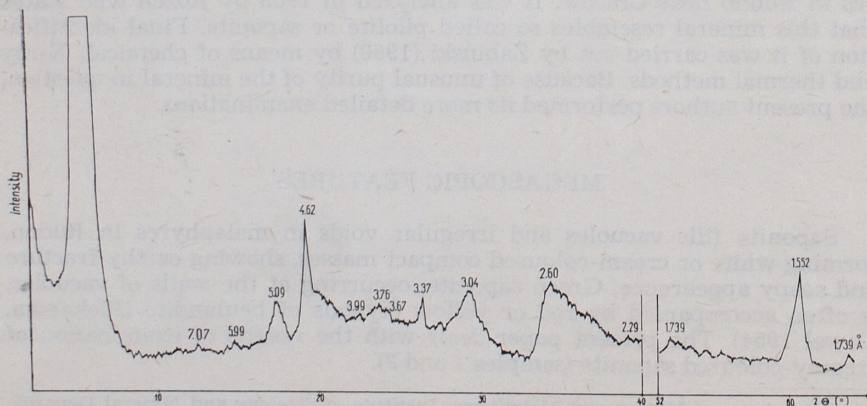


Fig. 1. X-ray diffractogram of saponite from Rudno

those obtained by Suquet *et al.* (1975) for saponite from Kozakov (Czechoslovakia) by means of Guinier camera. The most characteristic feature of X-ray pattern of saponite from Rudno are very sharp 020 and 060 peaks. Unit cell parameters calculated on the basis of 060 reflections are as follows:

$$\begin{aligned} a_0 &= 5.31 \text{ \AA}, \\ b_0 &= 9.20 \text{ \AA}, \end{aligned}$$

being identical with the values reported for saponite by Mac Evan (1961).

THERMAL INVESTIGATIONS

Thermal analysis of saponite was carried out with Derivatograph apparatus of Paulik's-Erdey system. Moreover, TG curves were recorded by means of Mettler' thermoanalyzer.

DTA, TG and DTG curves of saponite are presented in Figure 2. Double dehydration effect on DTA curve in the temperature range 50—350°C is characteristic of smectites containing bivalent exchange cation. This is in accord with crystallochemical formula of saponite in study, in which Ca^{2+} is the main exchange cation. The second strong endothermal effect in 850°C is connected with dehydroxylation of saponite. Similar DTA curves were obtained for saponites by Mackenzie (1957).

As follows from TG curve, the loss of OH groups begins already in temperature range 400—450°C and proceeds very slowly up to 720° when endothermal peak starts to develop. In this temperature range 1.5% water is evolved (sample 1), whilst in that of endothermal peak 750—900°C ca. 3.5% H_2O is lost. We have to note a bend on DTA curve at 740°C on the slope of endothermal dehydroxylation peak which indicates an overlapping of two closely situated peaks. Further studies are necessary to explain this phenomenon.

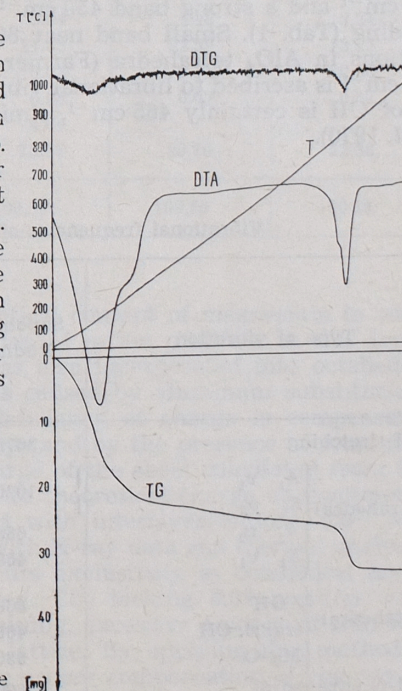


Fig. 2. Thermal analysis curves of saponite from Rudno

IR ABSORPTION SPECTRUM

Infrared absorption spectrum of saponite from Rudno was obtained with an UR-10 (Zeiss, Jena) spectrophotometer. KBr discs containing about 0.3% of the sample were used. The spectrum (Fig. 3) is typical of trioctahedral 2:1 layer silicate and shows a striking similarity to those obtained for saponite by Farmer (1958) and Farmer and Russell (1964).

In the OH-stretching region a small but sharp absorption band at 3675 cm^{-1} is visible, due to the OH stretch in the Mg_3OH groupings.

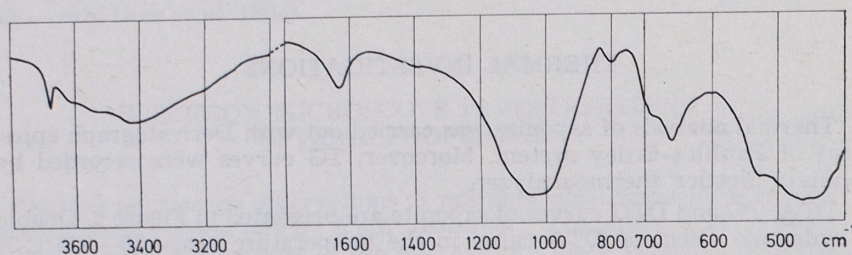


Fig. 3. IR absorption spectrum of saponite from Rudno

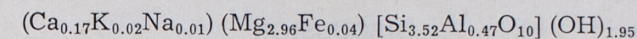
The most intensive bands correspond to the vibration of tetrahedral units. A strong but unresolved band near 1020 cm^{-1} , a smaller one at 685 cm^{-1} and a strong band 450 cm^{-1} arise from the Si-O stretching and bending (Tab. 1). Small band near 800 cm^{-1} is certainly due to Al-O vibrations in AlO_4 tetrahedra (Farmer and Russell 1964). A distinct band 660 cm^{-1} is ascribed to librational vibrations of OH. Translational frequency of OH is certainly 465 cm^{-1} , similarly as in the case of talc (Russell *et al.* 1970).

Vibrational frequencies of saponite and talc (cm^{-1})

Type of vibration	Saponite Rudno	Saponite (after Farmer 1958; Farmer, Russell 1964)	Talc (after Farmer, Russell 1964; Russell <i>et al.</i> 1970)
OH stretching	3675	3677	3676
tetrahedral	$\left. \begin{matrix} A_1 v_1 \\ E_1 v_3 \end{matrix} \right\}$	1056	1039
	$\left. \begin{matrix} A_1 v_2 \\ E_1 v_4 \end{matrix} \right\}$	1005	1014
	685	692	687
	450	450	460
octahedral	$\delta\text{ OH}$	660	669
	transl. OH	465	465
	Mg-O	530	535
Al-O tetrahedral	800	809	

CHEMICAL ANALYSIS

The results of chemical analyses of saponite samples examined are presented in Table 2, where earlier analyses of this mineral from Rudno (Żabiński 1960) are included for comparison purposes. Crystallochemical formula was calculated on the ground of chemical data for sample 1 which was found to be nearly pure saponite. Sample 2 was found to contain some sepiolite admixture. The formula is as follows:



The amount of OH groups was calculated from the amount of water evolved by this mineral in the temperature range $400\text{--}1000^\circ\text{C}$ determined by TG curve.

Table 2

Chemical analyses of saponites from Rudno

Component	Sample 1 *	Sample 2 *	after Żabiński (1960)	
SiO_2	47.57	45.26	45.12	45.66
Al_2O_3	5.13	8.22	8.28	5.65
Fe_2O_3	2.12	2.32	2.10	0.80
TiO_2	0.07	0.11	trace	trace
MnO	n.d.	0.05	0.04	0.06
CaO	2.08	2.04	1.48	2.24
MgO	26.86	21.83	22.59	23.27
Na_2O	0.09	0.03	0.11	0.06
K_2O	0.21	0.05	0.07	0.02
$\text{H}_2\text{O} + 450^\circ$	4.25	4.64		
H_2O^-	11.50	15.97	20.76	22.38
Total	99.88	100.52	100.55	100.14

* Analyst: mgr L. Budek.

It is worth to note a nearly theoretical content of magnesium in octahedral layer, indicating total occupation of cation positions in this layer. Small amount of iron determined was also incorporated into octahedral layer. The charge of saponite sheet is caused by aluminum substitutions in tetrahedral sites. The resulting deficiency of charge is compensated partly by some deficiency of OH groups and by the presence of some iron in octahedral layer. The resulting charge of the sheet calculated from the formula amounts to 0.37 and is close to theoretical charge of montmorillonite sheet (0.33). It is compensated with interlayer cations, Ca^{2+} and subordinate alkalis. This is in accord with X-ray data and thermal analysis.

By assuming that magnesium occurs exclusively in octahedral layer, it was nearly completely compensated. The lacking 0.04 position were supplemented by Fe^{3+} ions. The remaining, excessive amount of iron was considered to occur outside saponite lattice. By applying this method it was possible to get a formula showing proper compensation of charges by interlayer cations. However, it is also possible that some part of magne-

sium ions occurs in cation exchange positions and total amount of iron is fixed in octahedral layer.

The presence of Al in tetrahedra was confirmed by IR spectroscopy. It should be noticed that in saponite samples from Rudno and in numerous other samples of this mineral (Weaver, Pollard 1973) the most common alumina content is 5—6 weight %, corresponding to approx. 0.5 Al in tetrahedral position of crystallochemical formula of this mineral.

DISCUSSION

As follows from the obtained data, saponite from Rudno occurs locally in very pure form with no admixtures of other minerals and any mixed-layer structures. Similarly to formulas of typical saponites, collected by Weaver and Pollard (1973), it contains approx. 0.5 Al per 1/2 unit cell. Aluminum occurs nearly exclusively in tetrahedral sheets. Octahedral layers are nearly entirely occupied by Mg. Consequently, from chemical and structural point of view, saponite is an intermediate mineral form between talc and phlogopite:

talc	$\text{Mg}_3[\text{Si}_4\text{O}_{10}](\text{OH})_2$,
saponite	$\text{Mg}_3[\text{Si}_{3.5}\text{Al}_{0.5}\text{O}_{10}](\text{OH})_2$,
phlogopite	$\text{KMg}_3[\text{Si}_3\text{AlO}_{10}](\text{OH})_2$.

It can be, thus, defined as trioctahedral sheet aluminosilicate, in which ca 1/8 of silica atoms is replaced by Al. Lack of Al in octahedral coordination can be connected with the formation of saponites under hydrothermal conditions which are favouring for tetrahedral coordination of this element. The same refers to saponite from Rudno which is one of products of hydrothermal alteration of melaphyres.

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REFERENCES

- BEUTELSPACHER H., Van der MAREL H. W., 1968: Atlas of electron microscopy of clay minerals and their admixtures. Elsevier, Amsterdam.
- DEER W. A., HOWIE R. A., ZUSSMAN J., 1962: Rock-forming minerals. Longmans, London.
- FARMER V. C., 1958: The infrared spectra of talc, saponite and hectorite. *Miner. Mag.* 31, 829—845.
- FARMER V. C., RUSSELL J. D., 1964: The infrared spectra of layer silicates. *Spectrochim. Acta* 20, 1149—1173.
- MAC EVAN D. M. C., 1961: Montmorillonite minerals. X-ray identification and crystal structures of clay minerals (Brown G. — ed.). Mineralogical Society, London.
- MACKENZIE R. C., 1957: Saponite from Allt Ribhein, Fiskavaig Bay, Skye. *Miner. Mag.* 31, 672.
- PIEKARSKA E., GAWEL A., 1954: Heulandite from Rudno (Cracow district). *Ann. Soc. Géol. Pologne* 22, 367.
- ROZEN Z., 1909: Dawne ławy W. Ks. Krakowskiego. *Rozpr. Wydz. Mat.-Przyr. Pol. Acad. Umiej.* 49, s. A. Kraków.

RUSSELL J. D., FARMER V. C., VELDE B., 1970: Replacement of OH by OD in layer silicates and identification of the vibrations of these groups in infra-red spectra. *Miner. Mag.* 37, 869—879.

SUQUET H., DE LA CALLE C., PEZERAT H., 1975: Swelling and structural organization of saponite. *Clays and Clay Minerals* 23, 1—9.

WEAVER C. E., POLLARD L. D., 1973: The chemistry of clay minerals. Elsevier, Amsterdam.

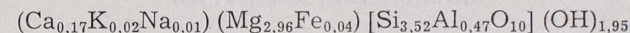
ZABIŃSKI W., 1960: Z badań krzemianowo-magnezowych produktów przeobrażenia melafirów krakowskich. *Spraw. z Pos. Kom. Nauk. O/PAN w Krakowie*, lipiec—grudzień, 1—2.

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SAPONIT Z RUDNA KOŁO KRAKOWA

Streszczenie

Przedstawiono wyniki badań mikroskopowych, rentgenowskich, termicznych, spektroskopowych w podczerwieni oraz chemicznych saponitu pochodzącego z pustek i pęcherzy pogazowych melafirów z Rudna. Wyliczono wzór strukturalny tego minerału:



Zwraca uwagę wysoka zawartość Mg w warstwie oktaedrycznej, zbliżona do wartości teoretycznej. Al występuje w koordynacji tetraedrycznej w ilości około 0,5 Al na 1/2 komórki elementarnej saponitu. Mineral ten zajmuje więc pod względem chemicznym i strukturalnym pozycję pośrednią między talkiem $\text{Mg}_3[\text{Si}_4\text{O}_{10}](\text{OH})_2$ a flogopitem $\text{KMg}_3[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$. Tetraedrycznej koordynacji glinu w saponitach sprzyjają warunki hydrotermalne w jakich na ogół minerały te powstają.

OBJAŚNIENIA DO FIGUR

- Fig. 1. Dyfraktogram rentgenowski saponitu z Rudna
 Fig. 2. Krzywe termiczne saponitu z Rudna
 Fig. 3. Widmo absorpcyjne w podczerwieni saponitu z Rudna

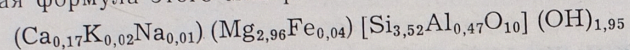
OBJAŚNIENIA FOTOGRAFII

- Fot. 1. Obraz elektronowy blaszek saponitu z Rudna o nieregularnych zarysach. Pow. $\times 45\,000$
 Fot. 2. Obraz elektronowy saponitu o wykształceniu listewkowym. Pow. $\times 45\,000$
 Fot. 3. Obraz elektronowy saponitu wykształconego w formie wachlarzowo ułożonych listewek. Pow. $\times 40\,000$

САПОНИТ ИЗ РУДНА ВБЛИЗИ КРАКОВА

Резюме

В работе представлены результаты микроскопических, рентгеновских, инфракрасных спектроскопических и химических исследований сапонита из пустот и газовых пузырей мелафиров из Рудна. Была рассчитана структурная формула этого минерала:



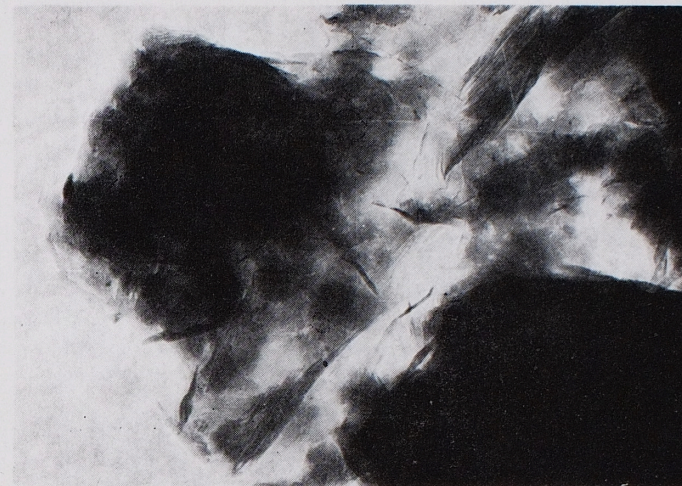
Надо обратить внимание на высокое содержание магния в октаэдрическом слое, которое весьма близко теоретической величине. Al содержится в тетраэдрической координации в количестве около 0,5 Al в 1/2 элементарной ячейки сапонита. Это значит, что этот минерал химически и по структуре занимает место между тальком $\text{Mg}_3[\text{Si}_4\text{O}_{10}](\text{OH})_2$ и флогонитом $\text{KMg}_3[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$. Тетраэдрической координации алюминия в сапонитах благоприятствуют гидротермальные условия, в которых главным образом эти минералы образуются.

ОБЪЯСНЕНИЯ К ФИГУРАМ

- Фиг. 1. Рентгеновская дифрактограмма сапонита из Рудна
Фиг. 2. Термические кривые сапонита из Рудна
Фиг. 3. ИК-спектр поглощения сапонита из Рудна

ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

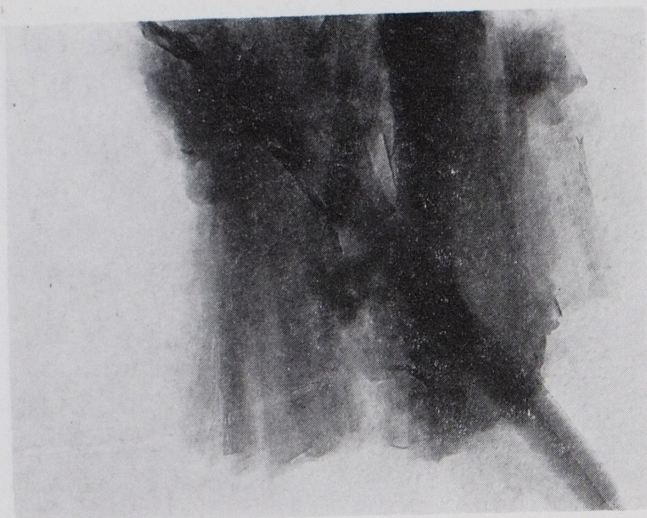
- Фот. 1. Электронномикроскопический снимок плиток сапонита из Рудна с неправильным контуром. Увеличение $\times 45\,000$
Фот. 2. Электронномикроскопический снимок сапонита планкообразной формы. Увеличение $\times 45\,000$
Фот. 3. Электронномикроскопический снимок веерообразно расположенных планочек сапонита. Увеличение $\times 40\,000$



Phot. 1. Electron micrograph of irregular particles of saponite from Rudno. Magn. $\times 45\,000$



Phot. 2. Electron micrograph of saponite lath. Magn. $\times 45\,000$



Phot. 3. Electron micrograph of fan-like aggregates of saponite laths. Magn. $\times 40\,000$