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THE USE OF CORRECTED THERMAL DECOMPOSITION TEMPERATURE IN THE GEOLOGICAL INTERPRETATION. I

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Abstract

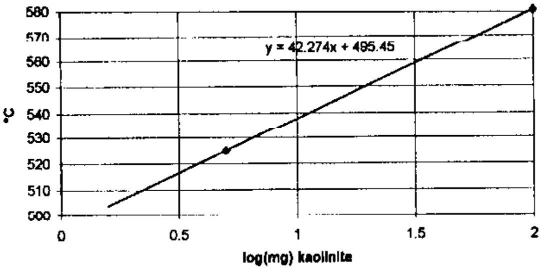
Dehydroxylation of kaolinite, thermal decomposition of calcite, dehydration of some cases of minerals bearing molecular water in the structure serve as example of the use of corrected temperature taking into the influencing quantity instead of the measured temperature. By using this, method data become more characteristic and comparable and the correction makes them suitable for further analysis, such as crystallinity, substitution, binding force, genesis etc.

Keywords: crystallinity, sample amount dependence, standard decomposition temperature

Introduction

There is a well-known fact that the peak temperature of a decomposition process due to the partial pressure of the decomposed gas or vapour product depends among others on its amount. The relation between peak temperature and concentration is

amount of kaolinite/mg	log(mg)	peak temperature of dehydroxylation/ °C
100	2	580
5	0.698970004	525



standard decomposition temperature=	peak temperature of 1mg kaolinite =	495.45 °C

Fig. 1 PA curve of the well-ordered kaolinite from Messa Alta (based on data measured by Smykatz-Kloss)

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logarithmic. Based on this connection for the quantitative determination of different minerals in the sample from the DTA curve the so-called PA (Proben Abhängigkeit) curves were introduced by Smykatz-Kloss [1] (Fig. 1).

In the case of geological samples the concentration is not only the single reason for the dispersion of the temperature data. The structure of the natural minerals depending on their genesis or geological past often differs from the ideal. This fact influences the decomposition temperature, too. A distinction between the two reasons is possible when we make a comparison between the decomposition reaction temperature of the same among of the investigated mineral sample and a reference mineral.

An extrapolation from the measured peak temperature and from the mass change during the decomposition process (measured by TG) to a standard quantity (e.g. 1 or 100 mg) of the decomposed product makes our data comparable (Fig. 2).

	measured amount of OH in kaolinite/mg	log(mg) OH	peak temperature of dehydroxylation/°C	peak temperature of dehydroxylation/°C
Messa Alta	13.94700139	1.14448	580	
as comparative curve	0.69735007	-0.1565	525	
Kaolinite sample for specification				
measured parameters	22	1.34242		558.6
extrapolation for 100 mg kaolinite*	13.95	1.14457		550.5
deviation**				-29.5

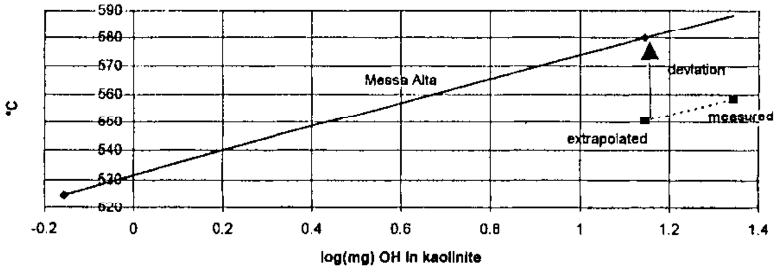

Fig. 2 Indirect parameters for the characterisation of material used in this work (*extrapolated decomposition temperature=peak temperature of 13.95 mg OH in 100 mg kaolinite, ** deviation=peak temperature difference between 100 mg kaolinite from Messa Alta and kaolinite examined)

From the differences among the comparative standard decomposition temperatures conclusions on other facts which influence the decomposition temperature (crystallinity, substitution, different geological processes as weathering, diagenesis, etc.) may be drawn.

Besides the earlier investigation of the dehydroxylation temperature in point of view of genetic type of kaolinite [2] measurements were carried out for different other mineralogical question as illite-muscovite series, octahedral substitution in montmorillonite lattice, crystallinity of different genetic of calcite, substitution and chemical composition of the carbonates of calcite series, interlayer cation in montmorillonite, Al substitution in goethite, zeolites, perlites etc. The calculations introduced enable to quantify the measurements.

Experimental

Thermal analysis was carried out by using a Derivatograph-PC, a computer conrolled simultaneous TG, DTG, DTA apparatus. The temperature of the furnace was egulated by a linear heating program at a rate of 10°C min^{-1}. The mass change of he sample was measured by the semi-microelectronic and automatic balance of the quipment. Other analytical conditions: air atmosphere, ceramic crucible, mass of amples about 100 mg, reference material Al_2O_3.

The temperature of the data measured in thermoanalysis besides the behaviour of he material depend on a lot of analytical factors (e.g. heating rate, instrument type, ample holder, sample amount). In the case of this type of the investigations there is bsolutely necessary to work under the same conditions (first of all important the gemetry of the crucible and the heating rate). Only data measured at the same instrunent and under the same conditions can be compared. Reference curves recomnended to make for another equipment with different dilution of the same material.

Studies on kaolinites

Different genetic types of kaolinite were investigated from the point of view of rystallinity (Table 1). The temperature of dehydroxylation peak of 153 kaolinite

Table 1 The genetic types of kaolinite examined

Genetic type	Localities	Number of samples
High temperature hydrothermal	Sárospatak, Mád (Hungary), Beregovo (Ukraine), Baia Mare, Cavnic (Romania)	9
Low temperature hydrothermal	Recsk, Asztagkő, Sárospatak, Mád, Budai Mt. (Hungary), Beregovo (Ukraine)	17
Low temperature weathering	Cserszegtomaj (Hungary), Sedlecz (Czech. Republic), Răzoare, Stejera (Romania)	54
Bauxite	Alsóörs, Gánt, Iharkút, Koldusszállás, Mesterberek, Nagyharsány, Németbánya, Uzsa (Hungary), Tahanovce (Slovak Republic)	51
Paleosol (Devonian)	Drake (Missouri)	6
Paleosol (Triassic)	Szentkirályszabadja, Hajmáskér (Hungary)	3
Paleosol (Pleistocene)	Hungary	4
Terrestrical sandstone	Felsőpetény, Sárisáp (Hungary), Nova Ves (Slovak Republic), Stejera (Romania)	25

bearing samples is found between 518–684°C (average 553, median 549°C). This interval is about four times as much as the temperature shifting influenced by the change of quantity in order of magnitude of the same kaolinite sample (42°C). The great difference due to the order of kaolinite, indirectly to the genetic of the mineral.

Measuring data of 169 kaolinite bearing samples are illustrated in Fig. 3.

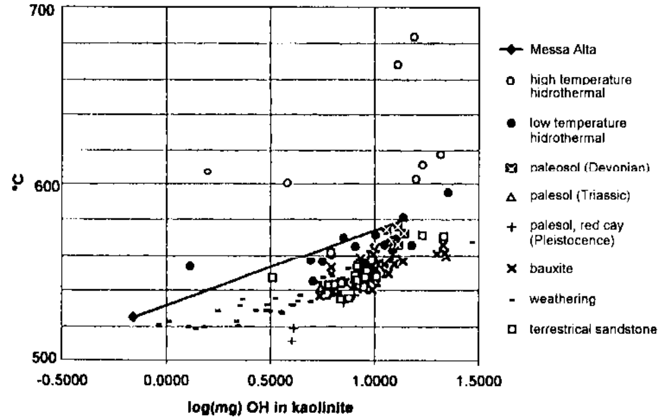

Fig. 3 Relationship between dehydroxylation temperature and OH content of different genetic types of kaolinite

The separation of genetic types is more expressive if the values of deviation are used (Fig. 4).

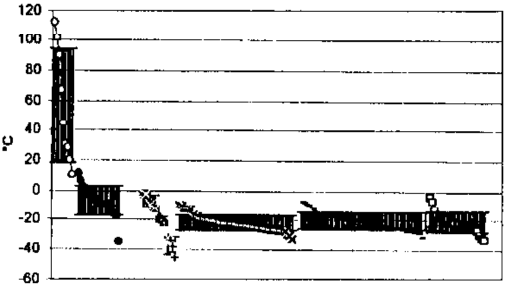

Fig. 4 Deviation in°C with dispersion (legends at Fig. 3)

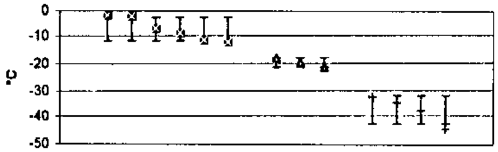

Fig. 5 Diagenesis of kaolinite in paleosol (legends at Fig. 3)

The temperature deviation shows with temperature of the exothermic peak the best correlation (for 181 pairs of data r=0.55, which corresponds to 0.1 of significance level) among other parameters, which are suitable for the characterization of the crystallinity of kaolinite. The shift of temperature of the dehydroxylation process is twice the shift of the temperature of the exothermic peak.

One of the uncountable possible cases is the investigation of diagenesis of kaolinite in paleosol [3] (Fig. 5).

Studies on calcites

The temperature data of decomposition process of about 100 calcite bearing rock samples according to the above mentioned in Fig. 6 are summarized. All the sample come from Hungary with the exception of marbles which come from Bulgaria and Cuba The measured temperatures of decomposition peak are between 647–940°C. The temperature shifting due to the change of quantity in order of magnitude of the same calcite sample is 95°C.

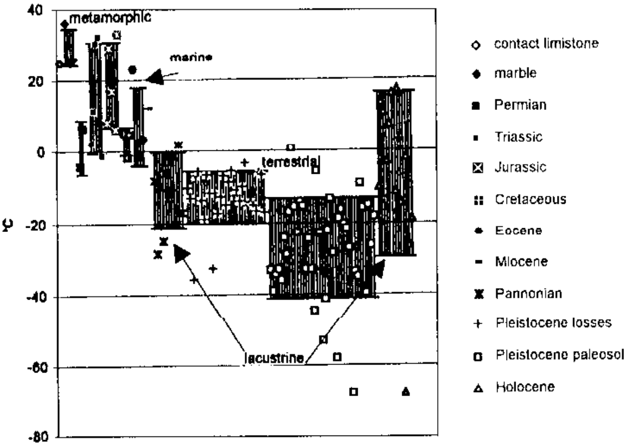

Fig. 6 Temperature deviation of thermal decomposition process of calcite in rocks of different genetic and age

It may be seen the differences of the carbonate decomposition according to the age or to the geological circumstances.

A case in point the shadowing of the pleistocene climatic history in a loess section of the Hungarian lowland [4]. Table 2 summarize the deviation of calcite decomposition temperature of the samples from borehole Udvari-2A. There are principal differences between the carbonate of loesses formed during the cold periods and of paleosoils formed during interglacial warm and wet periods. The lower decomposition temperature indicates the distroyed structure of carbonate effected by eluviation. Whereas one sample from the the lime accumulation horizon shows a very high decomposition temperature (temperature deviation + 6°C).

Table 2 Calcite decomposition temperature at the samples from borehole Udvari-2A

deep/m	Formation	Deviation from comparative standard/°C
10.8	paleosol	–33.3
23.3	loess	–10.4
31.3	loess	–13.1
36.1	paleosol	–39.0
41.6	loess	–35.8
46.8	loess	–7.0
51.8	loess	–5.7
58.8	loess	–13.7
62.8	loess	–18.8
68.5	paleosol	–34.4
68.7	paleosol	–33.1
71	paleosol	–36.1
73.8	loess	–6.6
74.4	loess	–11.7
79.7	paleosol	–24.3
79.7	loess	–32.8
84.7	loess	–11.8
89.4	loess	–17.3
91.3	paleosol	–29.1

Studies on minerals and rocks bearing water in molecular form

Molecular water can be bound in different ways in minerals. According to the temperature of dehydration process two main groups may be separated. The dehydration of the first group occurs in the temperature interval between 95–160°C (in order of bonding force water adsorption on the surfaces by van der Waals forces, 'zeolitic water' in channels more or less freely or bound to the internal surface of the channels formed by SiO_4 or AlO_4 tetrahedra, interlayer water in clay minerals, first step of crystal water in hydrated minerals bound by coodination forces around certain cations of the structure, gel water in amorphous minerals belong to the group). The dehydration of higher level take place generally in the temperature interval of 185–420°C (2nd, 3rd, etc. steps of hydrated minerals, water in zeolites coordinated to cations in the channels, water in natural glasses).

Taken the peak temperature of dehydration as a function of quantity of water may accurate the data. After the above mentioned extrapolation temperature data are suitable for further analysis.

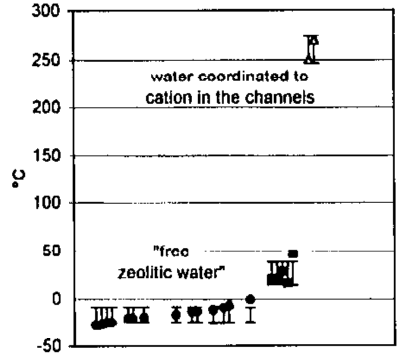

Fig. 7 Temperature deviation of dehydration process of clinoptilolite: ●, mordenite: ■ and natrolite: Δ

In the case of perlites the value of deviation may serve as an index-number to express the degree of alteration. The thermoanalytical data of a zeolitization series in the borehole No. 1. at Kishuta (Hungary) [5] show that during the lateness of the process the water content of the rock is greater and the temperature maximum of dehydration is lower. The deviation from the comparative curve (in this case the calibration curve of a montmorillonite sample with an equation T= 95.6°C+ 29*log(mg of water) (Fig. 8) express the connection of the change of two parameters (Table 3).

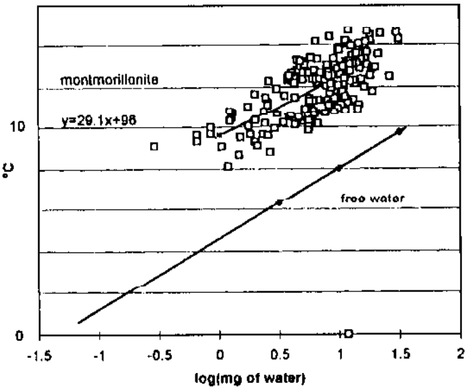

Fig. 8 Dehydration temperature of natural (Ca and Na) montmorillonites

The corrected dehydration temperature data of clinoptilolite and mordenite reflect the difference between the free aperture of main channels and the kinetic diameter of the two minerals. Data of natrolite show the difference in binding force between zeolitic water and water bond by coordination forces in zeolites (Fig. 7).

Table 3 Thermoanalytical data of the zeolitization series in borehole No. 1 at Kishuta

deep/m	Water content of the sample/%	Peak of dehydration/°C	Deviation/°C
104.3–107.5	6.8	260	112.2
355.3–358.3	8.0	200	50.5
321.4–324.3	8.2	195	45.2
337.6–340.3	8.7	160	9.3
332.8–334.3	9.3	120	−25.1

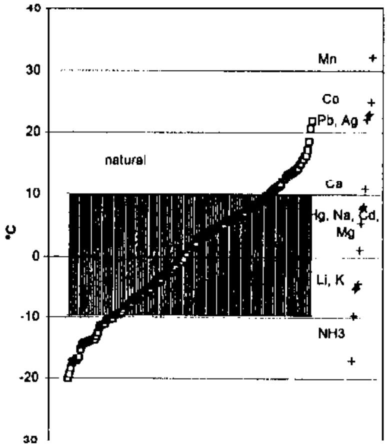

Fig. 9 Deviation of the main dehydration temperature at natural and cation exchanged montmorillonites

In certain cases the influence of the cation exchange on the main dehydration temperature of montmorillonite [6] can be observed (Figs 8, 9).

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