KAOLINITE-GENETIC AND THERMOANALYTICAL PARAMETERS

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Abstract

Different genetic types of kaolinite were investigated from the point of view of crystallinity. The measurements were carried out by means of different methods of thermal analysis, infrared spectroscopy and X-ray diffraction. The different parameters of the degree of crystallinity based on a series of 85 nearly monomineralic samples were critically studied. The estimated parameters of the different methods show relatively bad correlation. The reason for the difference in the data come from the fact that the methods give information about different parts and/or features of the mineral structure. The results are better if several parameters are simultaneously used. In the present paper the results of thermal parameters are summarized.

Keywords: kaolinite crystallinity, thermoanalytical parameters

Introduction

The occurrence of each mineral in the nature generally indicates different genetical conditions such as temperature, pressure, or concentration of the elements, etc. The same mineral may be frequently encountered in environments of different genetics. Conclusions on the genesis and antecendents of a mineral (for instance the temperature during its genesis, the bauxitization, the diagenesis, etc.) can be drawn by studying the form of appearance of the minerals. The degree of crystallinity can be a possible genetical feature of clay minerals, among them kaolinites.

Various instrumental analytical methods have been known for use in the determination of the polytype modifications, crystallinity and the degree of order of kaolinite.

When using an X-ray diffraction method, the crystallinity of kaolinites is indicated by the intensity conditions of certain reflections, the shape and 'd' value of basal reflections, and the extent of the splitting of reflections that are close to each other [4, 11, 20]. The reflection shifts obtained during various thermal and chemical (K-acetate, hydrazine etc.) treatment procedures are also suitable for the determination of the degree of crystallinity [33, 25].

Table 1 Ranges of characteristic peaks for kandites

	1.	2.	3.	4.	5.
	°C		A/B		°C
Dickite	680				
Nakrite	660				
Kaolinite	580	>575	0.78–1.5	0.8–1	980–1005
Fireclay		<575	1.5–2.4	1.2–1.4	940
Halloysite	560		2.5–3.8	1.8	

1 Peak temperature of thermal decomposition after Mackenzie (1957)
2 Peak temperature of thermal decomposition after Smykatz-Kloss (1974)
3 Slope ratio of the main endothermic peak after Bramao *et al.* (1952)
4 Slope ratio of the main endothermic peak after Robertson *et al.* (1954)
5 Peak temperature of the exothermic reaction after Smykatz-Kloss (1974)

Table 2 Kinetic data of the thermal decomposition

	1.	2.	3.
	kcal (g mol)$^{-1}$	the same /kJ mol^{-1}	
Dickite	48	200	
Kaolinite	38–40	158–168	1.06
Fireclay	22–30	90–125	
Halloysite	34–37	142–155	0.5–0.7

1–2 Activation energy (from isothermal weight loss) after Murray & White (1949)
3 Reaction order (from DTA) after Kissinger (1957)

When using IR-spectrometric analysis, the polytype modification of kaolinites, as well as the various degrees of crystallinity within the kaolinite are most frequently determined on the basis of the intensity ratios of the OH stretching vibrations [15, 22, 26, 34, 9, 29, 14, 7]. Kaolinites can also be featured by the intensity ratios of the OH deformation vibrations [2], the width of the OH valence vibrations, as well as the dimensions of the deformation band of water at 1630 cm^{-1} and the stretching band at 3440 cm^{-1} [12]. According to Gribina *et al.* [10] the absorbance ratio of the lattice vibrations is used to characterize the degree of crystallinity.

Table 3 Relation of α to ther symmetry parameter A/B

%	A/B
45	0.8
50	1.0
55	1.2
58	1.4
64	1.8

Of the thermoanalytical results, mainly the temperature and the geometric parameters of thermal effects appearing in the DTA curve (peak temperature, peak symmetry, peak width, intensity ratios of thermal reactions, etc.) can be used to draw conclusions on the degree of order [21, 5, 3, 17, 28, 6, 18, 30–31]. Murray & White [19] succeeded in distinguishing minerals of different kaolin groups on the basis of the activation energy of the decomposition reaction. Information is also supplied by the mass ratio of the interlayer and lattice waters determined from the thermogravimetric curve. The classification of kaolinite-type minerals based on different kinds of thermal parameters is presented below.

When using any of the methods listed above in actual practice, it is frequently experienced that measurements show a bad correlation. The reason for the difference in the data comes from the fact that the methods give information about different parts or features of the mineral structure. A great number of problems arise, when samples other than monomineralic are used for the determination of the degree of crystallinity of kaolinite. For instance, the application of Hinckley's index is disturbed if the sample has a high goethite or quartz content. In addition, the water content – OH ratio cannot be measured, unless the sample contains neither clay minerals of 2:1 structure nor any other water-bearing mineral. Interference by accompanying minerals (clay minerals, bauxite minerals, siderite, pyrite, etc.) can also disturb the determination carried out by means of thermoanalytical or IR-spectroscopic methods.

Our study described in the present paper is based mainly on computer controlled thermal analysis and gives the results of the critical investigation of each method, including the conclusion the be drawn therefrom.

Applied methods

Apparatus

Thermal analysis was carried out using a derivatograph-PC, a microcomputer automated apparatus, which is suitable for the simultaneous recording of thermogravimetric (TG), derivative thermogravimetric (DTG), thermogastitrimetric (TGT) and differential thermoanalytical (DTA) curves. If necessary, the device can also display graphically the DDTG, DDTA, DTGT curves, i.e. curves obtained by deriving the primary curves [23].

The mass of the sample was measured by the semi-microelectronic and automatic balance of the equipment (sample weight in this study was about 100 mg).

The temperature of the furnace was regulated by a linear heating program at a rate of $10^\circ C$ min^{-1}.

The software program for data processing and data handling permits calculation of the apparent kinetic parameters.

Evaluation.
The measured parameters of the thermoanalytical curves were as follows:

• Corrected peak temperature of thermal decomposition (determined from the DTG curve): This parameter was introduced for assessing the degree of crystallinity of kaolinite by the author of this study, because the temperature of decomposition depends not only on the degree of order or the possible substitution in the lattice (for instance by iron), but also on the concentration even under the same experimental conditions. The method based on the so-called 'Proben Abhängigkeit' curves show the temperature versus logarithmic concentration for a well-ordered kaolinite and a fireclay after Smykatz-Kloss [30], (Fig. 1). The difference in decomposition temperature between the two minerals – in the case of the same concentration – is 28°C. A curve with a similar slope has been obtained from our data
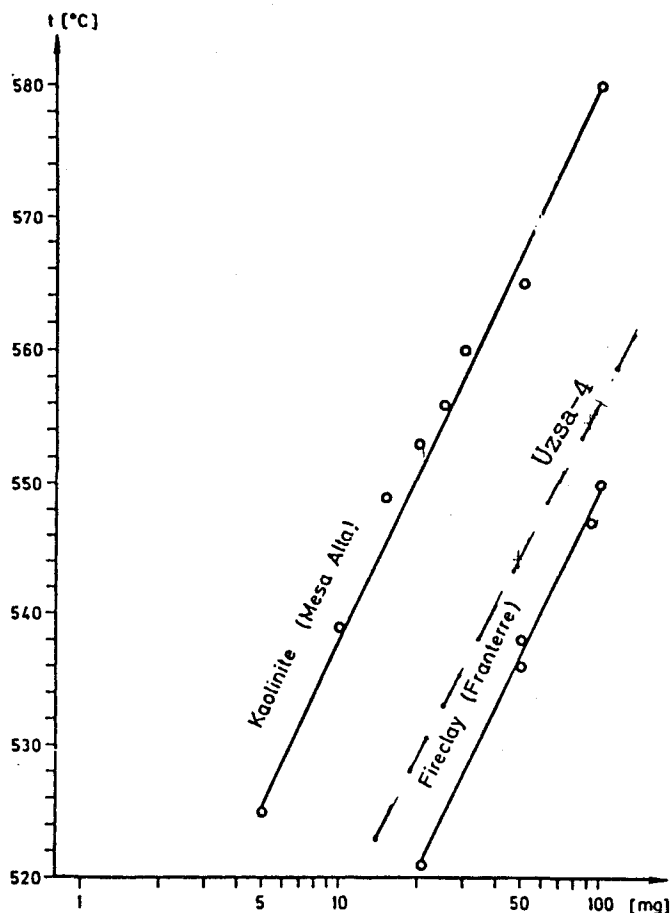

Fig. 1 PA-curves of different kaolinites slope of decomposition temperature *vs.* logarithmic concentration (after W. Smykatz-Kloss, 1974). Increasing the concentration by order of magnitude: 42.3°C (Mesa Alta), 41°C (Franterre), 41.3°C (Uzsa-4)

for a kaolinite sample of bauxites (in the middle). The corrected peak temperature is the calculated peak temperature for 100 mg of the measured kaolinite related to the temperature of 100 mg Mesa Alta kaolinite.

Method of calculation:

$$d = T_m - 495.3 + (42.3\log(m7.17))$$

where T_m = measured peak temperature; m = OH in mg during the dehydroxylation calculation for 100 mg

$$T_{cor} = 580 + d$$

• Width of the endothermic peak: according to Pokol et al. [24]

$$T(0.8 - 0.2)$$

• Sharpness of the endothermic peak: according to Pokol et al. [24]

$$\frac{T(0.8 - 0.2)}{1/(d\alpha/dt)}$$

• Symmetry of the endothermic peak: α

where α = percent of decomposed part at the maximum rate of the dehydroxylation reaction.

• Kinetic parameters for thermal decomposition (calculated from dynamic TG).

The computer calculates

• the apparent reaction order by the Kissinger method (13):

$$n = 1.26 \cdot (a/b)^{1/2}$$

• the activation energy according Arnold et al. (1):

$$E = \frac{n[\ln(1 - \alpha 1) - \ln(1 - \alpha 2)]}{(1/T1 - 1/T2)} * R$$

• Temperature of the exothermic peak.
• Intensity of the exothermic peak: $dT(DTA_{max} - DTA_{min})$. Values were obtained after enlargement, base line correction and were calculated for the same amount of kaolinite (100 mg). (This value corresponds to the endothermic peak intensity/exothermic peak intensity parameter used by others earlier.)
• Width of the exothermic peak: $T(DTA_{max} - DTA_{min})$
• Proportion of OH/H_2O

As the results of measurement show that the sharpness is highly dependent on the concentration, and the order of reaction shows good correlation with the symmetry, they were not analysed in the present study.

The following statements can be made based on the parameters:

• the OH/H2O ratio, temperature and activation energy of the decomposition re-action, the temperature and intensity of the exothermic reaction – although not al-ways in the same manner – reflect the dickite-kaolinite-fireclay-halloysite series.

• the iron oxide contamination on the surface of the particles has a great influ-ence on the size and shape of the exothermic peak.

As clearly shown by the data, the measured activation energy values are lower for dickites than for the highly crystalline kaolinites. This is especially striking when samples taken from the same locality (for example Beregovo or Mád) are con-cerned.

Table 4 Genetic types of kaolinite examined

Genetic type	Localities	Number of samples
High temperature post-volcanic alteration	Sárospatak, Mád (Hungary), Beregovo (Ukraine), Baia Mare, Cavnic (Romania)	7
Low temperature hydrothermal alteration	Recsk, Asztagkő, Sárospatak, Mád (Hungary), Beregovo (Ukraine)	9
Low temperature weathering	Cserszegtomaj (Hungary), Sedlecz (Czech. Republic), Ràzoare, Stejera (Romania)	10
Terrestrical sandstone	Felsőpetény, Sárisáp (Hungary), Nova Ves (Slovak Republic), Stejera (Romania)	8
Bauxite	Alsóörs, Gánt, Koldusszállás, Mesterberek, Nagyharsány, Németbánya, Uzsa (Hungary), Tahanovce (Slovak Republik), International standard	45
Paleosol (devonian)	Drake (Missouri)	6

Table 5 Results of OH/H_2O ratio measurements

Genetic type	Interval of data	Average
High temperature post-volcanic alteration	36.7 infinity	
Low temperature hydrothermal alteration	2.61 infinity	
Paleosol (devonian)	36.2–49	42.6
Terrestrical sandstone.	6.3–13.9	10.6
Low temperature weathering	0.7–14.8	6.5
Bauxite	1.4–20.8	5.3

Table 6 Corrected decomposition temperatures

Genetic type	Interval of data/°C	Average/°C
High temperature post-volcanic alteration	600–682	633
Low temperature hydrothermal alteration	560–586	576
Paleosol (devonian)	568–578	572
Terrestrical sandstone	548–574	561
Low temperature weathering	549–567	560
Bauxite	549–571	558

Table 7 Width of decomposition peak data

Genetic type	Interval of data/°C	Average/°C
High temperature post-volcanic alteration	89.5–110	99.3
Low temperature hydrothermal alteration	54–92	73.2
Paleosol (devonian)		
Terrestrical sandstone	70.8–117	89.6
Low temperature weathering	60–101.5	79.1
Bauxite	61–80	68.3

Table 8 Symmetry of decomposition peak data

Genetic type	Interval of data/°C	Average/°C	
High temperature post-volcanic alteration	49.1–80	61.9	
Low temperature hydrothermal alteration	41.7–60	53.5	
Paleosol (devonian)			
Terrestrical sandstone	31–57	44.7	*
Low temperature weathering	44–67	54.8	**
Bauxite	50–66	56.3	

* only 1 data > 50
** only 2 data < 50

These data are contrary to those published by Murray & White [19]. As experienced by Stoch & Waclawska [32] for dickites, the dehydroxylation process can be divided into two stages having a difference of approx. 20% in activation energy. The initial part that relates to the removal of one-third of the OH groups has an activation energy corresponding to that of poorly crystalline kaolinites, whereas the second part exhibited values corresponding to the highly crystalline kaolinites. The value of activation energy we have measured obviously corresponds to the average of them both.

Based on the results discussed above, it can be concluded that a combined application of several measured parameters should permit characterization of samples of

Table 9 Experimental activation energy data

Genetic type	Interval of data/kJ mol^{-1}	Average/kJ $mol-1$
High temperature post-volcanic alteration	71.9–130.3	110.4
Low temperature hydrothermal alteration	124.8–161	142.5
Paleosol (devonian)	132.6–141	137.2
Terrestrical sandstone	109.5–129	118.3
Low temperature weathering	106.4–159	134.3
Bauxite	113.5–165	131.8

Table 10

Polytype	Locality		kJ mol^{-1}
Kaolinite	Beregovo	1st class	161.5
Kaolinite	Beregovo	2nd class	154.0
Kaolinite	Beregovo	3rd class	143.9
Dickite	Beregovo		130.3
Kaolinite	Mád		124.8
Dickite	Mád		105.5

Table 11 Exothermic peak temperature data

Genetic type	Interval of data/°C	Average/°C
High temperature post-volcanic alteration	991.5–101	1002.1
Low temperature hydrothermal alteration	987.2–100	995.8
Paleosol (devonian)	989–1000	995.8
Terrestrical sandstone	950–995	983.9
Low temperature weathering	953–982	966.9
Bauxite	944–995	967.6

Table 12 Intensities of exothermic peaks

Genetic type	Interval of data/°C	Average/°C
High temperature post-volcanic alteration	0.53–2.62	1.23
Low temperature hydrothermal alteration	0.21–1.30	0.86
Paleosol (devonian)	0.58–1.00	0.77
Terrestrical sandstone	0.19–0.43	0.31
Low temperature weathering	0.15–1.00	0.64
Bauxite	0.21–0.49	0.49

different genenis. Only samples of genetic bauxite and weathering have similar parameters from all points of view.

Observation of fine changes in certain parameters of a certain locality, can also be very useful in following the geological processes.

At the Uzsa Kaolinite Deposit in Hungary, Upper Triassic dolomite chimneys and sink-holes contain the kaolin clay which, owing to its elevated position, was not involved in a bauxitization, that took place at other sites at that time. In the area a total of 34 samples from the filling of 2 sink-holes, were subjected to a detailed study. For these, only the data from thermal measurements are presented here, since the X-ray measurement of Hinckley's index was greatly disturbed by an interference caused by the high goethite content. On the basis of the data it was observed that the tendencies of the two profiles are different:

For the profile Uzsa-4, the data (Table 15) concerning the crystallinity of kaolinite show a scattered pattern within a limited range, only the corrected decomposition temperature indicates a minor increasing tendency toward the depth. How-
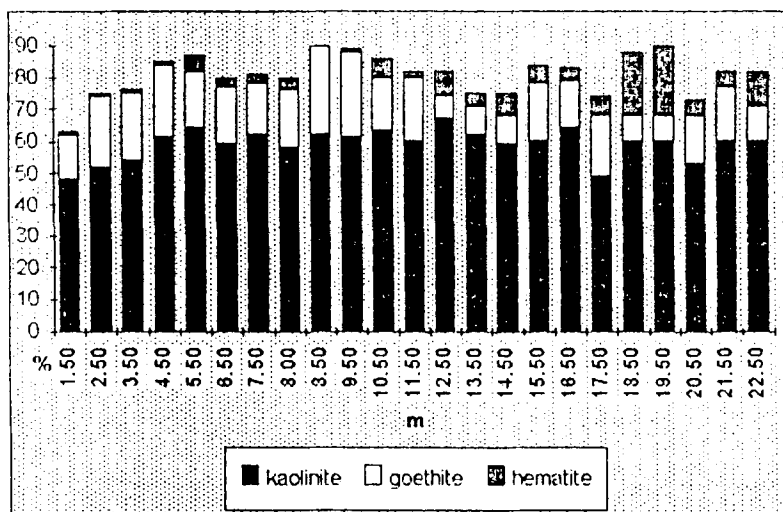

Fig. 2 Mineralogical composition of borehole Uzsa-4

Table 13 Width of exothermic peaks

Genetic type	Interval of data/°C	Average/°C
High temperature post-volcanic alteration	21.5–43.5	35.8
Low temperature hydrothermal alteration	18.5–44.0	31.6
Paleosol (devonian)	34.1–72.8	46.2
Terrestrical sandstone	28.0–41.0	34.9
Low temperature weathering	26.5–68.5	42.7
Bauxite	21.5–62.9	33.2

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Table 14 Characteristic ranges of the measured parameters

OH/H_2O		T_d	E	Pd_{width}	α	T_{ex}	Pex_{int}	Pex_{width}
>50	high temperature post-volcanic	>600	70–130	85–110	>50			
	low temperature hydrothermal	<590	120–160	50–95				
36–50	high temperature post-volcanic	>600	70–130					18–45
	low temperature hydrothermal	<590	120–160					
	paleosol (devonian)	<580	>130					34–72
<20	low temperature hydrothermal terristrical sandstone	>560				>585	>0.6	
	low temperature weathering bauxite	<575			<50	<595	<0.6	
<6	low temperature hydrothermal	>560			>50	>585	>0.6	
	low temperature weathering bauxite	<575				<595	<0.6	

Table 15 Mesured thermal parameters for the samples of the borehole Uzsa-4

m	OH/H$_2$O	T_{cor}/°C	$T_{20} - T_{80}$/°C	α/%	E/kJ mol^{-1}	T_{ex}/°C
1.5	4.1	553.9	63.6		136.1	960.3
2.5	4.0	554.8	62.1		141.1	956.1
3.5	4.5	549.6	64.5		140.4	953.8
4.5	5.0	555.4	66.4	57	151.3	974.0
5.5	5.3	548.0	66.3	57	129.2	968.9
6.5	4.6	559.6	67.7	56	129.2	968.9
7.5	4.6	556.2	71.0	54	128.7	966.8
8.0	5.0	559.4	70.0	57	121.2	966.5
8.5	4.4	552.7	67.2	56	126.2	954.1
9.5	4.5	554.9	66.6	55	129.9	964.0
10.5	5.3	557.3	67.5	58	124.4	961.3
11.5	5.1	557.9	66.4	56	127.1	961.9
12.5	4.9	560.7	70.0	52	130.1	966.5
13.5	5.3	563.3	71.6	55	122.2	974.2
14.5	4.6	559.4	67.8	56	131.4	965.2
15.5	4.3	560.4	66.4	58	129.3	962.0
16.5	4.9	555.9	71.1	53	125.9	960.1
17.5	3.8	556.6	72.6	52	126.8	966.2
18.5	7.7	560.2	66.5	54	134.5	989.2
19.5	8.4	558.9	68.7	56	128.8	980.8
20.5	4.8	553.4	68.2	50	144.6	962.0
21.5	4.2	556.7	61.9		150.3	958.3
22.5	5.2	561.8	69.0	55	123.7	968.2

ever, on the basis of two parameters (OH/H$_2$O and the temperature of the exothermic peak) there are two samples at 18.5 and 19.5 m considerably differing from the other samples of the profile and reflecting a higher degree of crystallinity.

These two samples have a goethite content of 5 and 6%, which is lower than the average of the other samples, and high hematite content, from 20 to 22%, as compared to the average of 4% of the other samples (Fig. 2).

	Goethite	Hematite
18.5–19.5	5–6%	20–22%
other samples	7–28(17)	0–11(4)

The higher degree of crystallinity of kaolinite, as well as the alteration of goethite to hematite, indicates that these two samples improved strongly by diage-

Table 16 Thermal parameters measured for the samples of the borehole Uzsa-6

m	OH/H_2O	T_{cor}/°C	$T_{20} - T_{80}$/°C	α/%	E/kJ mol^{-1}	T_{ex}/°C	Ex_{int}/°C
1.5	6.2	553.1	61.0	61	150.2	959.9	0.61
2.5	5.7	555.9	62.0	61	150.7	969.5	0.78
3.5	5.6	550.0	61.0	62	140.9	963.8	0.41
4.5	4.2	557.7	68.8	56	127.1	959.3	0.58
5.5	4.5	556.2	66.3	55	126.8	959.9	0.44
6.5	4.0	557.4	70.0	57	126.1	959.5	0.55
7.5	5.3	553.4	68.0	58	130.1	973.5	0.50
8.5	2.7	557.6	71.0	58	125.3	979.4	0.24
9.5	2.9	552.6	70.0	57	124.9	966.7	0.26
10.5	2.1	554.5	76.5	50	117.1	978.6	0.57
11.5	2.4	553.1	76.5	54	113.5	963.5	0.21

netic processes. These data have led us to the conclusion that the profile consists of samples which are transported from different sites and were subject to different processes.

For the profile Uzsa-6, which, from the point of view of mineral composition is similar to Uzsa-4, the measured parameters usually show a good correlation, showing a gradual change toward the depth (Table 16). Samples found at the top in the sink-hole seem to have the highest degree of crystallinity, according to the OH/H_2O ratio, the activation energy, the width and the symmetry of the decomposition reaction as well as the intensity of the exothermic peak. In this profile the transported samples underwent a further kaolinization in the sink-hole.

Conclusion

Based on the above examples it can be stated that in the detailed analysis of each locality, some parameters that were not significant in the case of kaolinites of the series of standards, can also be very useful. The application of more parameters at a time also offers a possibility to observe fine phenomena.

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