GEOLOGICKÝ ZBORNÍK — GEOLOGICA CARPATHICA XXIII, 2 — BRATISLAVA, NOVEMBER 1972

IVAN KRAUS, IVAN HORVÁTH, EVA ŠAMAJOVÁ, HELENA GERTHOFFEROVÁ*

STUDY OF INTERCALATION ABILITIES OF KAOLINITE GROUP MINERALS

(Figs. 1—6)

Abstract: Intercalation of minerals of the kaolinite group with the exception of dickite and nacrite was considered on the basis of X-ray analysis of reaction products after their treatment with K-acetate and hydrazine. The study of clay coming from Neogene sediments of the West Carpathians enabled to express some information concerning the existence of fire-clay mineral and mutual relations between kaolinite and halloysite.

Резюме: Включения минералов группы каолинов за исключением диккита и накрита характеризуются на основании рентгенографического анализа редукционных продуктов после их насыщения уксусно-кислым калием и гидразином. Изучение глин, происходящих из неогеновых осадков Западных Карпат предоставило возможность высказать некоторые данные касающиеся существования минерала огнеупорной глины (fire-clay) и взаимных связей между каолинитом и галлуазитом.

Introduction

Many-sided practical use of clay minerals has led to an intense study of their physical-chemical properties in the last years. To the specific properties of clay minerals belong their ability to bind organic ions and/or whole molecules. The ability of reaction depends in the first place from the crystal structure of the clay minerals. In this regard mainly three-layer minerals of the montmorillonite group are studied in detail. In spite of that the research of reaction abilities of kaolinite minerals with organic compounds is younger, it has provided much information till now, to a certain extent clarifying some questions in relations between the minerals of this group.

A. Weiss et all. (1966) divided intercalation complexes of kaolin minerals into two groups in essentials:

1. By the effect of organic compound which reacts with the clay minerals by means of a hydrogen bridge (for instance, formamide, acetamide, hydrazine) intercalation complexes with "d" values in the interval 9.5—11.4 Å.

2. Alkaline salts of lower aliphatic acids with easy to polarize, large univalent cations (K, Rb, Cs, NH_4) give with kaolin minerals reaction products with "d" values in the interval 14.0—14.5 Å.

More attention was rather paid to the second group of intercalation reactions[1]. This had mainly followed from better accessibility and unretentiousness of the work with alkaline salts of lower aliphatic acids. In this regard most frequently was used

---

[*] RNDr. I. Kraus, CSc., Department of Mineral Raw Materials Faculty of Natural Sciences of the Comenius University, Bratislava, Jirásková 12; Ing. I. Horváth, CSc., Institute of Inorganic Chemistry, Slovak Academy of Science, Bratislava, Dúbravská cesta; RNDr. E. Šamajová, CSc., Geological Institute, Faculty of Natural Science of the Comenius University, Bratislava-Petržalka, Zadunajská 15; RNDr. H. Gerthofferová, Geological Institute, Faculty of Natural Science of the Comenius University, Bratislava-Petržalka, Zadunajská 15.

[1] Under intercalation we understand the physical and chemical process, in which association of organic molecules with layers of clay mineral is taking place.

K-acetate and that mainly for investigation of intercalation abilities of halloysite M. D. C. MacEwan (1946, 1948), K. Wada (1961). Later it was established by K. Wada (1965) that with washing of intercalation complexes prepared by treatment of kaolin minerals with K-acetate H_2O complexes originate, stability of which depends on structural order of the mineral. This information was used for the purpose of identification (W. D. Miller, W. D. Keller 1963, V. D. Perlin 1966) as well as for classification of structural variability (C. T. Deeds et all. 1966, A. Alietti 1966, E. G. Kukovskij 1966). A. Wiewiora and G. W. Brindley (1969) extended the study of intercalation of kaolin minerals with K-acetate by the kinetic aspects of the process. Intercalation of kaolin minerals with hydrazine was observed by K. J. Range et all (1969). Qualitative and quantitative study of the intercalation process opens the way of objective control of the order of structure and brings new views, mainly of relations between kaolinite, fire-clay mineral[2] and halloysite.

Geological Position and Mineralogical Composition of Studied Clays

Intercalation abilities of minerals of the kaolinite group have so far been studied by the majority of authors on samples of the character of standards (kaolinite Georgia, kaolinite Sedlec, kaolinite Macon, kaolinite Spruce Pine, halloysite Indiana etc.). In the presented paper we are following intercalation abilities of kaolinite, fire-clay mineral and halloysite found in the West Carpathians. An exception form kaolinites from kaolin deposits of the Ukrainian SSR, in which we followed intercalation ability in dependence on the degree of structural order (tab. 4).

Kaolinites with well ordered structure come from the localities Horná Prievraná and Vyšný Petrovec in the Lučenecká kotlina Basin in Southern Slovakia. They represent so far the only kaolin deposit in the West Carpathians of economic importance. The original source rocks represent a variegated complex of volcanic-sedimentary origin epizonally metamorphosed prior to kaolinization. Kaolinization of porhyroids and phyllites of the Paleozoic of the Gemerides was taking place by the effect of hypergene processes in wide interval of time in the Paleogene and Sarmatian. A property characteristic of kaolin is the high content of hydromicas of dioctahedral type. Its mineralogical composition of hydromicas of dioctahedral type. Its mineralogical composition and technological properties are determined by the petrographic character of source rocks. I. Horváth (1969) arrived the conclusion that with weathering of porphyroids with high content of acid plagioclases conditions favourable for the origin of the Na-variety of a hyddromica close to brammalite with the value d_{001} 9.6 Å were formed, whereat comon hydromica with a high content of K_2O and d_{001} 10.0 Å originated mainly by weathering of phyllites (fig. 1, no. 1,2).

Minerals with disordered structure of fire-clay type represent extreme finely dispersed clays with fraction less than 1 micron predominating (tab. 2). They come from two separate areas. The samples from the Lučenecká kotlina Basin represent refractory, ceramic clays of the co called Poltár formation. It is a complex of clays, sands and gravels of Pliocene age, occurring in the overlier of kaolins and kaolin sands in the same area. The clays formed by fire-clay mineral, sometimes with insignificant admixture of hydromicas of dioctahedral type distinctly differ from primary kaolins and kaolin

---

[2] The term "fire-clay mineral" we apply in the sense of K. J. Range et all (1969) for a mineral of the kaolinite group with disordered structure and not intercalating with K-acetate and hydrazine.

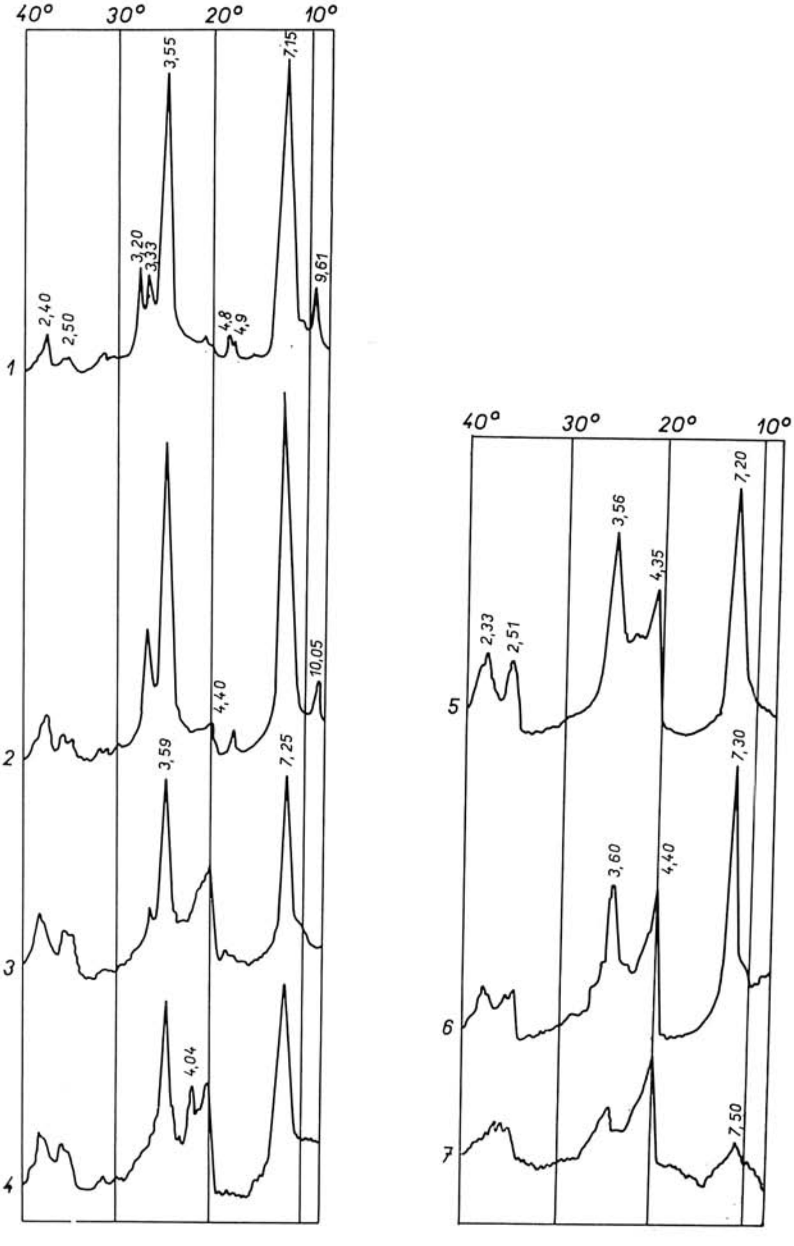

Fig. 1. X-ray diffractograms of studied clays. 1 — Kaolinite from Horná Prievraná, 2 — kaolinite from Vyšný Petrovec, 3 — fire-clay, Poltár Formation, 4 — fire clay, Podvihorlatská panva Basin, 5 — halloysite, Biela Hora near Michalovce, 6 — halloysite, Lučenecká kotlina Basin, 7 — halloysite, Slatinská kotlina Basin.

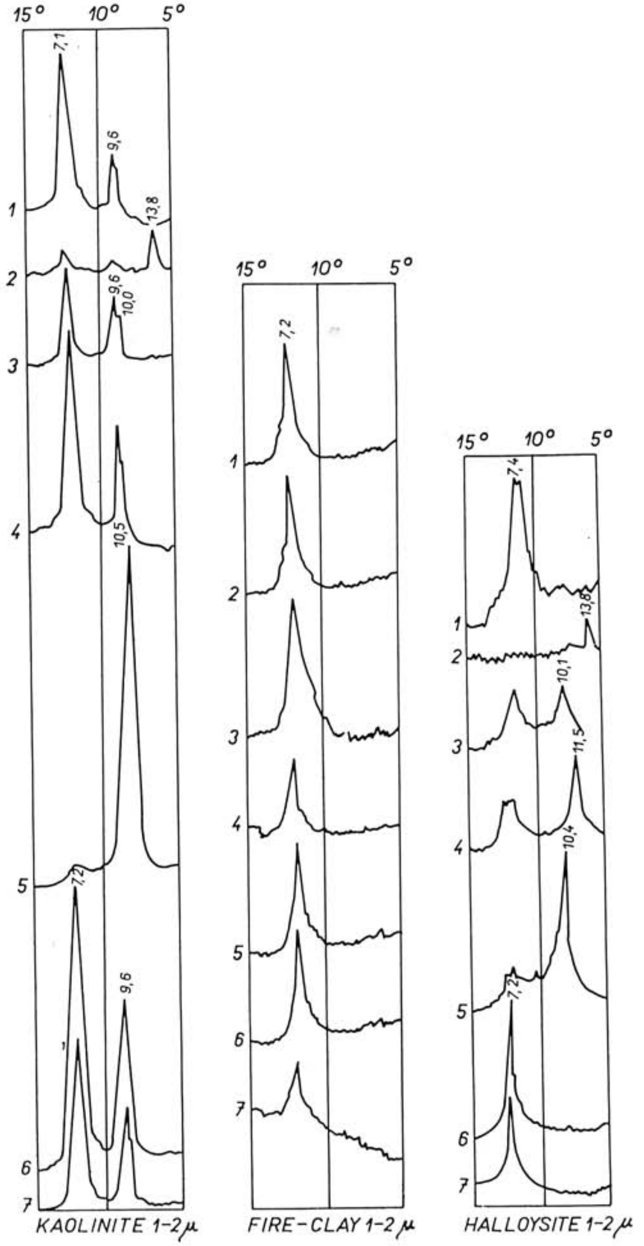

Fig. 2. X-ray diffractograms of kaolinite from Horná Prievraná, fire-clay mineral from the Podvihorlatská panva Basin and halloysite from the Lučenská kotlina Basin. 1 — sample in natural state, 2 — sample treated with K-acetate, 3 — sample washed with distilled water, 4 — sample treated with glycerol, 5 — sample treated with hydrazine, 6 — sample washed with distilled water, 7 — sample treated with glycerol.

sands redeposited at short distance in the order of their structure, size of particles, origin and technological properties. They represent the product of typical fluvio-limnic sedimentation of material derived from the southern slopes of the Veporide crystalline and having undergone a relatively long transportation into the present area of deposition after its origin in the original weathering crust.

The clays from the Podvihorlatská panva Basin in Eastern Slovakia are a part of the sedimentary filling of the Pliocene of the East Slovakian Lowland. Redeposited products of kaolinic weathering crusts are concerned, originated at the base of Lower Pliocene pyroxene andesites of the Vihorlat Mts. Beside the predominating fire-clay mineral they contain cristobalite and an insignificant admixture of halloysite. According to preliminary results the high content of Fe_2O_3 (tab. 1) is bound in the lattice of the studied mineral.

Halloysites with variously ordered structure and various degree of dehydration (fig. 1, no. 5, 6, 7) come from three separate areas.

Halloysite from the Lučenecká kotlina Basin (d_{001} 7,3—7,4 Å) is found in the complex of kaolin sands at the locality Kalinovo-Hrabovo in the form of so called armored mud balls. It was studied in detail by I. Kraus et all (1966). It is characteristic by the relatively good degree of structural order, low content of Fe_2O_3. The question of its origin and general distribution in kaolin sands has not sufficiently been clarified till now.

The halloysite from Biela Hora near Michalovce (d_{001} 7,2 Å) represents a sporadical accumulation of this material of economic importance in Europe. It has originated by weathering of rhyolite tuffs of Sarmatian age. The mineralogical study was carried out by A. Kochanovská (1955), J. Konta (1957), E. G. Kukovskij (1966). It contains cristobalite and a considerable admixture of fire-clay mineral.

Halloysite from the Slatinská kotlina Basin in central Slovakia (d_{001} 7,3—7,5 Å) forms irregular, little thick layers amidst decomposed pyroclastics of andesite volcanism Upper Tortonian in age. Originally the completely hydrated form was concerned (d_{001} 10,1 Å).

Table 1. Chemical analyses of studied samples

	Fire-clay Poltár Formation		Fire-clay Podvihorlatská panva Basin		Halloysite Lučenecká kotlina Basin		Halloysite Slatinská kotlina Basin	
	fraction < 1 μm	fraction 1—2 μm	fraction < 1 μm	fraction 1—2 μm	fraction < 1 μm	fraction 1—2 μm	fraction < 1 μm	fraction 1—2 μm
SiO_2	43,18 %	43,69 %	44,51 %	44,57 %	45,30 %	45,45 %	44,05 %	47,99 %
TiO_2	1.13	1,59	0,64	1,25	0,13	0,22	0.78	0,99
Al_2O_3	36,22	34,98	30,98	27,54	37,98	37,88	32,21	28,31
Fe_2O_3	1,97	2,19	4,03	6,92	0,63	0,78	7,81	8,20
FeO	0,56	0,74	traces	—	—	—	—	—
MnO	—	—	—	traces	—	—	—	—
MgO	0,14	0,25	0,49	0,47	0,10	0,10	0,32	0,62
CaO	0,58	0,58	0,87	0,82	0,71	0,72	0,88	0,87
Na_2O	0,38	0,46	0,54	0,23	0,09	0,05	0,10	0,20
K_2O	0,14	0,24	0,25	0,23	0,16	0,20	0,32	0,80
$-H_2O$	3,38	3,12	3,95	4,39	2,10	1,96	3,28	3,21
$+H_2O$	12,10	12,17	13,54	13,37	13,24	12,56	10,62	8,77
sum	99,78 %	100,01 %	99,80 %	99,79 %	100,44 %	99,92 %	100,37 %	99,96 %

Partial dehydration was taking place during deposition of the sample in the laboratory. It is characterized by relatively low degree of structural order, with distinct predominance of the fraction less than 1 micron. The tubular particles are of finely dispersive development (fig. 6). Remarkable is the high content of Fe_2O_3 — 7,81 %. On the basis of up to present study we have found that the presence of free Fe-oxides is insignificant. W. Engelhardt (1954) and D. P. Serdjučenko (1952) mention in the so called ferrohalloysite a content of Fe_2O_3 about 3,5 %.

Content of the Problem and Conditions of Experimental Study

We have focused the study of intercalation abilities on following of these problems:

1. Mutual comparison of intercalation with K-acetate and hydrazine.
2. Intercalation in dependence on the size of particles and structural order.
3. Existence of fire-clay mineral.
4. Relation between kaolinite and halloysite.

Treatment of samples with K-acetate we have carried out by methods mentioned by A. Wiewiora and G. W. Brindley (1969) and W. D. Miller, W. D. Keller (1963).

The first procedure we applied in solution of the first three problems[3].

The second procedure we applied in identification of tubular particles, of which we were in doubt wether they belong to halloysite[4].

The first procedure reliably indicates the course of intercalation and is also suitable for identification of mixtures of kaolinite with halloysite. On the contrary, the procedure modified by W. D. Miller and W. D. Keller (1963) is only suitable for the purpose of identification as with rubbing the structure of the studied minerals is partly disturbed.

Tratment of samples with hydrazine we carried out according to K. J. Range et all (1969)[5]. The oriented preparations determined for X-ray study we prepared under relative moisture 30 % in three forms: sample treated with K-acetate and/or hydrazine; sample washed with distilled water; sample treated with glycerol.

Intercalation of individual samples we expressed on the basis of the intensities of basal reflexes (001) of natural and treated sample. For K-acetate reflexes with values d 7.1 and 14,0 Å; for hydrazine 7,1 and 10,4 Å were concerned.

We took pictures of oriented preparations on X-ray goniometer GON-3 under Ni filtrated Cu K α radiation, 35 kV, 15 mA, ascending diaphragm 30′, entering diaphragm 2′, arm shift 1 °/min and time contant 10 sec. The electron micrographs mentioned in the paper are prepared on table electron microscope Tesla BS 242.

Mutual Comparison of Intercalation with K-acetate and Hydrazine

As it has confirmed, between intercalation of kaolinite, fire-clay mineral and halloysite there exists a directly proportionate dependence in their treatment with K-acetate and hydrazine (tab. 3). Well ordered kaolinites intercalate almost quantitavely, in the case of

---

[3] The separated clay fraction in an amount of 300 mg we treated in solution of 30 ml 8N K-acetate for 1 week, with occasional shaking. In closed wessels we left the samples in solution for another week.

[4] 500 mg of separated clay fraction and 400 mg of K-acetate we rubbed finally for $\frac{1}{2}$ hour in an agate dish.

[5] 300 mg of separated clay fraction we treated in 30 ml hydrazine hydrate at the temperature of 65 °C for one week.

hydrazine their reaction ability is somewhat higher. Characteristic of them is also that after washing by distilled water the complexes of K-acetate and hydrazine are very easily squeezed out. A certain shift of d_{001} from previous 7.1 Å to 7.2—7.3 Å is taking place there. Treatment of samples adjusted this way with glycerol does not exhibit any changes in well ordered kaolinites, on the contrary.

Insignificant or no intercalation after treatment with K-acetate and hydrazine is a property characteristic of clays, the essential component, of which is fire-clay mineral. This circumstance is markedly evident in clays from the Podvihorlatská panva Basin, having all marks of so called intercalation disorder in the sense of K. Range et all (1969).

In sediments of the Poltár Formation from the Lučenecká kotlina Basin, considered as typical representatives of clays of fire-clay type we have encountered such an intercalation disorder in one case only. The majority of studied clays from this area exhibit certain degree of intercalation, attaining 23 % as maximum with K-acetate and 34 % with hydrazine (tab. 3). This circumstance points at refractory, ceramic clays of the Poltár Formation containing probably also an admixture of well ordered kaolinite beside the dominating fire-clay mineral.

Certain differences between the clays of these two areas we may also follow in morphological development of the individual particles by aid of electron microscope (fig. 3, 4). The clays of the Poltár Formation from the Lučenecká kotlina Basin are formed by small particles with perfectly delimited sharp contours. Some of them are delimited geometrically and sporadically crystals are present, the edges of which show regular pseudohexagonal development. The clays from the Podvihorlatská panva Basin are characterized by completely irregular delimitation of particles with indistinct rims, what may be caused by bad planary orientation and formation of clusters. However, from morphological point of view a completely atypical kaolinite mineral is present there.

All the observed halloysites intercalate with K-acetate almost quantitatively. In contrast to the results of K. J. Range et all (1969) we have not recorded a quantitative intercalation in halloysites with hydrazine. Also no more distinct d_{001} shift towards lower angular vealues was taking place after glycerol of samples treated with hydrazine as well as with K-acetate. Remarkable is, that halloysite from Biela Hora near Micha-

Table 2. Grain size analysis of studied samples

Locality	% grain size fraction						
	>100 μm	100—50 μm	50—10 μm	10—5 μm	5—2 μm	2—1 μm	<1 μm
Kaolin Horná Prievraná	5,7	5,5	39,0	12,9	13,9	5,6	17,0
Fire-clay Poltár Formation	—	4,8	8,0	3,1	5,4	5,0	73,7
Halloysite Lučenecká kotlina Basin	12,1	5,1	18,9	8,8	13,5	6,9	34,7
Halloysite Slatinská kotlina Basin	3,0	1,6	5,0	5,3	7,7	0,8	76,6

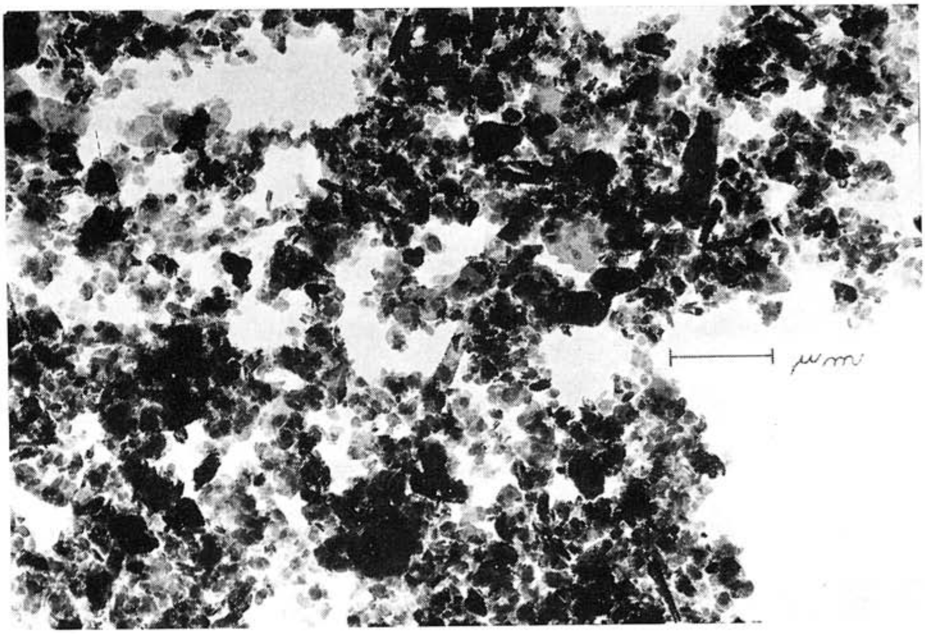

Fig. 3. Fire-clay, Poltár Formation.

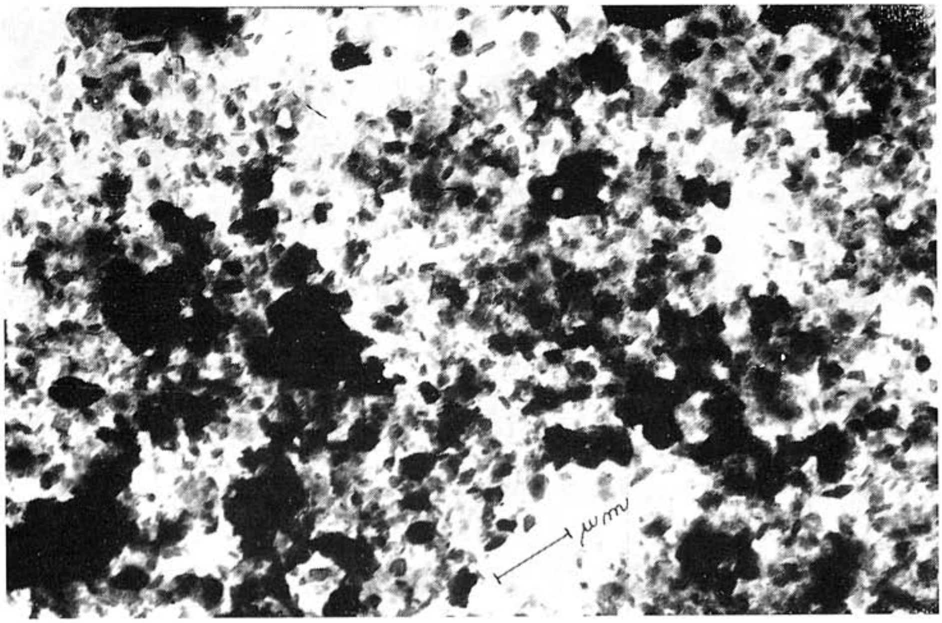

Fig. 4. Fire-clay, Podvihorlatská panva Basin.

lovce does not intercalate with hydrazine at all. So far we could not have cleared up the cause of this phenomenon.

Table 3. Intercalation of studied samples

Kaolinite	Fraction	Intercalation with K-acetate	Intercalation with hydrazine
Horná Prievraná "A"	1 µm	65 %	72 %
	1–2 µm	77	96
Horná Prievraná "B"	1 µm	68	94
	1–2 µm	100	96
Horná Prievraná "C"	1–2 µm	92	92
Vyšný Petrovec	1 µm	59	93
	1–2 µm	89	98
Fire-clay			
Poltár Formation "A" *	1–2 µm	13	34
Poltár Formation "C" *	1–2 µm	23	9
Poltár Formation "B" *	1–2 µm	10	0
Poltár Formation "D" *	1–2 µm	0	0
Podvihorlatská panva Basin "A"	1–2 µm	0	0
Podvihorlatská panva Basin "B"	1–2 µm	0	0
Podvihorlatská panva Basin "C"	1–2 µm	0	0
Podvihorlatská panva Basin "D"	1–2 µm	0	0
Halloysite			
Lučenecká kotlina Basin	1 µm	100	85
	1–2 µm	100	88
Slatinská kotlina Basin	1 µm	100	49
	1–2 µm	100	71
Biela Hora „A“	1–2 µm	78	0
Biela Hora „B“	1–2 µm	79	0

* The clays of the Poltár Formation contain an admixture of well ordered kaolinite beside fire-clay mineral.

Table 4. Relation between structure order and intercalation

Locality	„Index cristallinity“ according to D. N. Hinckley (1963)	Intercalation with K-acetate	Intercalation with hydrazine
Kaolinite Gluchoveckij**	1,44	81 %	90 %
Kaolinite Horná Prievraná	1,21	68	80
Kaolinite Prosjanovskij**	1,18	64	79
Kaolinite Dubrovskij**	0,83	52	16
Kaolinite Gluchovskij**	0,58	5	0
Fire-clay Poltár Formation	0,30	0	0
Podvihorlatská panva Basin	0,25	0	0

** Samples representing kaolin deposits of the Ukrainian SSR.

Intercalation in Dependence on the Size of Particles and Structural Order

The up to present results obtained in the study of intercalation abilities of clay minerals confirm that these reactions are of a course different in individual kaolin minerals. This circumstance is evident most markedly just at kaolinite. K. Wada (1961, 1965) was the first who called attention to the differences in intercalation of kaolinite with K-acetate. Later A. Alietti (1966) and A. Weiss et all (1966) have found kaolinite considered as well ordered on the basis of X-ray analysis to intercalate with K-acetate rapidly and quantitatively, disordered kaolinite to contain always the fraction intercalating only partly and/or intercalating at all, on the contrary. If the great influence of defects in kaolinite structure on its fundamental physical-chemical properties is generally recognized, a problem still remains clarification of their causes. The information obtained in X-ray study set out from the idea that the main cause of disorder in structure of kaolinite is the shift of layers in direction of axes „a" and „b". The importance of the study of intercalation abilities of kaolinite group minerals lies mainly in enlargement of our information in this way. Till now the largest problem remains right interpretation of this information.

On the one hand it is set out from the idea that of decisive influence on the order of structure and course of intercalation also in the case of two-layer clay minerals is substitution in tetrahedrons and octahedrons as well as the presence of inter-layer cations. On the other hand it is stressed that the course of intercalation is influenced mainly by the size of particles. According to A. Wiewiora and G. W. Brindley (1969) large particles have a greater density of structural defects than small ones and for that reason a more intense intercalation is to be seen in larger crystals than in small particles. According to them in kaolinite intercalation does not take place in particles less than 0,5 microns. The first idea sets out from the assumption that intercalations in minerals of the kaolinite group but mainly in fire-clay mineral is blocked by substitution in the whole crystal and the presence of inter-layer cations. The second idea explains intercalation as the process of penetration of organic substances only into "mechanical" defects in kaolinite crystal.

Based on the results of our work we conclude that the size of particles cannot be generally considered as first-rate factor affecting the course of intercalation. To a certain extent this influence is mainly shown in well ordered kaolinites. The results in tab. 3 prove that in the case of K-acetate intercalation is higher at particles in the fraction from 1—2 microns, in contrast to the fraction less than 1 micron. In the case of hydrazine the difference in intercalation of both fractions is insignificant. The different intercalation ability of kaolinite with K-acetate in dependence on the size of particles may be also caused by the admixture of kaolinite with more imperfectly ordered structure and/or the presence of fire-clay mineral. Different is the situation at clays of fire-clay type from the Podvihorlatská paňva Basin and Lučenecká kotlina Basin, which do not intercalate with K-acetate and hydrazine at all. We do not see the essentiality of this feature in the size of particles but in the structure of the discussed mineral at all. This circumstance is also confirmed by the directly proportinate dependence between the degree of structural disorder, which we have expressed quantitatively by the method according to D. N. Hinckley (1963) and the course of intercalation in tab. 4. Comparison of the results shows intercalation ability of kaolinite gradually diminishing with decreasing setructural order of the studied samples.

Existence of Fire-Clay Mineral

The study of intercalation of kaolinite group minerals has so far supplied most positive results in solution of mutual relations between kaolinite and fire-clay mineral. In contrast to up to present ideas considering the fire-clay as a variety of kaolinite with disordered structure K. J. Range et all (1969) prove an own mineral to be concerned with the following formula:

$(K^+, H^+)_x[Al_4(OH)_8(Si_{4-x}Al_x)O_{10}]$

where x varies in the interval from 0,08 to 0,12. Thus a structure is concerned, which enables to suppose isomorphous substitution in the frame of the whole crystal as well as the existence of inter-layer space filled out with K^+ and H_3O in contrast to kaolin structure. This circumstance is evident in fire-clay mineral not exhibiting intercalation with hydrazine and according to our observations even with K-acetate in contrast to kaolinite.

The observed essential differences in intercalation ability of kaolinite and fire-clay mineral, which we have found in Neogene sediments of the West Carpathians, fully support these assumptions. An argument important in the favour of this opinion is also the chemism of studied materials. The chemical analyses in tab. 1 show the clays considered by us as representatives of fire-clay mineral to be mainly characterized by increased content of Fe, alkalii and other components in spite of not to contain an admixture of other clay minerals and/or free Fe oxides. With the mentioned problem also relation between the structural order and course of intercalation is connected. The results in tab. 4 prove in this regard directly proportionate dependence indicating the pobability of the existence of an own series kaolinite—fire-clay.

A particular form of two-layer fire-clay mineral, characterized by isomorphous substitution in the whole crystal, the presence of inter-layer cations and high dispersion conditions many specific properties of these clays also from the standpoint of ceramics. In the first place we may mention their excellent plasticity, binding power and mainly easy sinterability under a very good thermal stability.

The mentioned shows that it will be necessary to call more attention to the problem of the existence of fire-clay mineral in the Neogene of the West Carpathians as the clays of this type differ much from well ordered kaolinites in their structure, chemism and technological properties. As natural, much obscurity remains there still. It is mainly the question of the boundary between kaolinite and fire-clay mineral, a thorough structural analysis of the fire-clay mineral as well as the problem of establishing of mechanical mixtures of kaolinite and fire-clay mineral, probably very frequent also in the Neogene of the West Carpathians.

Relation between Kaolinite and Halloysite

Although the period of the last 10 years has brought a vast amount of information, not existing till now, for clay-minerals of the kaolinite group, it is the mutual relation and position between the two most important minerals of this group — kaolinite and halloysite that always remains open. Following this important problem by aid of up to now existing methods (DTA, X-ray diffraction, electron microscopy) we often encounter contradictory results. We know cases that crystals of kaolinite perfectly delimited in morphology show marks typical of disordered structure in X-ray diffraction and on the other hand tubular particles are characterized by well ordered structure. In solution of these questions two contraversial ideas have formed.

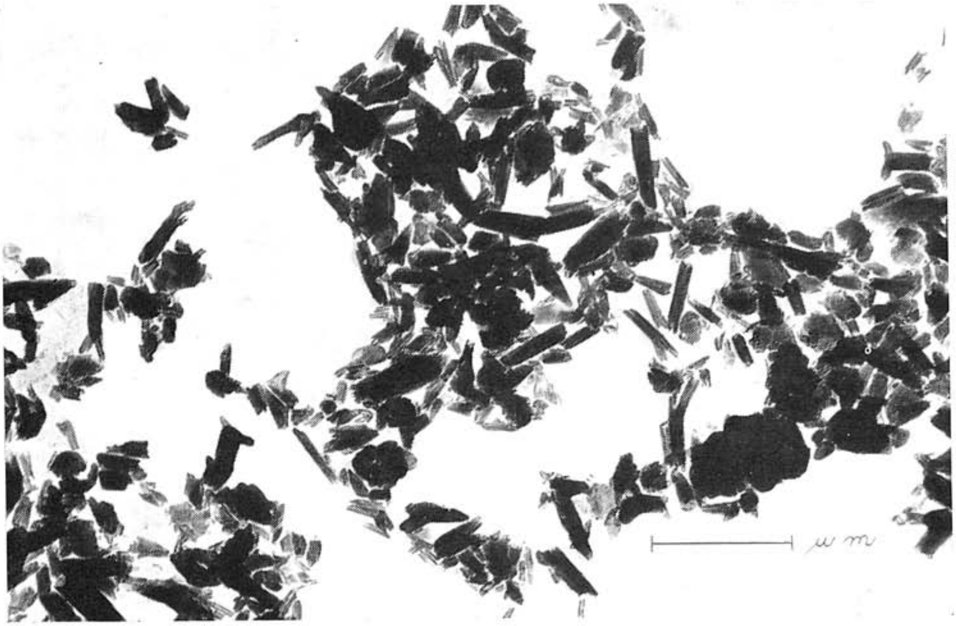

Fig. 5. Halloysite, Lučenecká kotlina Basin.

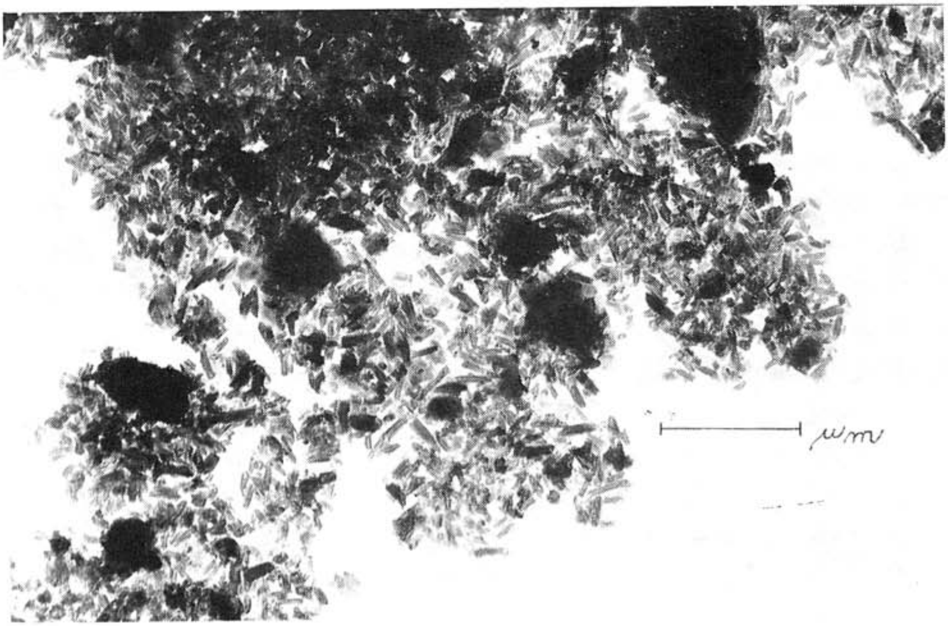

Fig. 6. Halloysite, Slatinská kotlina Basin.

G. W. Brindley and P. S. Santos (1968) have expressed the opinion that a continuous series of minerals exists with one structural layer per unit cell from kaolinite with highly ordered layer sequences, through mineral disordered mainly parallel to the "b"-axis — so called fire-clay with one — dimensionally disordered sequences, to halloysite with highly disordered parallel to the "a" and "b" axis, so called two-dimensionally disordered sequences.

F. V. Chukhrov and B. B. Zvyagin (1966) consider halloysite as own mineral characterized by monoclinic two-layer structure with parameters of elementary cell different from kaolinite. They prove the degree of structural order of halloysite to be changing in a range similar to that at kaolinite and for this reason exslude the possibility that halloysite is the terminal member of the series with the lowest degree of structure order. According to these authors the degree of structural order in halloysite decreases with highest content of water in inter-layer space. The so-called "tubular kaolinite", which according to G. Honjo et all (1954) and P. S. Santos et all (1965) has a triclinic two-layer structure is according to B. B. Zvjagin et all (1966) a typical halloysite with monoclinic two-layer structure, analogous to highly ordered kaolinite in this regard.

The X-ray diffraction and electron microscopic study of halloysites from the various localities in the Neogene of the West Carpathians, together with following of intercalation abilities points at considerable variability in their structural order. This moment is distinctly shown in the shape and position of basal reflexes (fig. 1), in morphological particularity of the individual particles (fig. 5, 6) and mainly in the chemism and different intercalation ability, especially with hydrazine (tab. 3). On the basis of these results we consider halloysite from the Lučenecká kotlina Basin, characterized by relatively sharp and high basal reflex during X-ray diffraction as well as an almost quantitative intercalation, as a mineral with higher degree of structure order in contrast to extremely finely dispersed halloysite from the Slatinská kotlina Basin with characteristic diffusive basal reflex, essentially lower intercalation ability and extraordinarily high content of Fe_2O_3, predominantly bound in the lattice of the studied mineral. The circumstance should be particularly mentioned that halloysite with admixture of fire-clay mineral from Biela Hora near Michalovce does not intercalate with hydrazine at all.

This information confirm the opinion that halloysite is an independent mineral, the degree of structure order of which is changing to a similar extent as at kaolinite. The idea of halloysite as an extreme, disordered member of the kaolinite series we consider as little probable so far.

Conclusions

Based on the study of intercalation abilities of kaolinite, fire-clay mineral and halloysite found in Neogene sediments of the West Carpathians we expressed some information concerning the problem of their mutual relations.

1. As it has been confirmed, between the intercalation of these minerals with K-acetate and hydrazine there exists a directly proportionate dependence. Well ordered kaolinites intercalate almost quantitatively. Insignificant or no intercalation is a property characteristic of clays, the essential component of which is fire-clay mineral. All the followed halloysites intercalate with K-acetate quantitatively. In contrast to up to present results mentioned in literature we have not recorded any quantitative intercalation with hydrazine in halloysite.

2. We suppose that the existence of fire-clay mineral in the Neogene of the West Car-

pathians is substantiated. We consider the fire-clay as a mineral of the kaolinite group with disordered structure which does not intercalate with K-acetate and hydrazine. The cause of this phenomenon we do not see in the size of particles but in the proper structure of this mineral. The directly proportionate dependence between the structure order and course of intercalation points at the probability of the existence of an independent series kaolinite — fire-clay.

3. The mineralogical study of halloysites together with following of intercalation abilities points at a considerable variability in their structure order. This information support the opinion that halloysite is an independent mineral, the degree of structure order of which is changing to a similar extent as at kaolinite. The idea of halloysite as an extreme, disordered member of the kaolinite series we consider as little probable so far.

Acknowledgements

We are deeply indepted to E. G. Kukovskij and his collaborators from the Institute of Physics and Geochemistry of Minerals at the Academy of Science of the USSR in Kiev for the samples of kaolinites from deposits of the Ukrainian Soviet Socialist Republik.

Translated by J. PEVNÝ.

REFERENCES

ALIETTI, A., 1966: Identification of disordered kaolinites. Clay Miner. (Oxford-Edinburg), 6, No. 3, p. 229—231.

BRINDLEY, G., W., SANTOS, P. S., 1966: New varietes of kaolin-group minerals and the problem of finding a suitable nomenclature. Proceedings Intern. Clay Conference (Jerusalem), 1, p. 3—9.

DEEDS, C. T., OLPHEN VAN, H., BRADLEY, W., F., 1966: Intercalation and interlayer hydration of minerals of the kaolinite group. Proceedings Intern. Clay Conference (Jerusalem), 1, p. 295—296.

ENGELHARDT VON, W., 1954: Ein Tonminerale der Kaolinit-Halloysitgruppe von Provins (Frankreich). Heidelberger Beitr. Mineral Petrog. (Heidelberg), 4, p. 319—324.

EWAN MAC, D., M., C., 1946: Halloysite organic complexes. Nature (London), 157, p. 159—160.

EWAN MAC, D., M., C., 1948: Complexes of clays with organic compounds. Trans. Faraday Soc., 44, p. 349—368.

HINCKLEY, D., N., 1963: Variability in "crystalinity" values among the kaolin deposits of the coastal plain of Georgia and south Carolina. Clays and Clay Minerals, Proceedings Eleventh Nat. Conference (Oxford-London—New York—Paris), p. 229—235.

HONJO, G., KITAMURA, N., MIHAMA, K., 1954: A study of clay minerals by means of simple crystal electron diffrection diagrams. The structure of tabular kaolin. Clay Miner. Bull. (London) 2, No. 12, p. 133—141.

HORVÁTH, I., 1969: Kaolin Horná Prievraná. Unpublished Dissertation Thesis, Bratislava.

CHUKHROV, F. V., ZVYAGIN, B., B., 1966: Halloysite, a crystallo-chemically and mineralogically distinct species. Proceedings International Clay Conference (Jerusalem), 1, p. 11—25.

KOCHANOVSKÁ, A., 1955: Roentgenografická studie halloysitového jílu z Michalovců. Technologie silikátů. Sborn. výskum. prací (Praha), 2, p. 7—18.

KONTA, J., 1957: Jílové minerály Československa. Praha, p. 1—319.

KRAUS, I., GERHOFFEROVÁ, H., KRIŽÁNI, I., 1966: The occurrence of halloysite in deposits of the Poltár Formation. Geol. zborn. Slov. akad. vied (Bratislava), 17, No. 1, p. 117—130.

KUKOVSKIJ, E., G., 1966: Osobennosti stroenija i fiziko-chimičeskie svojstva glinistych mineralov. Kijev, p. 1—130.

MILLER, W., D., KELLER, W., D., 1963: Differentiation between endelite-halloysite and kaolinite by treatment with potassium acetate and ethylene glycol. Clays and Clay Miner. Proceedings Tenth Nat. Conference (New York), 10, p. 244—253.

PERLIN, V., D., 1966: Metodika rentgenografičeskogo opredelenija galluazita. Rentgenografija mineraľnogo syrja (Moskva), 5, p. 132—137.

RANGE, K., J., RANGE, A., WEISS, A., 1969: Fire-clay type kaolinite or fire-clay mineral? Experimental classification of kaolinite-halloysite minerals. Proceedings Intern. Clay Conference (Tokyo), 1, p. 3—13.

SANTOS, P., S., BRINDLEY, C., W., SANTOS, H., S., 1965: Mineralogical studies of kaolinite-halloysite clays. Part III. A fibrous kaolin mineral from Piedade, Sao Paulo, Brazil. Amer. Mineralogist (Washington), 50, p. 619—627.

SERDJUČENKO, D., P., 1952: Mineraly kory vyvetrivanija na zmeevikach reki Malki. Kora vyvetrivanija (Moskva), 1, p. 23—63.

WADA, K., 1961: Lattice expansion of kaolin minerals by treatment with potassium acetate. Amer. Mineralogist (Washington), 46, p. 78—91.

WADA, K., 1965: Intercalation of water kaolin minerals. Amer. Mineralogist (Washington), 50, p. 924—941.

WEISS, A., THIELEPAPE, W., ORTH, H., 1966: Neue Kaolinit-Einlagerungsverbindungen. Proceedings Intern. Clay Conference (Jerusalem), p. 277—293.

WIEWIORA, A., BRINDLEY, G., W., 1969: Potassium acetate intercalation in kaolinite and its removal; effect of material characteristics. Proceedings Intern. Clay Conference (Tokyo), 1, p. 723—734.

ZVYAGIN, B., B., BERCHIN, S., I., GORŠKOV, A., I., 1966; Strukturnyje osobennosti galluazita po dannym difrakcii rentgenovskich lučej i elektronov. Rentgenografija mineraľnogo syrja (Moskva), 5, p. 69—93.

Review by M. HARMAN.