CHARACTERIZATION OF KAOLIN MINERALS OF DIFFERENT ORIGIN

(essentially from Hungarian deposits)

É. Kocsárdy and A. Heydemann

ABSTRACT

Kaolinite minerals from weathered rhyolite tuffs, from sedimentary kaolin clays, bauxites and argillaceous lignites were studied by X-ray diffractographic, infrared-spectroscopic and thermo-analytic methods. In addition to determining the mineralogical composition and the grain size distribution of bulk samples, the authors obtained closer characterization of various kaolinite minerals by measuring the polytypes and the crystallinity state of the minerals. X-ray diffractography was used for assessing the Hinkley index and the half-width of the 001-reflection, while infrared techniques were resorted to for assessing, among other things, the K_1-index ($K_1 = E_{3695 \, cm}^{-1} / E_{3620 \, cm}^{-1}$) and the K_2-index ($K_2 = E_{3670} + E_{3650} + E_{3620}/E_{3695}$).

All these results should be relied on for attempting to distinguish between kaolinites of different genesis.

INTRODUCTION

The various kaolin deposits of Hungary have already been studied mineralogically by many authors [among others: Nemecz, 1973; Mátyás, 1974]. According to these investigations some of the deposits were formed by postvolcanic activities, others by nearsurface weathering processes. Consequently, the kaolin minerals occurring in these deposits must have been formed under different physico-chemical conditions. The question is whether the differences in the genetic processes are anyhow reflected in the structure of the kaolin minerals, their polytypes or the degree of stacking.

Van der Marel and Krohmer [1969] examined the crystallinity of kaolinites, fireclay minerals and ball clays of various deposits by means of X-ray and infrared spectroscopic method. They found the degree of stacking to vary widely within each group, but they did not discuss whether differences in the genesis were responsible for this. Kato and Kanaoka [1978] while studying Japanese kaolins by means of special infrared spectroscopic techniques did succeed in differentiating between kaolinites of hydrothermal and weathering origin on the basis of their different structure. But their samples came from a restricted area.

Aim of the present work was therefore to examine to what extent differentiation between kaolin minerals of different origin and mode of occurrence is really possible.

EXPERIMENTAL

Methods

The kaolin samples were fractionated after ultrasonic treatment into the fractions $<2 \, \mu \, \varnothing$, $2-63 \, \mu \, \varnothing$ and $>63 \, \mu \, \varnothing$. X-ray diffraction analyses of oriented and randomly oriented samples were made with CuKα radiation and X-ray fluorescence analyses with W-radiation.

A Perkin Elmer grating IR spectrometer 457 was employed for IR-analyses using the KBr-pellet technique. Thermogravimetric analyses were made with a Mettler TA—1 Thermal Analyzer (heating rate: 10°/min, TG: 100/10 mg).

The mineralogical composition of the samples was determined by X-ray, IR- and thermoanalytic techniques [KOCSÁRDY, 1978, FLEHMIG and KURZE, 1974].

Material

Samples of various kaolin deposits from all over Hungary were investigated. In *Fig. 1* locality, mode of occurrence, genesis and mineral composition of the samplex are listed. Six samples from the Tokaj Mountains were selected as examples for hydrothermal kaolin formation. The deposits were formed predominantly in Sarmatian time by postvolcanic processes. Main source rocks were rhyolites. Kaolins
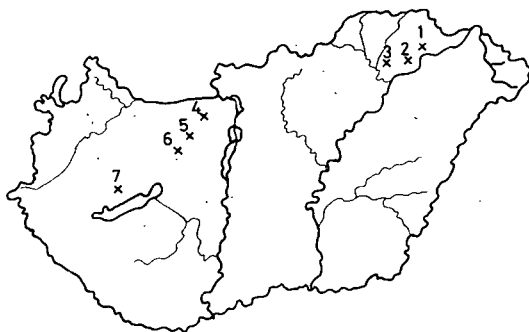
Samp-le	Localities	Occur-rence	Genesis	Mineral composition
1 KSZ	Szegilong / Tokaj M.	kaolin	hydroth.	
KBO	Bomboly / "	"	"	
2 KKP	Királyhegy / "	"	"	
KKD	Királyhegy / "	"	"	
3 KDR	Rátka / "	"	"	
KBR	Rátka / "	"	"	
5 B 16	Tatabánya	with	weath.	
B 41	"	brown	+	
B 42	"	coal	diagen?	
4 KS	Sárisáp / Visegrád	kaolin	weath.	
6 KBG	Gánt	in	weath. +	AL—HYDR.
7 KBH	Halimba	bauxite	diagen.	n. d.

kaolinite   quartz   illite   smectite   other min.   coal

Fig. 1. Kaolin samples from Hungary compared to one another regarding locality, genesis and mineral composition

occur partly as primary deposits but also sedimentary kaolins are present in the near-
by basins. Their material was mainly derived from the primary deposits in the sur-
roundings. Kaolin minerals and quartz are the major components, smectites, amor-
phous silica, volcanic glass and alunite occur occasionally. Three samples were
collected from the Eocene brown coal basin of Tatabánya. These are carbona-
ceous clays to clayey lignites. The mineral assemblage shows kaolin minerals as ma-
jor component together with quartz, illite and illite-chlorite mixed-layer minerals.
Investigations of the carbonaceous matter exhibits varying degrees of coali-
fication, notably sample B42 is most strongly coalified.

According to VARJÚ [1966] the kaolins of Sárisáp were formed by weathering
processes probably involving organic substances derived from the overlying lignite
seams.

The kaolin minerals occurring in the bauxites of Gánt and Halimba are believed
to provide additional examples for non-hydrothermal minerals. But from the geol-
ogical setting it cannot be decided whether they are formed by weathering or dia-
genetically by re-silicification of aluminum hydroxides.

In addition to this Hungarian material samples of other deposits were also
analyzed (Fig. 2). The kaolin of Wolfka (GDR) resulted from weathering of por-
phyry rocks, those from Karlovy Vary and Sedlec (Zettlitz, Czechoslovakia) from
granites and at Horny Briza arkoses were subjected to weathering. From similar
source rocks the kaolin of Georgia (USA) is derived. The kaolin of Keokuk (Iowa,
USA) originated from geodes.

Sample	Localities	Occur-rence	Genesis	Mineral compostion
KW	Wolfka (GDR)	kaolin	weath.	
KHB	Horny Briza (ČSSR)	kaolin	weath.	
KKV	Karlovy Vary (ČSSR)	kaolin	weath.	
KZ	Sedlec (ČSSR)	kaolin	weath.	
KG	Macon, Georgia (USA)	kaolin	weath.	
KK	Keokuk, Iowa (USA)	geode	diag.?	

kaolinite   quartz   illite

Fig. 2. The investigated kaolin samples from Europa and the USA and their mineral composition

Characterization of kaolin minerals

Mainly X-ray methods and IR spectroscopic techniques were chosen for the
characterization of the kaolin minerals.

X-ray diagrams from randomly oriented samples were used for the determina-
tion of the Hinkley index, H_i [HINKLEY, 1963]. Its determination is shown schema-
tically in *Fig. 3*. This index H_i, the crystallinity index, gives an estimation of the
extent of stacking imperfections. The values for H_i vary between zero for poorly
crystallized kaolin minerals and 1.6 for very well crystallized kaolinites.

X-ray diagrams of oriented samples were used to determine the peak width of
the (001)-reflection at half height *(Fig. 3)*. TRUNZ [1974] found a striking correla-

TABLE 1

IR-characteristics of kaolin minerals
(K: extinction ratios see Fig. 4)

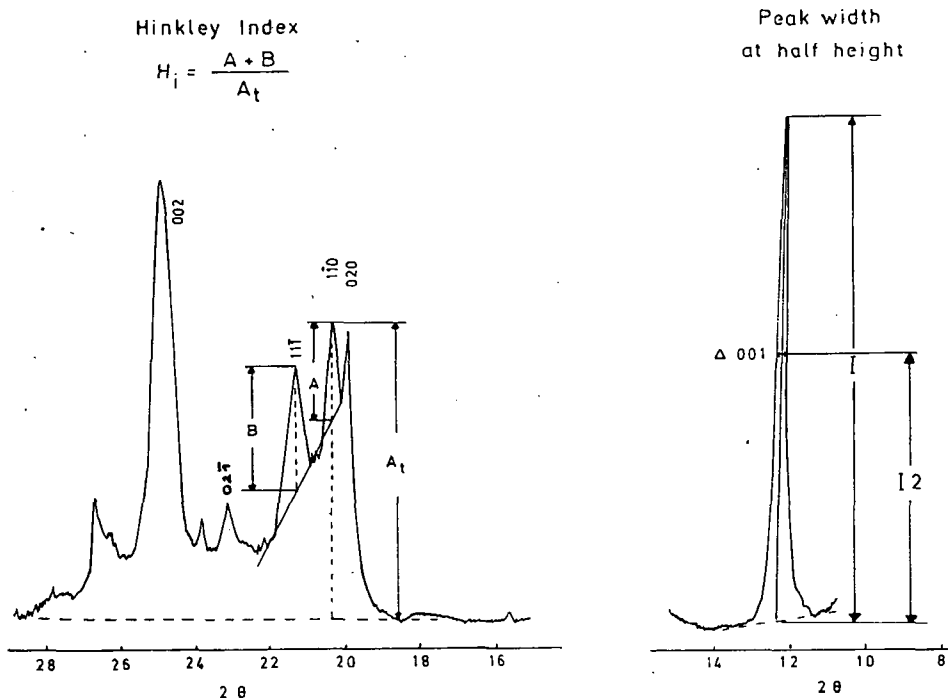|	Polytype		n_{OH}	K_1	K_2	K_3
kaolinite-D	T_d	monoclinic	3	1.1—1.5	—	>1.4
kaolinite	1T	triclinic	4	1.0—1.7	1.4—2.2	—
dickite	2M	monoclinic	3	0.5—1.1	—	1.5

Fig. 3. Definition of the Hinkley index (H_1) and the measure of half-width of the 001 line

tion between the Hinkley index and this width at half height. But he admitted that from a crystallographic point of view an increase in the broadening of the (001) peak with increasing stacking imperfections (decreasing crystallinity) does not seem plausible.

The IR spectra in the region of the OH-stretching vibrations (3700—3500 cm^{-1}) provided primarily information on the kaolin polytype present in the sample. The number of absorption bands (n_{OH}) together with the extinction ratio of the two strongest bands (at 3695 and 3620 cm^{-1}) were used for the differentiation between T_d kaolinite, 1T kaolinite and dickite (Table 1, Fig. 4).

But also information on the crystallinity of the various minerals were derived from the IR spectra. Already PARKER [1969] used the ratio Å 3695/Å 3620 for the
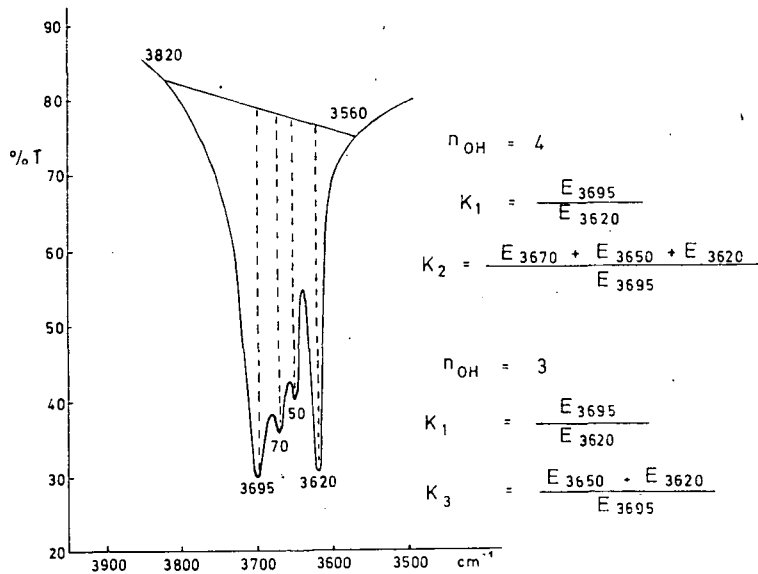
Fig. 4. Calculation of the crystallinity index from IR spectra at $n_{OH}=4$ and $n_{OH}=3$

characterization of kaolinites and discovered a relationship between the crystallinity. index H_i and this ratio.

Here the extinction ratios K_1, K_2 and K_3 were introduced. Definition and calculation of these terms are shown in *Fig. 4*. Only a very vague relationship between crystallinity index H_i and the extinction ratios could be detected.

RESULTS AND DISCUSSION

The preliminary results of this investigation are summarized in Table 2. Polytype, K-values, peak width (Δ 001) and crystallinity index H_i of the kaolin minerals together with grain size distribution of the samples are listed.

Most striking is the fact that there are samples which contain two kaolin polytypes side by side, for example T_d kaolinite in the $<2\,\mu$ fraction and 1T kaolinite in the $>2\,\mu$ fraction.

Kaolin clays consisting of mixtures of kaolin polymorphs have been described by KELLER [1967, 1978], who used electron optical methods. From X-ray analyses no such informations are available. Crystallinity indices can be obtained from the diagrams. But, it is impossible to decide whether the crystallinity represents an "apparent" one, derived from a mixture, or is the "true" crystallinity of a single kaolin polytype.

Also IR spectra are not conclusive, in general. In *Fig. 5* data from artificial mixtures of well crystallized 1T kaolinite and poorly crystalline T_d kaolinite (both $<2\,\mu\,\varnothing$) are presented. With increasing admixture of the T_d component the K_2 value decreases. In a monomineralic sample this would mean decreasing crystallinity. But here the value of K_2 depends exclusively on the composition of the mixture. It is also noteworthy that even in mixtures containing 70% of the T_d kaolinite, still the 1T polytype is predominant (in the OH-region of the IR spectra four bands are recorded).

95

TABLE 2

Polytypes, extinction ratios K_1, K_2, K_3 peak width at half height ($\Delta 001$) and Hinkley index H_i from the kaolin minerals present in the samples studied, in addition the grain size distribution
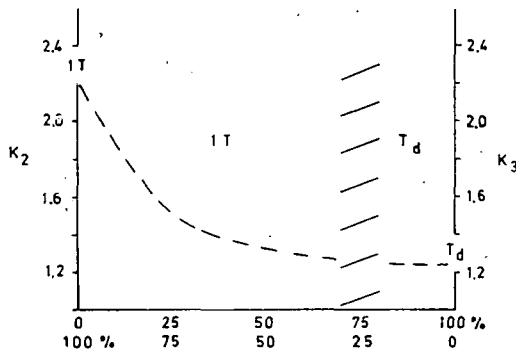

Fig. 5. Change of the crystallinity indices in 1T and T_d kaolinite mixtures

For the interpretation of the data in Table 2 these observations are of some importance. In samples, where IR analyses revealed two polytypes, all data are very likely only "apparent" ones, resulting primarily from the mixture of the two components. Differences between the grain size fractions can therefore exclusively be explained by changes in the composition of the mixture, for example T_d kaolinite

96

predominant in the $<2\ \mu$ and 1T kaolinite in the $>2\ \mu\ \varnothing$ fraction. But also variations in the properties of a single polytype with grain size may add to these differences. In samples where IR analyses revealed only one polytype, still two or more may be present. This can be demonstrated with a kaolinite from China. Electron optical studies indicated the presence of at least two polymorphs (pers. communication of Prof. KELLER), while the IR spectra and X-ray diagrams of both size fractions were almost identical, thus giving no hint to the presence of more than one polytype in this sample. These observations have to be considered further.

A first attempt of differentiating between kaolin minerals of different genesis was made by checking the influence of the environments on the formation of kaolin polytypes. All three, T_d kaolinite, 1T kaolinite and 2M dickite do occur in both hydrothermal and weathering-diagenetic environments.

The 2M polytype (dickite) was found, however, only in a few samples from the Tokaj territory and the Tatabánya coal basin. The dickite from the Tokaj Mountains came from zones directly adjacent to points of hydrothermal exhalations. Here hydrothermal genesis seems to be certain. The dickites from Tatabánya were found in those parts of the brown coal deposits where coalification of the surrounding lignites was the highest. It is assumed that these deposits were for some time locally subjected to higher temperatures. Under favourable conditions coalification coupled with alteration of pre-existing kaolin minerals into dickite must have taken place. Alteration of poorly crystalline kaolin minerals into dickite during high grade diagenesis was already described by SHUTOV [1970]. The presence of dickite consequently does not imply the conclusion of hydrothermal origin, but elevated temperatures apparently seem to be necessary.

The two kaolinite polytypes, 1T and T_d, have for a long time been known to occur in both the hydrothermal as well as in the weathering domains [SUDO and SHIMODA, 1978, among others], a fact also confirmed by the data presented here.

As far as the Hinkley index H_i and the K-values are concerned, similar variations are observed independent of the origin of the kaolin minerals.

Summarizing all the observations it can be stated that kaolin minerals of the same polytype and crystallinity occur in deposits formed under very different conditions. On the other hand different polytypes were observed side by side in deposits supposedly formed by the same process.

Already KELLER [1977] emphasized the importance of the geochemical environment for the formation of the various kaolin polytypes or polymorphs under weathering conditions. Also for hydrothermally formed kaolin minerals the geochemical parameters seem to be significant. This resulted from chemical and mineralogical investigations of kaolin samples from the Tokaj Mountains (Table 3).

The poorly crystalline T_d kaolinite from Szegilong (KSZ) is rich in iron, while the well crystallized 1T kaolinite from Bomboly (KBO) contains only very little iron in the structure. Similar relationships between iron content and crystall were also observed by MESTDAGH et al., [1980].

Not only variable iron content, but also variation of the zinc concentrations emphasize differences in geochemical environment during mineral formation. Although KÖSTER [1969] stated that the trace element of kaolin minerals is largely determined by the source rock, in the Tokaj area certainly both, composition of the hydrothermal solution and source rock (mainly rhyolitic tuffs) were important geochemical parameters.

KELLER [1977] called also attention to the possiblity of changes of the primarily formed kaolin minerals by diagenetic processes, particularly in older kaolin deposits.

To what extent such diagenetic alterations changed already the primary composition of the kaolins studied here is difficult to say. The formation of dickite in the brown coals from Tatabánya were explained by such processes.

Iron, zinc and kaolin mineral content in the < 2 μ fraction of samples from the Tokaj area (samples were treated with buffered sodium dithionite solution for removal of iron oxyhydrate coatings)

Sample	Kaolin min. content	Polytype	Fe %	Zn ppm
KSZ	>95	T_d	4.9	500
KKP	>95	1T	1.6	150
KBO	90	1T+2 M	0.3	240

Considering all the observations and data it seems very unlikely that differentiation between kaolin minerals of different origin should be possible if it is based exclusively on investigations of crystal structure, polytype or crystallinity as determined by X-rays and IR spectroscopy. Even if all available data from geological, chemical, mineralogcial analyses are considered in addition, differentiation seems still to be rather difficult.

REFERENCES

BÁRDOSSY, G. [1966]: Les minéraux hydrosilicatés (argileux) de la bauxite. Acta Geologica Hung., X, 233—248.

FLEHMIG, W., KURZE, R. [1973]: Die quantitative infrarotspektroskopische Phasenanalyse von Mineralmengen. N. Jb. Miner. Abh. 119, 101—112.

HINKLEY, D. N. [1963]: Variability in crystallinity values among the kaolin deposits of the coastal plain of Georgia and South Carolina. Clays and Clay Minerals 11 229—235.

KATO, E., KANAOKA, S. [1978]: Differentiation of hydrothermal kaolinite from weathered kaolinite by IR spectra in OH region. Sixth International Clay Conference, Oxford,

KELLER, W. D., HAENNI, R. P. [1978]: Effects of microsized mixtures of kaolin minerals on properties kaolinites. Clays and Clay Minerals 26, 384—396.

KELLER, W. D. [1977]: Scan electron micrographs of kaolin collected from diverse environments of origin. IV. Georgia kaolin and kaolinized source rocks. Clay and Clay Minerals 25, 311—345.

KOCSÁRDY, E. [1978]: Die IR-Spektroskopie der Kaolinitpolytypen. XXI. Ungarische Spektroskopische Tagung, Szeged, Ungarn.

KÖSTER, H. M. [1969]: Beitrag zur Geochemie der Kaoline. Intern. Clay Conference Tokyo, 273—280.

MAREL, VAN DER H. W. [1969]: OH-stretching vibrations in kaolinite and related minerals. Contr. Mineral and Petrol., 22, 78—82.

MÁTYÁS, E. [1974]: Volcanic and postvolcanic processes in the Tokaj Mountains on the basis of geological data of raw material prospecting. Acta Geological Sci. Hung., 421—455.

MESTDAGH, M. M., VIELVOYE, L., HERBILLON, A. J. [1980]: Iron in kaolinite: II. The relationship between kaolinite crystallinity and iron content. Clay Minerals 15, 1—13.

NEMECZ, E. [1981]: Clay minerals. Akadémiai Kiadó, Budapest.

PARKER, T. W. [1969]: A classification of kaolinites by infrared spectroscopy. Clay Minerals 8, 135p.

SHUTOV, V. D., ALEKSANDROVA, A. V. [1970]: Genetic interpretation of the kaolinite group in sedimentary rocks. Sedimentology 15, 69—82.

SUDO, T. SHIMODA, S. [1978]: Clay sand Clay Minerals of Japan. Developments in Sedimentology, Elsevier.

TRUNZ, V. [1974]: Untersuchung zu Fehlordnungserscheinungen des Kaolinites: eine röntgenographische Linienprofilanalyse mit Hilfe der Variant Methode. Dissertation, Clausthal.

VARJÚ, G. [1968]: Kaolin deposits of Hungary. XXIII. Intern. Geological Congress, Prague, 179—200.

ANNEROSE HEYDEMANN
Department of Mineralogy
University of Göttingen
Göttingen
FRG

ÉVA KOCSÁRDY
ALUTERV-FKI
Department of Material Science
1509 Budapest
P. O. B. 5
Hungary