

Dedicated to Professor Ferenc Paulik on the occasion of his 75th birthday

USE OF THE SECOND DERIVATIVE OF TG CURVES FOR INVESTIGATION OF THE EXCHANGED INTERLAYER CATION IN MONTMORILLONITE

M. Földvári¹, P. Kovács-Pálffy¹, N. M. Nagy² and J. Kónya²

¹Hungarian Geological Survey, Budapest, Stefánia út 14, H-1143

²Isotope Laboratory, Kossuth University, Debrecen, H-4010, Hungary

Abstract

Various cation-exchanged montmorillonites (Li^+ , Na^+ , Ba^{2+} , Mg^{2+} , Ca^{2+} , Mn^{2+} , Co^{2+} , Cu^{2+} , Ag^+ , Cd^{2+} , Hg^{2+} , Al^{3+} , Pb^{2+} and NH_4^+) were prepared from calcium montmorillonite and their properties were studied by means of X-ray diffraction and thermal analysis. The two methods give information on the cation exchange in the interlayer space only. X-ray diffraction studies at room temperature are mainly suitable for estimation of the exchange of cations of different valencies. At 500°C, when the structure is completely collapsed, the d value of montmorillonite depends on the non-hydrated ionic radius of the interlayer cation, but the measurement interval is limited for fine interpretation. The thermoanalytical method is suitable for a better distinction of different exchangeable cations of higher hydration energy on the basis of the DTG or DDTG curve.

Keywords: cation exchange, montmorillonite, thermogravimetry, X-ray diffraction

Introduction

The montmorillonite crystal lattice consists of two layers of silica tetrahedra separated by one layer of alumina octahedra. In the tetrahedral layer, some silicon ions are replaced by aluminium ions, and in the octahedral layers aluminium ions may be replaced in general by iron(II), iron(III) or magnesium ions. These natural substitutions of silicon and aluminium result in a negative charge, which is balanced by the presence of exchangeable cations, commonly divalent calcium or monovalent sodium. For these reasons, montmorillonites from different locations demonstrate varying chemical and physical properties, and these differences are further compounded by the different types of mineral impurities that may be present. An outstanding feature of the montmorillonite structure is that water (and other polar molecules) can enter between the unit layers, causing the lattice to expand in the c direction.

The presence of different ions as exchangeable cations greatly influences the properties of montmorillonite and especially the all-important swelling characteristics (engineering geology). A knowledge of the properties of cation-exchanged montmorillonites is very important from the point of view of their industrial use and in studies of the contamination and decontamination of aqueous and soil systems and the interfacial reactions between microelements, toxic ions, soils and rocks (agriculture specific environmental studies, etc.). A great number of papers have been published recently on the various artificially cation-exchanged montmorillonites (e.g. as catalysts in organic syntheses, etc.).

In present paper, various cation-exchanged montmorillonites and their properties are studied, involving

- ions in macro-concentrations in rocks and soils: Ca^{2+} , Mg^{2+} , K^+ and Na^+
- toxic elements: Cd^{2+} , Co^{2+} , Cu^{2+} , Pb^{2+} , Mn^{2+} , Hg^{2+} , Al^{3+} and (Li^+)
- a radioactive waste end-product: Ba^{2+}

Experimental

Two types of montmorillonite were applied as basic materials: One is calcium bentonite from Buru, Romania, which X-ray diffraction studies show a montmorillonite content of about 60%. The other Ca-montmorillonite is a natural substance from Istenmezeje, Hungary, with a montmorillonite content of about 80%.

Preparation of various cation-exchanged montmorillonites

The fraction $<2 \mu\text{m}$ was separated by sedimentation in water. Suspensions were made of air-dried calcium montmorillonite in different metal nitrate or chloride solutions with concentrations of from 0.01 to 1 mol dm^{-3} , in ratios of from 1:5 to 1:50, or in different chloride solutions in concentrations from 1 mol dm^{-3} . The mixtures was stirred for several hours, and then centrifuged. The supernatant was poured off, fresh electrolyte solution was added, and the mixture was then stirred and centrifuged again. This procedure was repeated from 3 to 10 times. Finally, the solid product was washed with alcohol or water and dried in air or in some cases at 105°C (Mn, Co, Ag and Pb). The conditions are detailed in Table 1.

The quantities of exchanged metal ions in the montmorillonite were determined by an X-ray fluorescence method.

The structural modifications of the various cation-exchanged montmorillonites were determined by means of X-ray diffraction, using a computer-controlled Philips PW1710 diffractometer with a Cu anticathode, operating at 30 mA and 40 kV and with a graphite monochromator. The scanning rate was $2^\circ 2\Theta \text{ min}^{-1}$.

Thermal analysis was carried out with a Derivatograph-PC, a computer-controlled simultaneous TG, DTG DTA apparatus. This can display graphically the

Table 1 Procedure used for the preparation of cation-exchanged montmorillonites

	Mass of Ca-montmorillonite/ g	Solution	pH	Number of treatments	Temperature of drying/ °C
Ag-montmorillonite	10	25 cm ³ 0.03 mol dm ⁻³ AgClO ₄	3.9	3	105
Ag-montmorillonite	10	25 cm ³ 0.03 mol dm ⁻³ AgClO ₄	2.9	3	105
Al-montmorillonite	20	100 cm ³ 0.002 mol dm ⁻³ Al(NO ₃) ₃	3.2	7	105
Al-montmorillonite	20	20 cm ³ 0.012 mol dm ⁻³ Al(NO ₃) ₃	3.5	7	25
Ba-montmorillonite	1	50 cm ³ 0.05 mol dm ⁻³ BaCl ₂	6-7	1	25
Ca-H-montmorillonite	10	100 cm ³ HClO ₄	4.44	1	105
Ca-H-montmorillonite	10	100 cm ³ HClO ₄	3.18	1	105
Cd-montmorillonite	5	50 cm ³ 0.01 mol dm ⁻³ Cd(NO ₃) ₂	6.5	7	25
Co-montmorillonite	5	60 cm ³ 0.01 mol dm ⁻³ Co(ClO ₄) ₂	7	7	105
Cu-montmorillonite	20	10 cm ³ 0.05 mol dm ⁻³ Cu(ClO ₄) ₂	4-4.5	7	105
Cu-montmorillonite	20	20 cm ³ 0.05 mol dm ⁻³ Cu(ClO ₄) ₂	4-4.5	7	105
Hg-montmorillonite	5	50 cm ³ 0.05 mol dm ⁻³ HgCl ₂	6-7	7	25
K-montmorillonite	1	50 cm ³ 0.05 mol dm ⁻³ KCl	6-7	1	25
Li-montmorillonite	1	50 cm ³ 0.05 mol dm ⁻³ LiCl	6-7	1	25
Mn-montmorillonite	10	100 cm ³ 0.01 mol dm ⁻³ Mn(ClO ₄) ₂	6.5	7	105
Na-montmorillonite	1	50 cm ³ 0.05 mol dm ⁻³ NaCl	6-7	1	25
NH ₄ -montmorillonite	5	50 cm ³ 0.02 mol dm ⁻³ NH ₃	10	7	25
NH ₄ -montmorillonite	5	50 cm ³ 0.02 mol dm ⁻³ NH ₄ ClO ₄	7.8	7	25
NH ₄ -montmorillonite	1	50 cm ³ NH ₄ OH		1	25
Pb-montmorillonite	5	10 cm ³ 0.1 mol dm ⁻³ Pb(ClO ₄) ₂	2.9	3	105

DDTG curve obtained by differentiating the primary thermogravimetric data. The temperature of the furnace was regulated by a linear heating program at a rate of $10^{\circ}\text{C min}^{-1}$. The analytical conditions: air atmosphere, ceramic crucible, mass of sample about 100 mg, reference material Al_2O_3 .

X-ray diffraction studies

X-ray diffractograms were made on non-oriented powder samples, oriented samples, and oriented samples heated at 490°C for 4 h, respectively.

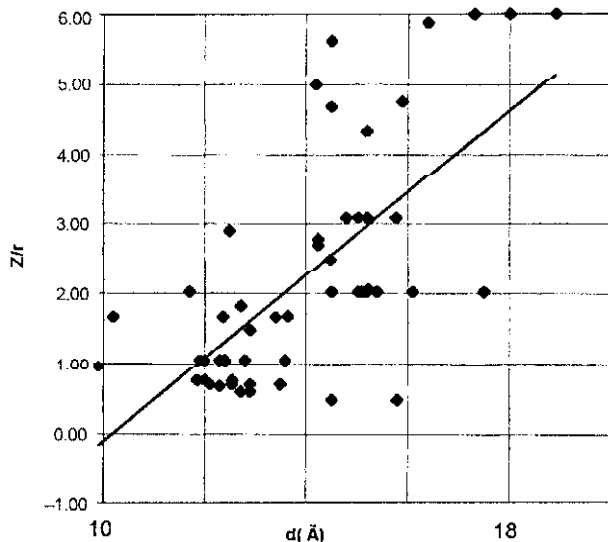


Fig. 1 Ionic potential vs. d value of base reflection for different cation-exchanged montmorillonites, after literature data

About 80% of the exchangeable cations of montmorillonite are in the interlayer space. X-ray diffraction gives information on the cation exchange in the interlayer space only, and not on adsorption on the surface. The extent to which the clay mineral expands as a result of the adsorption of water into the interlayer space is about 9.5 \AA along the c axis. This expansion can be followed by X-ray diffraction: mainly (001) base reflections were determined. The c axis dimension of montmorillonite depends on the thickness of the water layers. The structure of the interlayer water is a resultant of various superimposed effects, one of which is the nature of the exchangeable cations located in the interlayer space. Exchangeable ions are mainly hydrated, due to the electrostatic forces between the ion and the electric dipole of the water molecule. The size of the cation hydration zone and the number of water layers determining the size of the interlayer space (the thickness of each layer is approximately $3 \mu\text{m}$) decrease with increasing ionic size and increase with increasing ionic charge.

The literature data on different cation-exchanged montmorillonites ([1–9] and present paper) (Fig. 1) reveal that the ionic potential and the d value show some correlation, but there is not a strictly functional relationship between the variables. The reasons for the scattering are as follows:

- The literature data on a given cation-exchanged montmorillonite differ. Unfortunately, very important parameters, such as the experimental conditions, the temperature, the relative humidity, or the degree of cation exchange, are frequently not given in the literature. Data on the hydration of ions are highly controversial [10]. The variation in the d value, depending on the relative humidity, may be several Å, and the c spacing values can vary with electrolyte concentration and indicate partial cation exchange.

- There are water molecules in the interlayer space which do not belong directly to the cation hydration zone (the ordered water zone of the oxygen plane, and the disordered water zone which separates the two ordered water zones).

- In some cases, there is a gibbsite-like layer in the interlayer space, because OH ions can coordinate around the cation (Al or Li).

- The d values of exchanged montmorillonites involving cations with different valencies follow different theoretical rules (Fig. 2). For tri- or tetravalent cations, the trend is particularly marked. In the case of monovalent cations, the ionic size is of great importance, while the water cosphere around these large ions is very thin. The data relating to the middle line in Fig. 2 show that the bivalent cation-exchanged montmorillonites cannot be distinguished by X-ray diffraction studies. Consequently, X-ray diffraction studies at room temperature are mainly suitable for study of the exchange of cations of different valencies.

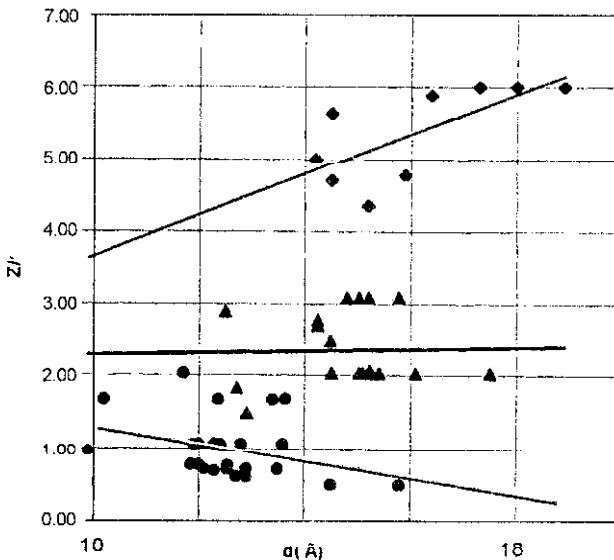


Fig. 2 The data of Fig. 1 separated according to valency

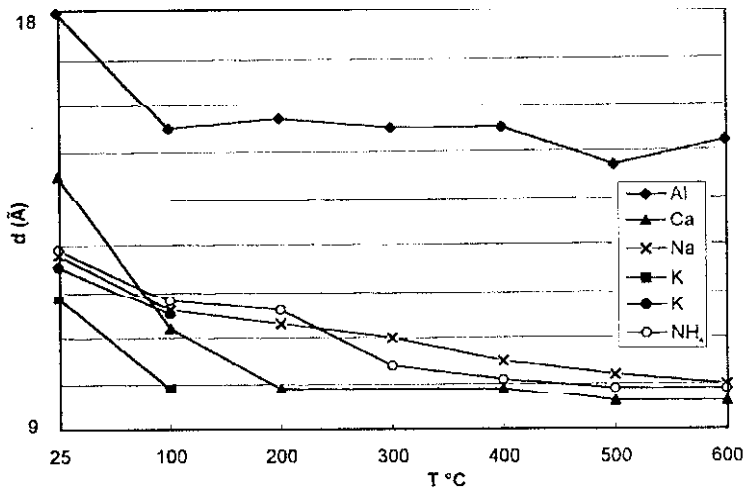


Fig. 3 Change in d value of base reflection for different cation-exchanged montmorillonites during heating

During heating and partial dehydration, the size of the c spacing decreases step by step (Fig. 3). At 500°C, when the structure is completely collapsed, the d value of the montmorillonite depends on the non-hydrated ionic radius of the interlayer cation, analogously as for mica minerals with different interlayer cations. Interpolation from data for Na, K, Ca, Ba and NH₃ mica minerals (Fig. 4) suggests that d value range is 9–11 Å. The interval is too limited for the identification of cations with similar ionic radii. There are some cations (Ni and Li) which can migrate from the initial interlayer position to the vacant octahedral sheet (at about 250°C), thereby becoming unexchangeable.

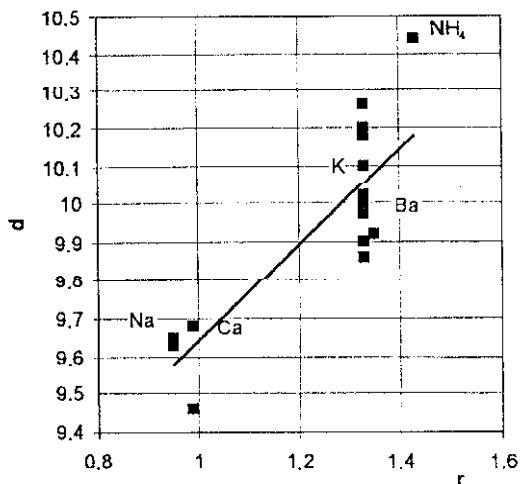


Fig. 4 d value of base reflection for micas with different interlayer cations, after data of

Thermoanalytical studies

Thermoanalytical studies furnish different possibilities for investigation of the cations in the interlayer space. One is the measurement of the binding energy of water molecules coordinated by the cations. The greater the hydration energy, the higher the temperature of elimination of the water coordination to the cation. The hydration energy is closely connected with the charge and radius of the cation: the greater the charge and the smaller the radius, the greater the hydration energy (Fig. 5). The temperature of dehydration of the hydrated cation in °C is of the same order as the hydration entropy (Table 2). It may therefore be supposed that there is a greater possibility for the identification of different cations on the basis of the thermal dehydration reaction.

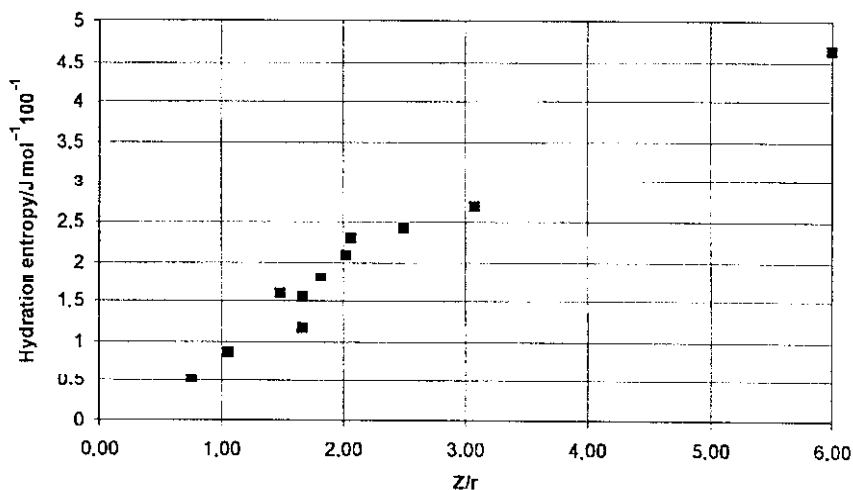


Fig. 5 Ionic potential vs. hydration entropy after data of Bohn *et al.* (1979)

The elimination of water coordinated to cations and that of other forms of water in the interlayer space are distinguished in the DTA and DTG curves only when the hydration energy of the cation is sufficiently great (Mg, Mn, Ca, Cu, Li, etc.) (Figs 6 and 7). The thermal reaction at 242°C is probably due to the dehydroxylation of LiOH to be found in the interlayer space.

As attempt was made to separate the elimination of water coordinated to the interlayer cations with small hydration energy by means of the second derivative (DDTG) of the low-temperature water elimination reaction (Ba, Hg, Cd and Ag) (Fig. 8a, b, c). The temperature difference between the DTG peak and the DDTG minimum for these reactions is about 8°C.

In the case of monovalent ions (due to their large size and only small electric charge), the hydration zone of the exchangeable cation and the binding energy are small, and this water therefore forms a unit with other water in the interlayer space in the DTG and DDTG curves (Na, NH₄, etc.) (Fig. 9a, b).

Table 2 Characteristic parameters of cations used for saturation of montmorillonite

	Ionic radius/ Å	Valency	Ionic potential	Entropy/ J mol ⁻¹	T _p / measured	Remarks
Al	0.50	3	6.00	464.7	543	overlapped by dehydroxylation?
Mg	0.65	2	3.08	267.9	336	measured on DTC (data from other measurements: 240–295°C)
Cu	0.69	2	2.90		343	measured on DTC
Co	0.74	2	2.70			uncertain data
Mn	0.80	2	2.50	242.8	258	measured on DTC
Cd	0.97	2	2.06	230.2	192	minimum of DDTG+8°C
Ca	0.99	2	2.02	209.3	197	measured on DTC
Hg	1.1	2	1.82	180	179	minimum of DDTG+8°C
Li	0.60	1	1.67	117.2	170	measured on DTG
Pb	1.20	2	1.67	154.9		uncertain data
Ba	1.35	2	1.48	159	152	minimum of DDTG+8°C
Na	0.95	1	1.05	87.5	130	peak temperature of total dehydration
Ag	1.26	1	0.79		163	minimum of DDTG+8°C
K	1.33	1	0.75	51.8	115	peak temperature of total dehydration
NH ₄	1.43	1	0.70		132	peak temperature of total dehydration

Entropy: Hydration entropy (after Bohn *et al*)T_p=peak temperature of cation dehydration

The results obtained from the measurements on Co and Pb-montmorillonite cannot be interpreted so far.

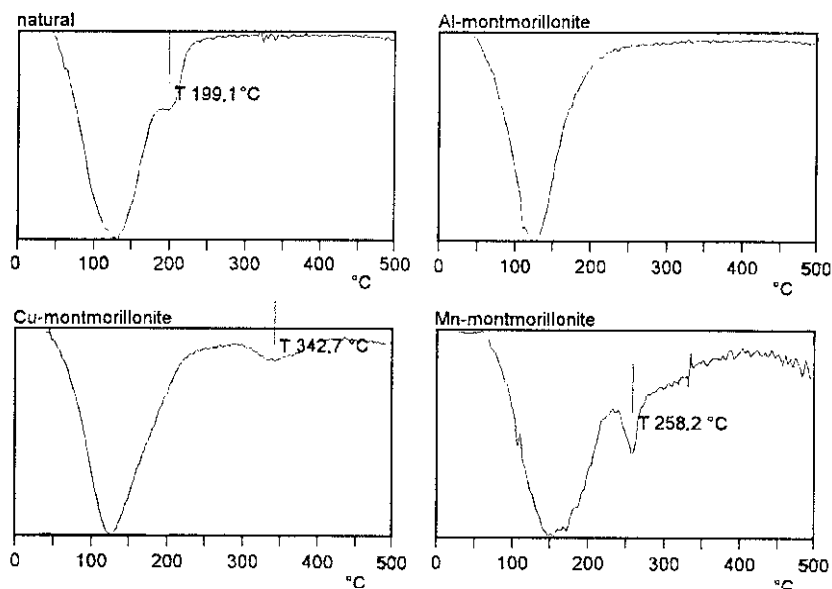


Fig. 6 DTG curves of montmorillonite from Istenmezeje

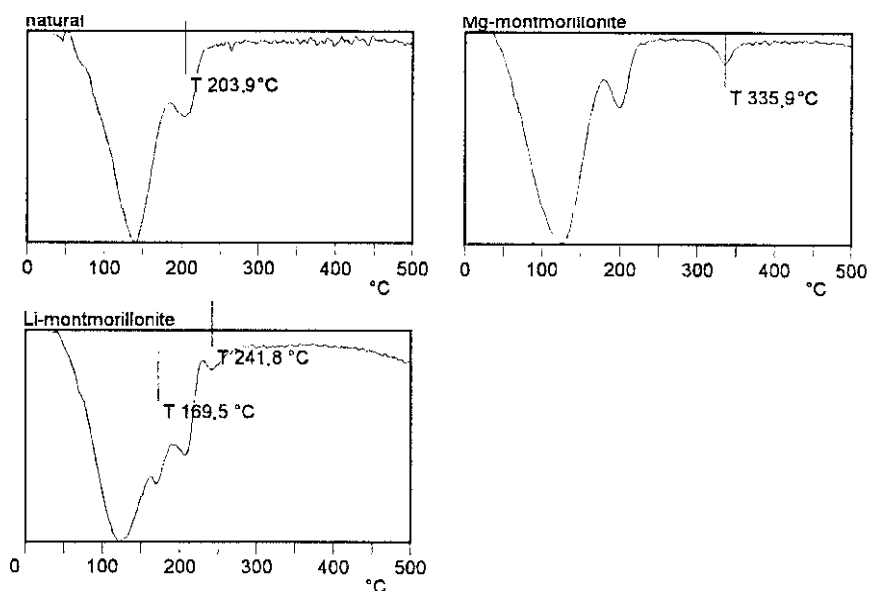


Fig. 7 DTG curves of montmorillonite from Buru

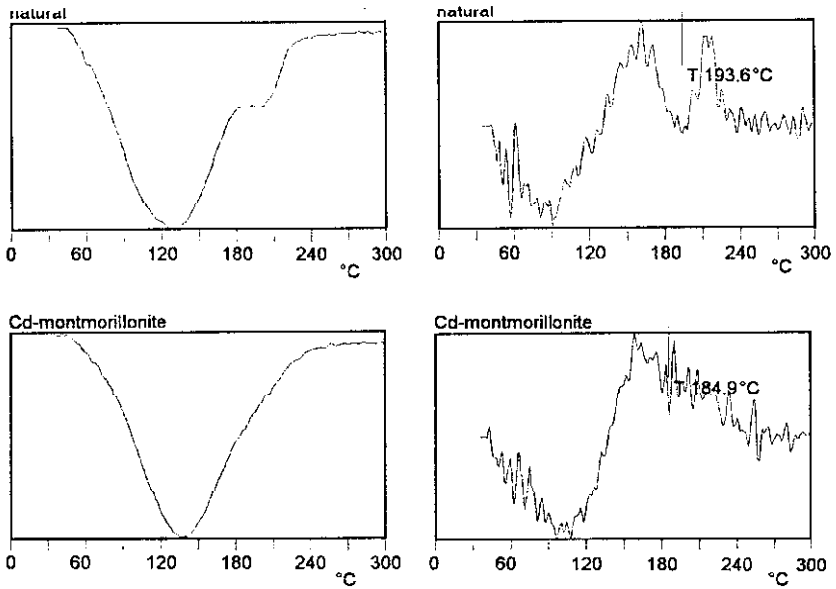


Fig. 8/a DTG and DDTG curves of montmorillonite from Istenmezeje

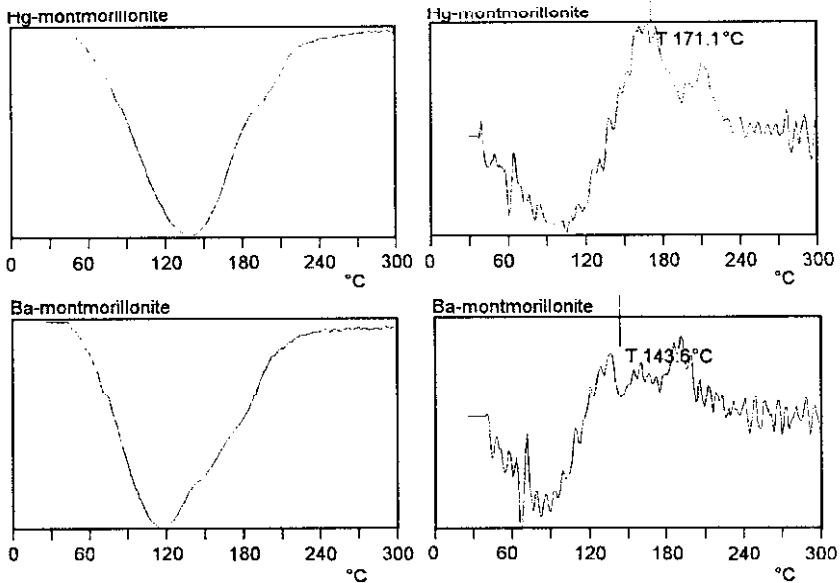


Fig. 8/b DTG and DDTG curves of montmorillonite from Istenmezeje

The temperature data measured in thermoanalysis depend considerably on many parameters (e.g. heating rate, instrument type, sample holder and sample

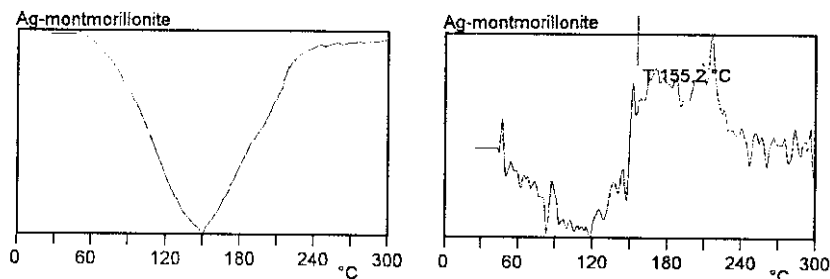


Fig. 8/c DTG and DDTG curves of montmorillonite from Istenmezeje

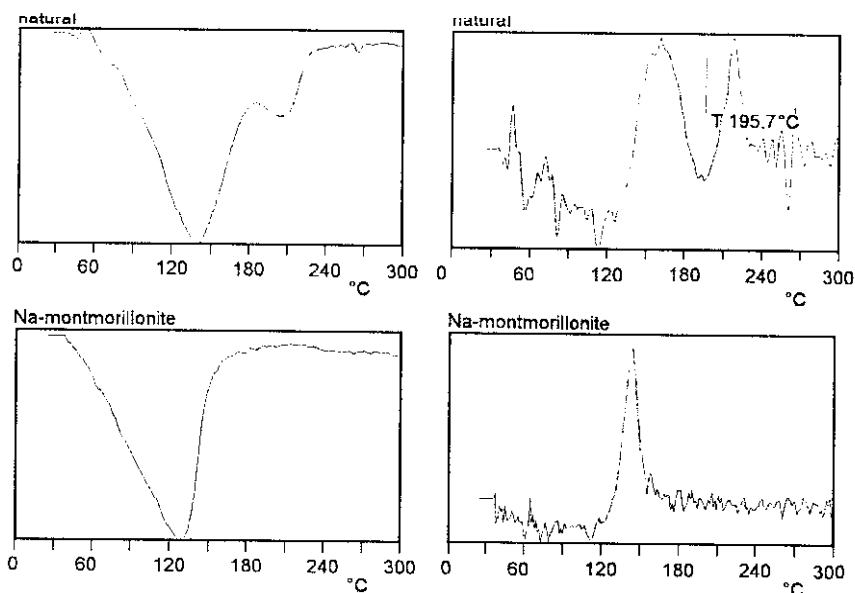


Fig. 9/a DTG and DDTG curves of montmorillonite from Buru

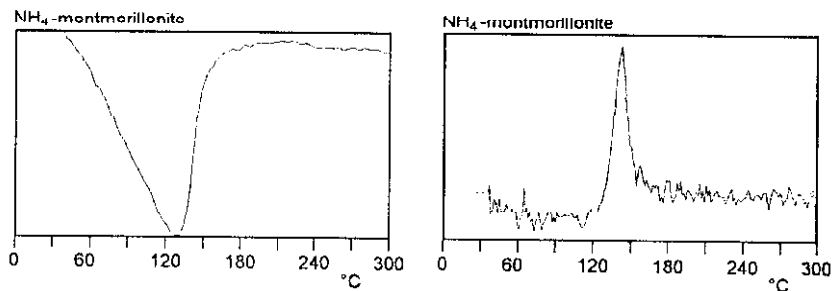


Fig. 9/b DTG and DDTG curves of montmorillonite from Buru

amount). For this reason, only data measured with the same instrument and under the same conditions can be compared.

References

- 1 I. Barshad, *The Amer. Mineral.*, 35 (1950) 225.
- 2 L. Heller-Kallai and C. Moser, *Clays and Clay Minerals*, 43 (1995) 738.
- 3 E. G. Kukovskij, *Osobennosti stroeniya i fiziko-khimicheskiye svoystva glinnistikh mineralov*. Akademia Nauk SSSR, Kiev, 1966.
- 4 M. Lacher, N. Lahav and S. Yariv, *J. Thermal Anal.*, 40 (1993) 41.
- 5 M. Lacher, N. Lahav and S. Yariv, *J. Thermal Anal.*, 39 (1993) 1233.
- 6 M. Lacher, N. Lahav and S. Yariv, *J. Thermal Anal.*, 42 (1994) 13.
- 7 I. Pálinkó, Gy. Kiricsi, K. Tasi and J. Varga, *J. Thermal Anal.*, 39 (1993) 197.
- 8 M. Patel, *Clays and Clay Minerals*, 30 (1982) 397.
- 9 M. Stadler and P. W. Schindler, *Clays and Clay Minerals*, 41 (1993) 288.
- 10 B. Rohn, I. McNeal and G. A. O'Connor, *Soil Chemistry*. John Wiley and Sons, New York, Chichester, Brisbane, Toronto 1979.