

Jerzy FIJAŁ*

THE EFFECT OF FLUORINE IN THE CRYSTAL LATTICE OF MONTMORILLONITE ON ITS SURFACE PROPERTIES

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Abstract. A correlation was studied between the structure and morphological features of montmorillonite fluoroderivatives and their surface, specifically acid and catalytic, properties. The crystallochemical function of fluorine in the crystal lattice of silicates and its effect on their physico-chemical properties were determined. Fluorine enhances particularly the acid properties of silicates. Its presence causes disturbances in the crystal field round Si—OH groups, leading to weakening of the bond energy of protons, which facilitates their displacement at elevated temperatures. Consequently, the samples show high activity in the reaction of cumene cracking. It seems most probable that fluorine present in the structure of the acid form of montmorillonite lowers the energy barrier for thermal motion of protons. Due to this, the samples acquire high surface (catalytic) activity at considerably lower temperatures compared with untreated samples.

INTRODUCTION

The surface properties of silicates can be significantly modified by fluorine ions introduced into their crystal lattice. It is one of the methods of modifying the acid, catalytic and sorption properties of silicates. Sometimes fluorination is effected by treating silicates with fluoride solutions. This way of activation was used, e.g. for porous silicate glasses (Chapman, Hair 1963, 1965; Elmer *et al.* 1963; Cant, Little 1968), silica gels (Sidorov, Nejmark 1964), aluminosilicate gels (Peri 1968) and layer silicates of the kaolinite and montmorillonite groups (Fijał, Tokarz 1975; Fijał *et al.* 1976; Brückman, Fijał *et al.* 1976).

* Institute of Geology and Mineral Deposits, Academy of Mining and Metallurgy, Cracow (Kraków, al. Mickiewicza 30).

This paper aimed to establish a correlation between the structural features of montmorillonite fluoroderivatives and their surface properties, specifically their surface acidity and catalytic activity. Special emphasis was laid on the crystallochemical function of fluorine in the silicates studied.

EXPERIMENTAL

Samples of varying degrees of fluorination were obtained by activation NH_4F solutions of an almost monomineral montmorillonite sample separated by sedimentation from bentonite from the Chmielnik deposit. The way of obtaining the fluoroderivatives was discussed in an earlier publication (Fijał *et al.* 1976), which also established the nature of structural changes occurring in montmorillonite during fluorination and determined the changes in sorption properties induced by that reaction. The content of fluorine in fluorinated samples, the nature of the secondary fluorides formed during activation of montmorillonite, as well as the degree of degradation of its structure were defined using X-ray diffractometry, IR spectroscopy and electron microscopy.

The paper aimed to determine the content of acid protons on the surface of some montmorillonite fluoroderivatives and to define the catalytic properties of the latter using a test of cumene cracking*. Prior to investigations, all the samples, the untreated sample *M-0* included, were subjected to calcination at 450°C for 2 h.

The content of surface protons in Si-OH groups was determined by two methods: 1 — from the amount of Mn^{2+} substituting for protons, and 2 — by measuring (from IR spectra) the amount of pyridine molecules sorbed as pyridinium ions as a result of reaction with acid protons. The catalytic activity was tested in a microreactor, using pulse technique. The reaction products were analysed in a gas chromatograph with a flame ionization detector (silicone oil column, 150°C). The temperature of cracking reaction was 350°C .

RESULTS

The results of investigations of some physico-chemical properties of the untreated sample *M-0* and fluorinated samples *M-1*—*M-7* are presented in Tables 1 and 2. In their interpretation the results of former sorption and structural studies must be considered (Fijał *et al.* 1976). The activation of montmorillonite leads to the formation of aggregates consisting of strongly defect crystallites and domains. Their structure becomes rigid and loses its ability to swell due collapsing of the layer structure following the thermal decomposition of NH_4^+ (from NH_4F) on the exchange positions

* The catalytic test was made in the Research Laboratories of Catalysis and Surface Chemistry of the Polish Academy of Science in Cracow.

Table 1
Physico-chemical properties of montmorillonite fluoroderivatives

Sample number	Surface area, m^2/g	Fluorine content, weight %	Amount of surface Si-OH groups, mval/100 g
<i>M-0</i>	127.0	0.00	12.3
<i>M-1</i>	132.22	12.2	6.42
<i>M-3</i>	156.5	15.6	5.66
<i>M-4</i>	162.7	17.0	4.91
<i>M-7</i>	54.20	44.6	n.o.

Table 2
Results of cumene cracking reaction

Sample number	Activity, %				Selectivity to benzene, %				Selectivity to α -methylstyrene, %			
	1*	5	10	15	1	5	10	15	1	5	10	15
<i>M-0</i>	16.36	13.96	6.75		n.d.	n.d.	n.d.	n.d.	31.2	17.9	71.7	
<i>M-1</i>	99.3	99.3	99.2	98.2	85.68	65.01	77.30	80.62	0.0	0.0	0.0	0.0
<i>M-3</i>	99.1	99.1	98.0	99.1	67.67	77.30	60.15	65.87	0.0	0.0	0.0	0.0
<i>M-4</i>	99.3	99.3	99.0	99.1	84.78	67.41	71.58	82.11	0.0	0.0	0.0	0.0
<i>M-7</i>	33.0	28.0	29.0	22.0	8.15	7.48	6.97	9.62	6.63	10.50	12.36	10.78

* Amount of following cumene pulses.

and the migration of protons to the octahedral layers. Fluorine atoms, partly disseminated through the defect lattice of montmorillonite, concentrate predominantly in the most intensely degraded marginal zones of the aggregates (Fijał *et al.* 1976). Depending on the way of activation, fluorine can not only substitute for OH groups in the crystal lattice of montmorillonite but also occupy the oxygen sites, which process is attended by disruption of Si-O-Si and Si-O-Al oxygen bridges.

As activation is prolonged, the fluorine content in the samples increased from 12.2 to 17.0% (samples *M-1* to *M-4*). If the concentration of NH_4F solution is high (3N), fluorination leads soon to a nearly complete breakdown of the structure of montmorillonite, attended by the formation of secondary crystalline phases, fluorosilicates and fluoroaluminates (the content of fluorine in sample *M-7* is 44.6 wt. %). X-ray investigations have shown that mild activation with fluorine compounds permits introducing about 3 wt. % of F into the structure montmorillonite without giving rise to secondary phases detectable by X-ray methods. Further fluorination results in both the degradation of the structure of montmorillonite and the systematic increase in the amount of secondary phases.

As appears from the data listed in Tables 1 and 2, the surface and catalytic activity of the samples is the highest when they have a F content of a dozen or so per cent (*M-3* — 15.6%, *M-4* — 17.0%). Moreover, those

samples show the highest surface area values determined from argon and *n*-hexane sorption (Fijał *et al.* 1976). When the fluorine content in a sample is higher (*M-7*), this element is mainly fixed in the form of secondary fluorides. In that case, the catalytic activity of the sample, as well as its sorption capacity, decreases markedly (Table 2) due to the reduced percentage of the active substance, i.e. the acid form of fluorinated montmorillonite.

The above results indicate that the presence of fluorine in the products of montmorillonite fluorination alone is not a sufficient test of their high surface activity because the secondary phases resulting from the decomposition of montmorillonite possess no significant sorption or catalytic properties. The above statements are consistent with the inferences made by Chapman and Hair (1963) and Elmer *et al.* (1963), who studied fluorinated porous silicate glasses.

The catalytic reaction of cumene dealkylation (Table 2) requires the participation of strong proton and nonproton acid centres. It can be therefore treated, on one hand, as a reaction yielding data on the catalytic activity of the samples and, on the other, as a test for the acid properties of catalysts (Covini *et al.* 1967; Brückman *et al.* 1976). The kind and amount of products of cumene decomposition differ markedly for respective samples, which is an essential source of information on the nature of their surface centres. Samples exhibiting the highest catalytic activity (*M-1*, *M-3*, *M-4*) yield mainly benzene and propylene and only a small amount of ethylbenzene and trace amounts of toluene as the reaction products. Such products evidence that the reaction proceeds with the formation of carbonium ions (Covini *et al.* 1967; Antipina 1975), which requires the presence of strong Brönsted and Lewis acid centres. The highly fluorinated sample *M-7* shows a considerably lower conversion of cumene and reduced selectivity towards benzene. α — methylstyrene forms in large amounts. Its presence in the reaction products is a result of cumene dehydrogenation, which requires centres of a different nature, capable of forming free radicals (Brückman *et al.* 1976). The influence of the surface of the catalysts studied on polymerization of α — methylstyrene may cause a rapid drop in the activity of samples due to the formation of coke.

The increase of general acidity of montmorillonite fluoroderivatives was proved by the investigation of chinoline sorption carried out at 350°C. The results of these investigations will be presented in a separate paper.

DISCUSSION

The surface activity of montmorillonite fluoroderivatives is to be viewed in the light of the specific structural, morphological and surface properties of that mineral. The method of activation used in the present investigations gives rise to aggregates consisting of strongly defect crystallites and domains of montmorillonite with a rigid structure, incapable of swelling in water. This is a result of collapsing of the layer structure due to the thermal decomposition of NH_4^+ ions on the exchange positions and the migration of protons to the octahedral layers. The fluorine atoms, partly disseminated through the defect structure of montmorillonite, concentrate

predominantly in the most intensely degraded marginal zones of the aggregates (Fijał *et al.* 1976). Under certain conditions of activation, fluorine not only substitutes for OH groups but also occupies the oxygen sites, disrupting Si-O-Si and S-O-Al oxygen bridges.

The fact that the montmorillonite fluoroderivatives in question display a high activity in cumene cracking testifies to the presence of strong proton and nonproton acid centres on the surface of fluorinated samples. Brönsted acidity is due, e.g. to the presence of Si-OH groups and H_3O^+ ions which are proton donors. Only a small part of those groups, located on the surface of crystalline aggregates (Table 1), may participate at room temperature in the reaction with organic molecules, while the bulk of silanol groups and hydronium ions arising due to migration of protons into the layers are inaccessible to those molecules. The number of protons migrating into the layers corresponds to the exchange capacity of samples (the amount of NH_4^+ ions on the exchange position), which, in turn, depends on the degree of fluorination. The exchange capacity of samples *M-0* to *M-4*, measured before thermal activation, varies from about 120 mval/100 g to about 50 mval/100 g.

The amount of surface silanol groups was determined from the reaction with pyridine sorbed at room temperature (i.e. from the number of pyridinium ions formed), as well as from the exchange of protons available in the surface zone for Mn^{2+} ions (Table 1, column 3). The data obtained do not correspond to the catalytic activity of samples (Table 2, column 1). It appears that the amount of Si-OH groups in fluorinated montmorillonite samples is relatively small, decreasing slightly as fluorination is prolonged; it is even smaller than in the untreated sample *M-0*. Yet, fluorinated samples (*M-1* to *M-4*) show a high, stable catalytic activity, reflected in the amount of cumene conversion (about 99%) during a series of 15 pulses. It is several times higher than the activity of sample *M-0*. This proves unequivocally the crystallochemical activity of fluorine in the lattice of silicates, specifically its effects on their acid properties. Basing on the results obtained, it can be assumed that in the range of low temperatures the protons of the silanol groups and hydronium ions located inside the crystallites fail to show sorption or catalytic interaction with molecules of organic bases used in test reactions. There are several reasons for the lack of reactivity of those groups, e.g. steric reasons, inability of calcinated and fluorinated samples to swell, or limited mobility of the constituent protons at low temperatures at which test reactions of that type are carried on. Only when temperature is raised up to about 300°C and sufficient activation energy is supplied to protons, which become fairly mobile under those conditions, the samples acquire strong acid properties. The F^- ions present in the structure of silicates cause disturbances in the crystal field round Si-OH groups, leading to attenuation of the bonding energy of protons and thus promoting their displacement. It follows, therefore, that in the course of cracking the crystal lattice of fluorinated montmorillonite becomes a sort of *conductor* for protons performing thermal motion (jumps) towards oxygen or fluorine atoms having an excess negative charge at that moment. That state permits the intracrystalline acid protons to participate in catalytic reactions proceeding at elevated temperatures. The evidence of the active role of fluorine in the crystal lattice of samples is provided by sample *M-0*, which fails to exhibit high activity in cumene

cracking (350°C) despite high total acidity and a similar degree of crystalline defectiveness as in fluorinated samples. In the light of theory adopted here, the low activity of sample M-0 is to be accounted for by too small a mobility of its acid protons at 350°C, which is an optimum temperature for fluorinated catalysts. It can be expected that an elevated temperature of the test reaction with cumene, affecting the mobility of the intracrystalline protons, would cause an increase in both the surface acidity and the activity of the sample in dealkylation reaction.

The theory adopted to explain the active role of fluorine in the structure of surface-reactive silicates is consistent with the results of earlier studies of Fripiat (1971) and Chapman and Hair (1963). Basing on NMR spectra, Fripiat (1971) explained the phenomenon of proton displacement occurring in aluminosilicates with acid properties at elevated temperatures. Chapman and Hair (1963) suggested that the enhancement of acid properties noted in fluorinated samples of porous silicate glasses is due to polarization of O-H bonds in silanol groups under the influence of neighbouring F atoms. These authors assumed that the electronegativity of fluorine caused displacement of electrons in the nearest-neighbour atoms, which could result in attenuation of the bonding strength of protons. Objections to this theory were raised by Cant and Little (1968), who pointed out that the absorption bands of free O-H groups in the infrared spectra of fluorinated silicate glass failed to be displaced. Yet, as appears from our investigations (Fijał, Tokarz 1975), infrared spectra of some fluorinated silicates, e.g. kaolinite, reveal a change in orientation of O-H groups in the structure of that mineral, which does not induce any changes in the length of O-H bonds. Moreover, the spectra of acid forms of fluorinated montmorillonites recorded at high temperatures (up to 500°C) have shown that the absorption bands produced by Si-OH vibrations become more diffuse above 300°C than the bands attributed to these groups in the spectrum of untreated H-montmorillonite.

It is possible to find other sources of surface proton acidity of montmorillonite, e.g. strongly dissociated H₂O molecules coordinated by Lewis centres. The evidence for that statement is provided by a catalytic test with cumene carried out on fluorinated montmorillonite in which acid protons were replaced by potassium ions, as well as on montmorillonite fluorinated with KF solution (Brückman *et al.* 1976). It has been found that the samples show some catalytic activity which disappears when successive doses of cumene are supplied. Seeing that potassium ions fail to be hydrated and knowing, on the other hand, that cumene cracking requires the participation of protons to yield benzene and propylene, H₂O molecules coordinated by Lewis centres have been assumed to be the source of protons. It is feasible that fluorination contributes to an increase in the amount and strength of those centres as well (Cant, Little 1968). The studies of Granquist and Kennedy (1967) have revealed that high-temperature (about 500°C) sorption of H₂O molecules on synthetic fluorinated mixed-layer montmorillonite/micas increases in relation to untreated forms. According to these authors, the greater strength bonds between H₂O molecules and the fluorinated surface accounts for that phenomenon. It is conceivable however that fluorinated minerals exhibit a higher strength of Lewis centres, which enhances their reactivity with H₂O molecules.

The surface activity of montmorillonite fluoroderivatives, specifically their acidity and catalytic properties, are not a simple function of the

content of fluorine in the sample. It has been found that highly active catalysts of cracking must show appropriate proportions between the total amount of acid centres and the content of fluorine in the crystal lattice. A catalyst is said to possess optimum catalytic properties when it has a largest possible number of acid protons while the fluorine content is such as not to reduce excessively the number of exchange positions nor to give rise to excessive amounts of secondary fluorides. On the other hand, fluorine would cause certain disturbances in the structure, breaking the continuity of the crystal lattice and leading to its distortion.

The differences in the surface properties of montmorillonite fluoroderivatives are primarily due to the lowering of the energy barrier for thermal motion of protons. For that reason, the fluoroderivatives become surface-active at considerably lower temperatures than non-fluorinated samples. This would account for the apparent lack of correlation between the low content of surface silanol groups and the high catalytic activity of those samples (Tables 1 and 2). It is, therefore, imperative to select appropriate methods of determining surface acidity, depending on the working conditions of the catalyst.

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**WPLYW OBECNOŚCI FLUORU W SIECI KRystalicznej
MONTMORILLONITU NA JEGO WŁASNOŚCI
POWIERZCHNIOWE**

Streszczenie

Badano korelację między strukturalnymi i morfologicznymi cechami fluoropochodnych montmorillonitu a ich własnościami powierzchniowymi (kwasowymi i katalitycznymi). Zwrócono uwagę na krystalochemiczną funkcję fluoru w sieci krystalicznej badanych krzemianów i jego wpływ na niektóre ich własności fizykochemiczne, a w szczególności własności powierzchniowe. Wskazano na niewątpliwy wpływ tego pierwiastka na krystaliczne pole sił wokół grup Si-OH, co prowadzi do osłabienia energii wiązania protonów, ułatwiając ich delokalizację w podwyższonych temperaturach. Stąd wysoka aktywność próbek w reakcjach krakingu kumenu. Wydaje się, iż rozproszony w strukturze kwasowych form montmorillonitu fluor wpływa na obniżenie bariery energetycznej dla termicznych ruchów protonów, co pozwala na osiągnięcie wysokiej aktywności powierzchniowej (katalitycznej) przy znacznie niższych temperaturach w stosunku do próbek niefluorowanych.

Ежи ФИЯЛ

**ВЛИЯНИЕ ПРИСУТСТВИЯ ФТОРА В КРИСТАЛЛИЧЕСКОЙ
РЕШЕТКЕ МОНТМОРИЛЛОНИТА НА ЕГО ПОВЕРХНОСТНЫЕ
СВОЙСТВА**

Резюме

Изучалась связь между структурными и морфологическими свойствами фторопроизводных монтмориллонита и их поверхностными свойствами (кислотными и каталитическими). Было обращено внимание на кристаллохимические функции фтора в кристаллической решетке изучаемых силикатов и на его влияние на некоторые их физикохимические свойства, а особенно на поверхностные свойства. Было указано несомненное влияние этого элемента на кристаллическое силовое поле вокруг групп Si-OH, что ведёт к ослаблению энергий связи между протонами, облегчая их перемещения в повышенных температурах. Из этого вытекает высокая активность образцов во время реакций крекинга кумола. Кажется, что рассеянный в структуре кислотных форм монтмориллонита фтор влияет на обнижение энергетического барьера для термических движений протонов. Это позволяет достигнуть высокой поверхностной (каталитической) активности при значительно обниженных температурах по сравнению с образцами, которые не подвергались воздействию фтора.

Barbara KWIECIŃSKA *, Grażyna CICHON **

**SOME REMARKS ON THE MORPHOLOGY OF SEPIOLITE
AND Palygorskite FROM RUDNO**

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Abstract. Electron micrographs were taken of sepiolite and palygorskite coexisting in fissures of the melaphyre from Rudno. It has been found that, despite similar structure and genesis, these minerals differ markedly in the morphology of crystallites. Electron micrographs have revealed that sepiolite has a lamellar, platy and lath-like form whereas palygorskite exhibits a fibrous, hair-like structure.

INTRODUCTION

Sepiolite and palygorskite belong to layer magnesium silicates with a ribboned structure. The details of their structure became better known due to the use of electron microscopy (Vivaldi, Robertson 1971; Serna *et al.* 1974). The principal structural elements of both sepiolite and palygorskite are ribbons made up of silicon-oxygen chains. A ribbon of sepiolite consist of three and that of palygorskite of two Si-O chains. The tetrahedrons of the Si-O layer in sepiolite are linked by Mg²⁺ cations which are surrounded by oxygens of the free tetrahedra corners and by OH groups. They form the octahedral layer which, together with two tetrahedral layers, makes up a talc like sheet. The structure of sepiolite is generally shown as a rectangle consisting of five elements arranged in such a way that four of them occupy the corners and the fifth the centre of the rectangle (Fig. 1). Free oxygen corners of the tetrahedral layer in the neighbouring ribbons have opposite directions. Between the ribbons there are empty channels filled with molecules of zeolitic water. The unit cell parameters deter-

* Academy of Mining and Metallurgy, Institute of Geology and Mineral Deposits, A. Mickiewicza 30, Kraków.

** Silesian University, Institute of Geology, Sosnowiec.

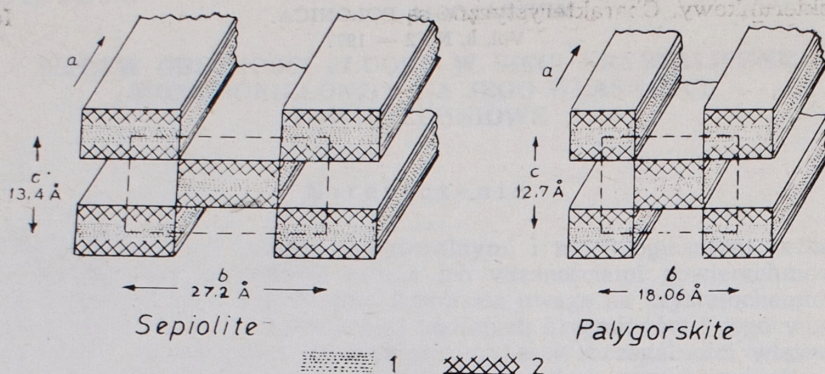


Fig. 1. Scheme of linkage of ribbons in structure of sepiolite and palygorskite (Vivaldi, Robertson 1971)
1 — octahedral layers, 2 — tetrahedral layers

mined by Zwiagin *et al.* (1963) are: $a_0 = 13.4 \text{ \AA}$, $b_0 = 27.2 \text{ \AA}$, $c_0 = 5.24 \text{ \AA}$. Palygorskite has a ditrioctahedral structure. The tetrahedral layers are linked by Mg^{2+} and Al^{3+} cations which, together with the surrounding oxygens and OH groups, form the octahedral layer. Due to the presence of two Si-O chains in the ribbon of palygorskite, the parameter b_0 of the unit cell is only 18.6 \AA (Zwiagin *et al.* 1963).

The structure of sepiolite and palygorskite finds its external reflection in the morphology of crystallites, which exhibit a needle-like or fibrous habit, conspicuous on electron micrographs. The available data seem to imply that the coexisting sepiolite and palygorskite show in some cases a nearly identical, and in others quite different morphology. For example, from the data published by McLean *et al.* (1972) it appears that the two minerals found in sedimentary rocks have a similar morphology, making it impossible to distinguish them on electron micrographs. The present authors used transmission electron microscopy to study the morphology of sepiolite and palygorskite which formed as secondary minerals in melaphyres, presumably under hydrothermal conditions.

The minerals in question occur in fissures in melaphyres, forming small lamellar or wool-like aggregates. Pure sepiolite, free from admixtures of other minerals, appears in the form of friable snow-like platelets up to several mm in thickness (Cichoń 1977a), whereas palygorskite forms soft, wool-like aggregates of white colour (Cichoń, 1977b). Saponite is a frequent admixture in the sepiolite and palygorskite aggregates; its intergrowths with palygorskite have a frayed form showing a woodlike structure. However, samples prepared for electron microscope studies did not contain saponite.

EXPERIMENTAL

Samples for electron microscope studies were prepared using suspension technique. The copper grids were evaporated with spec-pure carbon. Both alcohol and ammonia water solution were used as a dispersing liquid.

No mechanical dispersing agents or ultrasounds were employed to avoid the possible break-down of the particles or changes in their shape.

Electron micrographs were taken on a Jeol JEM-100C microscope operated at an accelerating voltage of 100 kV. It has been found that preparations obtained from the same samples but applying varying time of evaporation reveal no differences in the geometry of morphological images. The experimental procedure has been intentionally described at it is well known that the proper interpretation of electron micrographs depends in large measure on the way of sample preparation (Vivaldi, Robertson 1971; Beutelspacher, Van der Marel 1968; Rautureau, Tchoubar 1976).

RESULTS

Electron microscope studies have revealed slight but, in the authors' opinion, significant differences in the crystal morphology of sepiolite and palygorskite from Rudno. Those differences are a deviation from the fibrous habit of crystals, generally accepted for the two minerals.

Sepiolite crystals exhibit a lath-flaky or wool-like structure. Larger forms are aggregates of single fine fibres, laths, flakes and plates (Phot. 1—4). It is difficult to define the size of such aggregated forms except for the maximum length of individual fibres ($5\text{--}6 \mu\text{m}$) and the breadth of the finest, flat laths (about $0.1 \mu\text{m}$). The mode of packing of laths sets, sheets, or bundles is absolutely random and unoriented. The ends of fine fibres are frequently split and flattened, resembling splinters. It seems possible that it is connected with the tendency of sepiolite crystals to fold at elevated temperatures (Serna *et al.* 1975) which may arise during taking electron micrograph. The edges of flaky aggregates are folded, curled, sometimes overlapping (Phot. 1, 3).

Compared with sepiolite, palygorskite crystals are considerably more elongated (Phot. 5—8). In consequence, it is easier to determine the size of single fibres: their length varies from some to a dozen or so μm and their breadth from 500 to 200 \AA . It is evident that the fibres are much thinner and more elastic, grouped in broader bands and parallel ribbons branching off at the ends (Phot. 7). The thinnest needles are strongly bent, assuming the shape of loops which show a striking similarity to asbestiform palygorskite from Lemesurier Island, Alaska (Vivaldi, Robertson 1971) (Phot. 8). The ends of fibres or needles resembling hair-like forms are at an acute or right angle. When the fibres are crossing or overlapping, they are not subject to fraying as is the case in sepiolite crystals. Sometimes they resemble tubular forms reported by, e.g., Vivaldi and Robertson (1971) (Phot. 6). Some fibres exhibit distinct striation, running parallel to the longer axis of needles.

The above remarks and observations confronted with the data published by other authors substantiate the statement that the morphology of sepiolite and palygorskite crystals is sometimes similar, e.g. under the conditions of formation of sedimentary rocks (McLean *et al.* 1972), and sometimes markedly different, specifically when the two minerals occur under the same hydrothermal conditions. In the latter case, palygorskite is acicular, hair-like and needle-like whereas sepiolite exhibits a platy,

lamellar or flat, rigid fibrous structure. Sepiolite and palygorskite show such morphology in the melaphyre quarry at Rudno.

Owing to some interesting surface properties, sepiolite and palygorskite are of great importance in several chemical technologies (Stoch 1974). It seems, therefore, that every contribution increasing the knowledge of their properties has both a cognitive and practical significance.

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Barbara KWIECIŃSKA, Grażyna CICHON

UWAGI O MORFOLOGII SEPIOLITU I PAŁYGORSKITU Z RUDNA

Streszczenie

Wykonano zdjęcia elektronowe sepiolitu i palygorskitu występujących obok siebie w szczelinach melafiru w Rudnie. Zwrócono uwagę na to, że mimo podobieństwa strukturalnego tych minerałów oraz podobnej ich genezy (zapewne hydrotermalnej) różnią się one znacznie morfologią kryształów.

Sepiolit wykazuje budowę blaszkowo-listewkową. Tworzy zwykle skupienia krystalitów, w których sposób upakowania poszczególnych listewek

w zespoły lub wiązki jest dowolny, bezkierunkowy. Charakterystyczne są formy spłśnione, skudłone i zwinięte, zwłaszcza na brzegach blaszek.

Palygorskit odznacza się znacznie silniejszą elongacją i elastycznością włókien. Częste są struktury włoskowe i igielkowe. Igły zebrane są czasem w równoległe, rozwidlające się pasma lub wstęgi. Najcieńsze igły są silnie powyginane, przyjmując niekiedy kształt pętli.

OBJAŚNIENIE FIGURY

Fig. 1. Schemat połączenia wstęg w strukturze sepiolitu i palygorskitu (Vivaldi, Robertson 1971)

OBJAŚNIENIA FOTOGRAFII

- Fot. 1. Kryształy sepiolitu wykazujące budowę płytkowo-listewkową. Pow. $\times 66\ 000$
- Fot. 2. Sepiolit. Większe skupienia blaszek i płytek o nieregularnych zarysach. Pow. $\times 66\ 000$
- Fot. 3. Sepiolit. Formy płaskich listewek skudłone na końcach i zwinięte na brzegach. Pow. $\times 100\ 000$
- Fot. 4. Kryształy sepiolitu wykazujące budowę *kudetkową*. Mają tendencję do spłśnienia. Pow. $\times 32\ 000$
- Fot. 5. Palygorskit igielkowy. Krystality wykazują znaczną długość i elastyczność. Pow. $\times 40\ 000$
- Fot. 6. Cienkie wydłużone włókna palygorskitu przypominające formy rurkowe. Zakończenia włókien są pod ostrym lub prostym kątem. Pow. $\times 66\ 000$
- Fot. 7. Palygorskit o strukturze włoskowej. Widoczne pojedyncze włókna o szerokości od 500 do 200 Å, zebrane w równoległe, rozwidlające się wstęgi. Pow. $\times 32\ 000$
- Fot. 8. Palygorskit o strukturze długich elastycznych igieł przyjmujących kształt pętli. Wyraźne podobieństwo do azbestu. Pow. $\times 52\ 000$

Барбара КВЕЦИНЬСКА, Гражина ЦИХОНЬ

НЕКОТОРЫЕ ЗАМЕЧАНИЯ ПО ПОВОДУ МОРФОЛОГИИ СЕПИОЛИТА И ПАЛЫГОРСКИТА ИЗ РУДНА

Резюме

Были сделаны электронномикроскопические снимки сепиолита и палыгорскита, которые появляются поблизости друг от друга в трещинах мелафира в Рудне около Кракова. Обращено внимание на то, что, не смотря на структурное сходство этих минералов и похожий генезис (вероятно гидротермальный), они значительно отличаются морфологией кристаллов.

У сепиолита пластинчато-планочное строение. Даёт он обыкновенно накопления кристаллитов, в которых способ упаковки одиночных пластинок в комплексы или связки является произвольным, ненаправленным.

Очень характерны фетровые, взлохмоченные и свёрнутые формы, особенно по краям пластинок.

Пальгорскит отличается значительно более удлиненной формой и эластичностью волокон. Очень часты *волосатые* и игольчатые структуры. Иглы очень часто собраны в параллельные, разветвляющиеся полосы или ленты. Самые тонкие иглы очень сильно выгнуты, иногда даже в форме петли.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Схема соединения лент в структуре сепиолита и пальгорскита (Вивальди, Робертсон 1971)

ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

- Фото. 1. Кристаллы сепиолита, которые обнаруживают пластинчато-планковое строение. Увел. $\times 66\ 000$
- Фото. 2. Сепиолит. Большие скопления плиток и пластинок с неправильным контуром. Увел. $\times 66\ 000$
- Фото. 3. Сепиолит. Плоские формы планок взлохмоченных на концах и свёрнутые по краям. Увел. $\times 100\ 000$
- Фото. 4. Кристаллы сепиолита обнаруживающие лохматое строение. Эти кристаллы склонны к фетрованию. Увел. $\times 32\ 000$
- Фото. 5. Игольчатый пальгорскит. Кристаллиты обнаруживают значительную длину и эластичность. Увел. $\times 40\ 000$
- Фото. 6. Тонкие, удлиненные волокна пальгорскита напоминают трубчатые формы. Окончания волокон остроконечные или прямоугольные. Увел. $\times 66\ 000$
- Фото. 7. Пальгорскит с волосатой структурой. Видны одиночные волокна шириной от 500 до 200 Å собранные в параллельные, разветвляющиеся ленты. Увел. $\times 32\ 000$
- Фото. 8. Пальгорскит со структурой в форме длинных эластичных игл, которые свёрнуты в петли. Очень отчетливое сходство с асбестом. Увел. $\times 52\ 000$



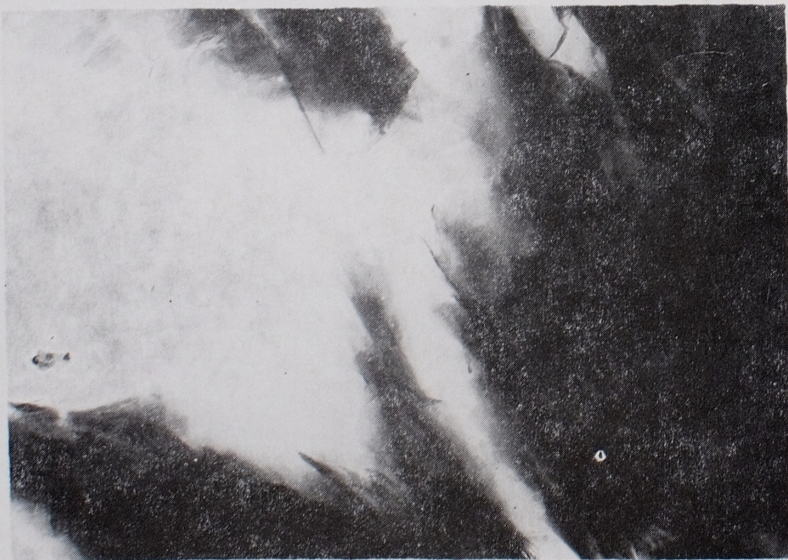
Phot. 1. Sepiolite crystals exhibit a lath-flaky structure. Magn. $\times 66\ 000$



Phot. 2. Sepiolite. Larger aggregate of plates and flakes with irregular shape. Magn. $\times 66\ 000$

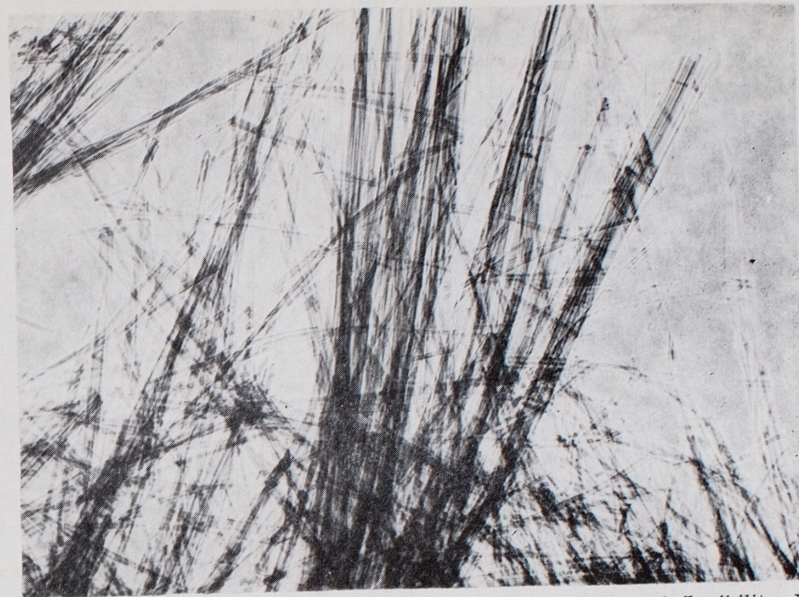


Phot. 3. Sepiolite. Forms of flat laths tangled at the ends and folded at the edges. Magn. $\times 100\ 000$

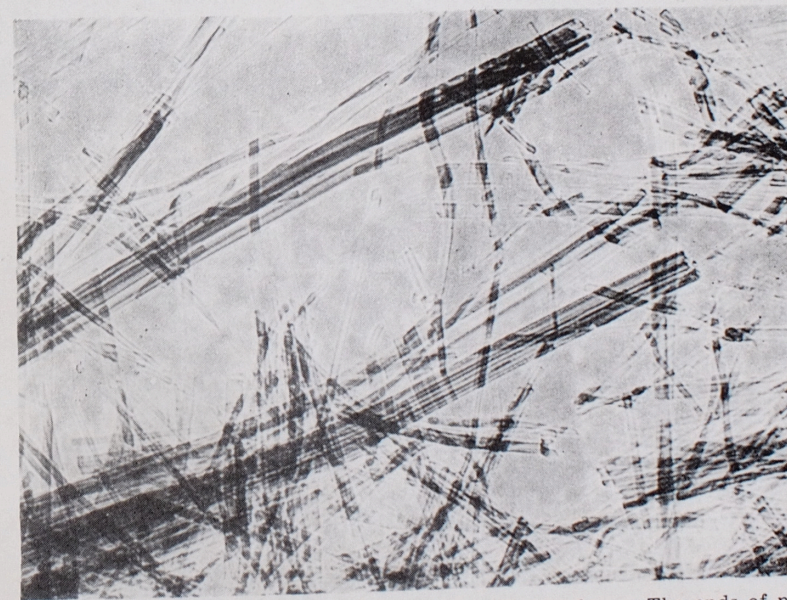


Phot. 4. Sepiolite crystals showing a wool-like habit. They have tendency to fray. Magn. $\times 32\ 000$

Barbara KWIECIŃSKA, Grażyna CICHON — Some remarks on the morphology of sepiolite and palygorskite from Rudno



Phot. 5. Acicular palygorskite. Crystallites show great length and flexibility. Magn. $\times 40\ 000$

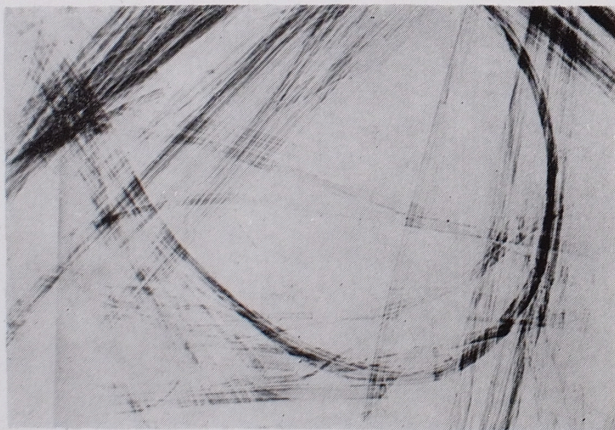


Phot. 6. Thin, long-fibred palygorskite resembles tubular forms. The ends of needles are at an acute or right angle. Magn. $\times 66\ 000$

Barbara KWIECIŃSKA, Grażyna CICHON — Some remarks on the morphology of sepiolite and palygorskite from Rudno



Phot. 7. Hair-like structure of palygorskite. Width of single fibres varies from 500 to 200 Å. They are grouped in parallel branching off ribbons. Magn. $\times 32\ 000$



Phot. 8. Palygorskite with structure of elongated flexible needles assuming the shape of loops. Distinct similarity to asbestiform palygorskite. Magn. $\times 52\ 000$