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THERMAL BEHAVIOUR OF SOME MINERALS

Differential thermal analysis and determination of PA curves for different heating rates

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Thermal behaviour of some minerals (kaolinite, halloysite, two montmorillonites, quartz and calcite) for different sample amounts and heating rates has been investigated using differential thermal analysis. On the basis of the DTA analysis carried out, the PA curves of each mineral have been obtained for different heating rates. These diagrams can be employed in the semi-quantitative evaluation of identical substances contained in uncharacterized polymineral samples.

A great deal of information on the minerals here concerned is to be found the literature [1, 5] and, for some of them, the relative PA curves (Probenabhängigkeit), i.e. the ultimate objective of this work, are also provided. The PA curve (curve of sample amount dependence) of a substance can be determined only when the endothermic effect is due to dehydration, dehydroxylation and/or structure decomposition. In this case, the relative peak temperatures basically depend upon sample amount and heating rate [2, 4]. If standard PA curves can be obtained from pure enough monomineral samples, the interdependence between these parameters allows to determine the amount of unknown samples that undergo dehydration or decomposition during heating. Consequently the minerals contained in a polymineral unknown sample can be determined semiquantitatively.

As it will be explained later, the tests have been performed keeping some parameters constant and varying others. Finally, on the basis of the results, the PA curves of all the studied minerals have been obtained. Moreover, any discrepancies between the literature data [4] and our experimental data are discussed.

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Experimental

Material and methods

The Stanton Redcroft STA 780 Series apparatus, used for the analysis, gives simultaneous thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) records, for sample amounts up to 100 mg, depending on density and packing.

The sample and reference material crucibles are in Pt–Rh with a volume of about 135 mm^3 and a diameter of 6 mm. The thermocouples, in Pt–Rh too, are exterior to and in contact with the sides of the crucibles.

The analysis of the present study have been carried out in static air.

The microprocessor-based control unit of the electronic microbalance guarantees high accuracy in weight determination (around μg).

Identification of the minerals

The mineral studied by thermal analysis are the following four clay international standards:

1) kaolinite ≠ 5, Bath, South Carolina 48W0250;
2) halloysite ≠ 13, Dragon Iron Mine, Eureka, Utah 48W0130;
3) montmorillonite 22b (cream), Amory, Mississippi 48W1222;
4) montmorillonite 22a (cream), Amory, Mississippi 48W1221.

All these standards are supplied by the World's Natural Science Establishment Inc., P.O. box 1712, Rochester, New York 14603.

In addition calcite and quartz samples, derived from large monocrystals, have also been studied.

Calcite, quartz and clay minerals have been previously subjected to chemical and XRD analysis and, only once their purity had been ascertained, they were studied by DTA.

Table 1 gives the chemical analysis for the major elements and their proportional formulas. For calcite some trace elements have also been determined, as their presence can have a marked effect on reaction temperatures [2]. However, Pb and Mn are only present in minute quantities or are absent altogether.

As mentioned in the foregoing, the temperature variation of the endothermic reactions has been calculated by differential thermal analysis for different minerals, changing the sample amount and keeping some other parameters constant. Table 2 shows the test conditions.

Calcined Al_2O_3 has been used as inert reference material in all the tests. As Table 2 shows, sample amounts ranging between 1 and 70 mg have been tested at heating rates of 10 deg/min, 15 deg/min and 20 deg/min. In the case of the montmoril-

Table 1 Chemical analyses and proportional formulas of the analyzed minerals

	Montmorillonite 22a			Montmorillonite 22b			Kaolinite		Halloysite		Quartz	Calcite		
SiO_2	56.64			59.34			45.02		46.10		98.88			
TiO_2	0.72			0.68			1.07		—		—			
Al_2O_3	20.63			20.06			40.29		39.20		0.23	CaO →	55.23	
Fe_2O_3	8.57			5.08			—		—		0.03	MgO →	0.30	
MgO	1.77			2.42			—		—		—	Fe_2O_3 →	0.04	
CaO	1.23			2.24			—		0.34		0.34	MnO →	0.04	
Na_2O	0.24			0.16			—		—		—	PbO →	—	
K_2O	1.10			0.95			—		—		0.01	CO_2 →	43.60	
ign. loss	9.74			9.96			13.79		14.94		—			
	100.64			100.89			100.17		100.58		99.49		99.21	
	Numbers of ions on the basis of													
	20 (O)–4 (OH)			20 (O)–4 (OH)			10 (O)–8 (OH)		10 (O)–8 (OH)		2 (O)	3 (O)		
Si	6.87		8.00	7.09		8.00	3.88		3.92		1.00			
		1.13			0.91									
Al	2.95			2.83			4.09	4.16	3.93	3.93	0.01	Ca	0.99	1.00
		1.82	2.99		1.92	2.73						Mg	0.01	
Ti		0.07			0.06		0.07		—		—	Fe^{3+}	—	
Fe^{3+}		0.78			0.46		—		—		—	Mn	—	
Mg		0.32			0.29		—		—		—	Pb	—	
Ca		0.16	0.39		0.43	0.61	—		0.03	0.03	—	C	1.00	
Na		0.06			0.04		—		—		—			
K		0.17			0.14		—		—		—			
(OH)		4.00			4.00		7.93		8.47		—			
H_2O		3.88			3.94		—		—		—			

Table 2 Experimental and calculated values of $w-T$ couples, equations of straight-lines for the analyzed samples

Sample	Experimental values						Straight-lines equations ($y = m \log x + b$)	Calculated values on the regression straight-lines					
	10 deg/min		15 deg/min		20 deg/min			10 deg/min		15 deg/min		20 deg/min	
	+W	++T	W	T	W	T		W	T	W	T	W	T
Halloysite (100 °C)	1.08	45	1.22	55	1.10	51							
	3.20	55	3.26	57	3.19	55	10 deg/min	3	51	3	52	3	54
	5.09	60	5.38	63	5.28	66	$y = 36.71 \log x + 33.23$	5	59	5	62	5	65
	9.82	67	10.23	73	10.50	83	15 deg/min	10	70	10	75	10	80
	20.38	78	20.41	86	20.55	95	$y = 44.98 \log x + 30.38$	20	81	20	89	20	95
	30.38	83	29.69	94	30.50	104	20 deg/min	30	87	30	97	30	104
	40.27	92	40.92	105	39.82	111	$y = 30.42 \log x + 49.74$	40	92	40	102	40	110
	50.05	97	50.50	107	50.25	114		50	96	50	107	50	114
	60.09	104	60.65	114	59.91	119		60	99	60	110	60	119
Halloysite (500 °C)	1.08	486	1.22	497	1.10	503							
	3.20	494	3.26	499	3.19	501	10 deg/min	3	491	3	493	3	500
	5.09	500	5.38	504	5.28	509	$y = 29.59 \log x + 477.21$	5	498	5	502	5	509
	9.82	504	10.23	512	10.50	523	15 deg/min	10	507	10	514	10	521
	20.38	512	20.41	520	20.55	531	$y = 38.97 \log x + 474.88$	20	516	20	526	20	534
	30.38	519	29.69	527	30.50	544	20 deg/min	30	521	30	532	30	541
	40.27	525	40.92	538	39.82	548	$y = 41.52 \log x + 479.69$	40	525	40	537	40	546
	50.05	529	50.50	544	50.25	550		50	527	50	541	50	550
	60.09	533	60.65	550	59.91	552		60	530	60	544	60	553
Kaolinite	1.69	512	1.90	512	1.55	518	10 deg/min	3	511	3	520	3	518
	3.20	515	3.08	521	3.25	521	$y = 37.86 \log x + 493.19$	5	520	5	528	5	530
	5.12	518	5.20	526	5.12	530	15 deg/min	10	531	10	540	10	547
	10.35	530	10.00	544	9.96	548	$y = 38.28 \log x + 501.37$	20	542	20	551	20	564
	21.56	544	19.56	548	20.00	561	20 deg/min	30	549	30	558	30	574
	32.25	548	31.23	557	31.90	575	$y = 56.09 \log x + 491.11$	40	554	40	563	40	581
	40.30	557	43.30	566	41.00	584							
Montmorillonite 22b (100°C)	10.63	63	10.43	69	10.84	80	10 deg/min	10	61	10	67	10	78
	20.00	78	20.50	83	20.03	97	$y = 57.37 \log x + 3.31$	20	78	20	84	20	94
	30.92	87	30.16	94	30.31	101	15 deg/min	30	88	30	95	30	103
	40.36	95	40.45	104	40.48	107	$y = 59.18 \log x + 7.36$	40	95	40	102	40	110

	50.59	101	50.23	107	50.70	118	20 deg/min	50	101	50	108	50	115
	60.33	107	60.73	114	60.13	120	$y = 52.45 \log x + 25.93$	60	105	60	113	60	119
Montmoril-lonite 22b (700°C)	10.63	644	10.43	649	10.84	658	10 deg/min	10	646	10	652	10	657
	20.00	652	20.50	662	20.03	658	$y = 9.30 \log x + 636.85$	20	646	20	657	20	659
	30.92	652	30.16	662	30.31	658	15 deg/min	30	651	30	660	30	660
	40.36	652	40.45	662	40.48	662	$y = 16.68 \log x + 635.41$	40	652	40	662	40	661
	50.59	652	50.23	662	50.70	662	20 deg/min	50	653	50	663	50	661
	60.33	652	60.73	664	60.13	662	$y = 6.60 \log x + 650.20$	60	653	60	665	60	662
Montmoril-lonite 22a (100 °C)	10.13	63	10.30	74			10 deg/min	10	63	10	71	10	69
	20.39	80	20.54	81	20.41	91	$y = 55.98 \log x + 11.22$	20	79	20	86	20	89
	30.08	89	30.12	94	30.36	105	15 deg/min	30	88	30	94	30	103
	40.34	94	40.42	105	40.69	110	$y = 49.81 \log x + 20.88$	40	94	40	101	40	112
	50.11	98	50.14	105	50.79	118	20 deg/min	50	100	50	105	50	119
	59.82	105	60.09	108	60.16	127	$y = 72.12 \log x - 3.6$	60	104	60	109	60	125
	70.36	107	70.23	114				70	107	70	113	70	129
Montmoril-lonite 22a (700 °C)	20.39	656	20.54	658	20.41	666	10 deg/min	10	655	10	652	10	665
	30.08	657	30.12	658	30.36	666	$y = 3.55 \log x + 651.24$	20	656	20	656	20	666
	40.34	656	40.42	661	40.69	666	15 deg/min	30	656	30	659	30	666
	50.11	657	50.14	659	50.79	666	$y = 14.14 \log x + 638.08$	40	657	40	661	40	666
	59.82	658	60.09	664	60.16	667	20 deg/min	50	657	50	662	50	666
	70.36	658	70.23	666			$y = 1.45 \log x + 663.90$	60	658	60	663	60	666
								70	658	70	664	70	667
Calcite	1.44	778	1.24	767	1.55	772							
	3.49	780	3.05	790	3.49	795	10 deg/min	1	753	1	756	1	752
	5.38	791	5.08	804	5.36	812	$y = 79.99 \log x + 737.25$	3	775	3	791	3	793
	10.13	826	10.31	832	10.39	838	15 deg/min	5	793	5	808	5	811
	20.84	842	20.94	855	20.08	858	$y = 74.72 \log x + 755.70$	10	817	10	830	10	836
	30.31	855	30.54	864	30.25	871	20 deg/min	20	841	20	853	20	861
	40.15	866	41.00	876	40.70	890	$y = 83.41 \log x + 752.37$	30	855	30	866	30	876
	51.36	872	50.92	884	50.10	897		40	865	40	875	40	886
	60.40	880	60.94	892	60.71	902		50	873	50	883	50	894
								60	879	60	889	60	901

+W = weight (mg)
++T = temperature (°C)

lonites the amount of the samples was not less than 10–20 mg, because otherwise the reaction temperatures become illegible, due to insufficient definition of the peaks.

The DTA curves obtained for the different minerals have the following features in common:

1) the endothermic reaction temperatures for identical amounts, are directly correlated with heating rates;

2) for the same heating rate, the endothermic reaction temperature is a function of the amount of substance tested according to a log-normal law (as will be demonstrated later) for almost all studied minerals.

Generally, the best DTA curves, from a qualitative point of view, have been obtained under the following conditions:

— amount of sample analyzed: >10 mg;
— recorded output sensitivity: 10 mV;
— heating rate: 15 deg/min.

It has been observed that with sample amounts of less than 10 mg, reaction temperatures cannot be satisfactorily defined due to the very broad peaks; they could be better defined by increasing the recorder sensitivity to 2.5 mV. However, this results in a worse diagram quality since the DTA curves exhibit considerable drift. This trend is also observed when heating rate is increased and therefore heating rate of 15 deg/min appeared appropriate. Figures 1 (a, b, c) show a series of DTA curves which are good examples for such phenomena. These have been plotted for the same amount of kaolinite (~ 30 mg) at 2.5, 5 and 10 mV recorder output (Fig. 1a); for ~ 10 mg of kaolinite at 10, 15 and 20 deg/min with a recorder sensitivity of 10 mV (Fig. 1b); for about 5, 10, 20, 30 and 40 mg of the same halloysite sample at 15 deg/min and 10 mV (Fig. 1c). We also found that varying the amount of inert substance it had no effect on the endothermic reaction temperature, in agreement with the literature data [1, 4].

Results and discussion

For each mineral the weight versus temperature ($w-T$) curves obtained at heating rates of 10, 15 and 20 deg/min have been plotted on semi-logarithmic diagrams.

On the basis of the experimental $w-T$ values, a linear regression has been carried out: the results are shown in Fig. 2.

It can be seen, that the experimental points are not very scattered around the regression line, except in a few cases. The correlation coefficient R ($E = m\sigma x/\sigma y$ where m is the slope of the straight-line) calculated for each equation that defines the relative curve, allows to evaluate the points scattering. In some diagrams the first $w-T$ couple for 1 mg of analyzed substance has not been taken into account in data interpolation. In fact, its inclusion had a detrimental effect in the approximation of the regression line, owing to the difficulties encountered in reading the temperature from the diagram (very broad and poorly-defined peaks).

Before analyzing the obtained experimental results for the other minerals, we make a short comment on quartz. This test has been carried out to verify if its

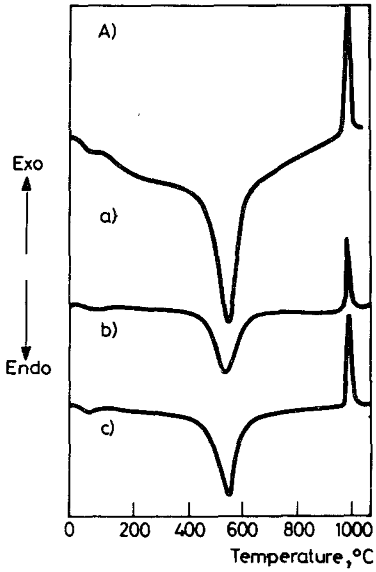

Fig. 1a DTA curves for kaolinite (heating rate 15 deg/min; sample weight ~30 mg). a) recorder output sensitivity: 2.5 mV; b) recorder output sensitivity: 5.0 mV; c) recorder output sensitivity: 10.0 mV

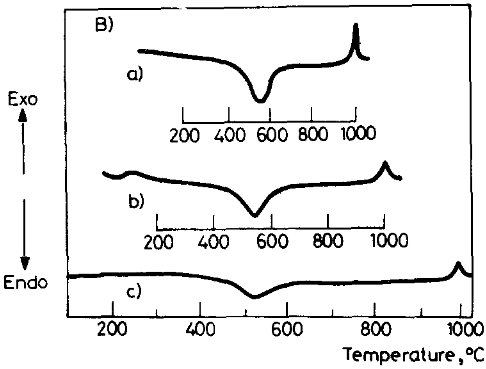

Fig. 1b DTA curves for kaolinite (sensitivity 10 mV; sample weight ~10 mg). a) heating rate: 20 deg/min; b) heating rate: 15 deg/min; c) heating rate: 10 deg/min

reaction temperature, at about 587°, keeps constant as heating rate and weight of the sample vary. In fact, we did not find significant variations for the endothermic peak temperature, because the reaction is due to a structural transformation from α-quartz to β-quartz. For the above-mentioned reasons the $w-T$ values are not reported on the graph.

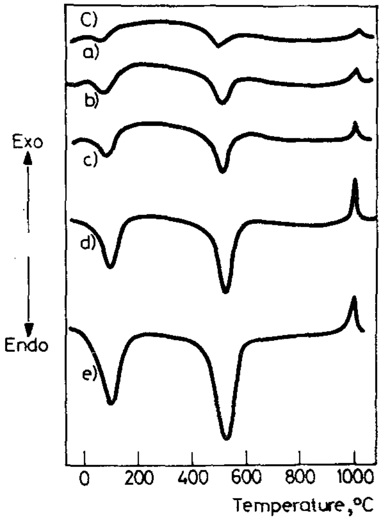

Fig. 1c DTA curves for halloysite (heating rate 15 deg/min; sensitivity 10 mV). Sample weight: a) 5.38 mg; b) 10.23 mg; c) 20.41 mg; d) 26.69 mg; e) 40.92 mg

The experimental results obtained for the other minerals are reported, as mentioned above, in Fig. 2 where the regression straight-lines for the 100° and 500–700° peaks are plotted.

Only three, between the analyzed minerals (the halloysite and two montmorillonites) show the endothermic reaction at about 100°. The diagrams of Figs 2d and 2e denote a direct correlation between temperature, heating rate and the amount of sample, pointed out by each $w-T$ couple reported on the graph. Particularly, for the halloysite the points are more clustered around the line representing the 20 deg/min heating rate ($R = 0.9991$) while at 15 deg/min ($R = 0.9910$) and 10 deg/min ($R = 0.9811$) the scattering is greater. The $w-T$ values corresponding to the endothermic peak around 100° due to the 22a montmorillonite dehydration, show considerable scattering at 15 deg/min ($R = 0.9788$), decreasing to $R = 0.9890$ at 20 deg/min and $R = 0.9976$ at 10 deg/min (Fig. 2b). The best approximation of the straight-line for the 22b montmorillonite is obtained at a heating rate of 10 deg/min ($R = 0.9975$); at 15 deg/min ($R = 0.9960$) and 20 deg/min ($R = 0.9849$) the fit becomes worse and worse (Fig. 2e).

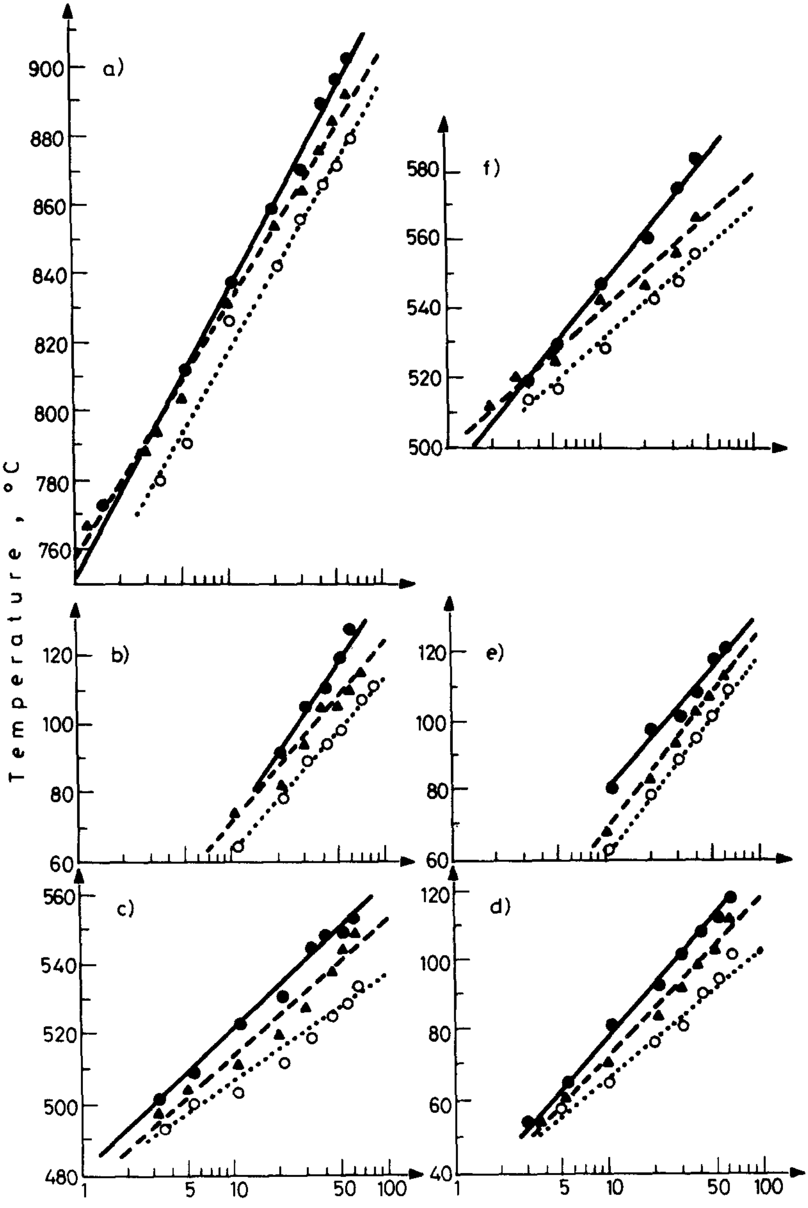

Fig. 2 Regression lines of the analyzed minerals. a) calcite decomposition peak: b) montmorillonite 22a dehydration peak; c) halloysite dehydroxylation and decomposition peak; d) halloysite dehydration peak; e) montmorillonite 22b dehydration peak; f) kaolinite dehydroxylation and decomposition peak. ——— ● straight-lines and points at 20 deg/min; – – – – ▲ straight-lines and points at 15 deg/min; .... ○ straight-lines and points at 10 deg/min

It emerges, from these results, that no optimal common heating rate exists for the minerals studied here.

As regards the minimum and maximum temperatures relative to the dehydration reaction of the above-mentioned minerals, in the weight ranges considered, we have obtained the following results.

For the halloysite dehydration peak the lowest temperature observed was 45° (~1 mg and 10 deg/min) and the highest 119° (~60 mg and 20 deg/min). The temperature variation of 22a montmorillonite is also considerable: from a minimum of 63° for ~10 mg at 10 deg/min to 127° for ~60 mg at 20 deg/min. For the 22b montmorillonite they are 63° (~10 mg and 10 deg/min) and 120° (~60 mg and 20 deg/min). Also the endothermic peak that refers to dehydroxylation and structural decomposition of the clay minerals shows the same general, above described trend depending on the heating rate and the amount of the sample. Again it does not point out common optimal heating rates for all minerals. In fact, the halloysite shows, for the peak around 500°, a correlation coefficient better for the 20 deg/min ($R = 0.9954$) than for 15 deg/min ($R = 0.9743$) and 10 deg/min ($R = 0.9839$). The kaolinite shows the same behaviour; in this case the scattering around the respective straight-lines is slightly more pronounced at a lower heating rates (10 deg/min: $R = 0.9900$; 15 deg/min: $R = 0.9911$; 20 deg/min: $R = 0.9970$) (Fig. 2f).

The dehydroxylation and decomposition reaction for the halloysite shows a peak value ranging from 486° (~1 mg and 10 deg/min) up to 552° (~60 mg and 20 deg/min). The same peak for kaolinite varies from 512° (~1 mg and 10 deg/min) up to 584° (~40 mg and 20 deg/min).

A quite different behaviour was oberved for all the montmorillonite samples; opposite to the data reported in the literature [1, 4] they did not show significative reaction temperature variation related to the amount of the sample and/or of the heating rate variations. The experimental results obtained for the 22a montmorillonite show, in fact, a difference of only 2° (Table 2) over the entire range from 20 to 70 mg at 10 deg/min; the variation at 15 deg/min is 8° and at 20 deg/min only 1°. The 22b montmorillonite shows that 10 deg/min a temperature of 644° for about 10 mg of sample while for 20 to 60 mg it remains constant at 652°; at 15 deg/min and 10 mg of the analyzed substance the temperature is 649° and for 20–60 mg 662–664°; finally at 20 deg/min the temperature excursion is only 4° for weights that vary between 20 and 60 mg (Table 2).

The peak at about 700° is attributed, in the literature, to a combined dehydroxylation and decomposition reaction [1, 4]. However, our findings, theoretically infinite slope of PA-curves (parallel to the X-axis), do not support this claim. In fact, on the basis of analyses of some montmorillonites reported in the literature, the slope of the PA-curve for the endothermic reaction is considerable being the difference of temperature, between minimum and maximum amount analyzed, in excess of 70° [4]. To confirm whether the thermal behaviour of the two samples tested here could be extended to other montmorillonites or whether it was peculiar to them, three natural samples of montmorillonites originated from Cabo de Gata (Spain), Nurri and Uras (Sardinia, Italy), have been tested. In this case it emerged that the endothermic peak temperatures do not vary substantially for different sample weights and heating rates (only by a few degrees). Therefore it is possible that the endothermic reaction of montmorillonite at 650–700° is not attributable to dehydroxylation and/or decomposition reaction but to a structural transformation.

The endothermic reaction temperatures depend, apart from on P_{H_2O} (as for the above-mentioned clay minerals) also on P_{CO_2} and this is of fundamental importance in the case of calcite. The CO_2, i.e. a reaction product of the carbonate decomposition, delays the reaction. In the absence of gas flow, it accumulates above the sample, being heavier than air. There is an increase of the partial pressure of CO_2 above the sample that hinders the decomposition reaction: the greater the amount of carbonate, the greater the amount of CO_2 generated and as a result the greater is the delay in the reaction. This is why the reaction temperature increases [1, 4]. The variation in endothermic reaction temperature of calcite, as a function of sample amount, is attributed to structural decomposition [1, 4, 5]. For the same heating rate the increase of endothermic reaction temperature is considerable, as the regression line slope shows (Fig. 2a), for the different sample weights. In this case too, at fixed amounts direct correlation can be observed between reaction temperature and heating rate. The scattering is greater at 10 deg/min ($R = 0.9950$) than at 15 deg/min ($R = 0.9981$) and 20 deg/min ($R = 0.9978$).

In conclusion the most important results that emerge from this study are the following:

— direct correlation between sample weights, heating rates and the reaction temperatures for all analyzed minerals;

— anomalous behaviour of the montmorillonite reaction at about 700°, as compared to literature data;

— no optimal heating rate exists for the minerals studied here. The regression lines of best fit do not always correspond to the same heating rate but there is an optimal rate for each mineral. On the basis of our results, these are: 20 deg/min for kaolinite, 15 deg/min for calcite, 10 deg/min for the peak around 100° of montmorillonites and 15 deg/min for the 600–700° one; 20 deg/min for both halloysite peaks;

— finally the results obtained allow a better knowledge of the thermal behaviour of the minerals studied at different heating rates and amounts. The relative diagrams, reported for each substance analyzed, can be employed for a semiquantitative evolution of identical substances contained in unknown polymineral samples.

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Zusammenfassung — Mittels Differentialthermoanalyse wurden für verschiedene Probenmengen und Aufheizgeschwindigkeiten das thermische Verhalten einiger Minerale (Kaolinit, Halloysit, Quarz, Kalkspat und zwei Montmorillonite) untersucht. Auf Grundlage der durchgeführten DTA-Analyse wurden für jedes einzelne Mineral die PA-Kurven für verschiedene Aufheizgeschwindigkeiten erhalten. Diese Diagramme können bei der halbquantitativen Bestimmung der entsprechenden Substanzen in unbekannten polymineralen Proben dienen.

Резюме — Методом ДТА. изучено термическое поведение некоторых минералов (каолин, галлоизит, два монтмориллонита, кварц и кальцит) с разным количеством образца и при разных скоростях нагрева. На основании проведенных ДТА исследований, получены кривые ПА для каждого минерала при различных скоростях нагрева. Такие диаграммы могут быть использованы для полуколичественного определения идентичных веществ, содержащихся в неохарактеризованных полиминералах.