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APPLICATION OF DIFFERENTIAL THERMAL ANALYSIS IN MINERALOGY*

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In mineralogical research differential thermal analysis can be applied as either a single or a combined method for three purposes:

1. for the qualitative identification of minerals and the (semi-)quantitative determination of the components of rocks and soils,
2. for the characterization of crystal-physical and crystal-chemical properties, including the study of kinetics and the determination of thermodynamic data, phase and reaction equilibria,
3. for special petrogenetic investigations concerning the interrelation of mineralogical properties with the formation, decomposition or recrystallization of minerals.

The presented results were obtained under strongly standardized and reproducible conditions of analysis and by means of some methods recently developed by the author. They include the construction of key diagrams of ΔT versus peak temperatures to identify unknown minerals; the dependence of dehydration and decomposition peak temperatures on the partial pressure of gaseous reaction products (= PA curves); the determination of chemical and crystal-chemical parameters of minerals by using the dependence of dehydroxylation peak temperatures on solid solution (chlorites, smectites) or by using the interrelation between the peak temperatures of structural transformations and crystal-chemical substitutions (sulfides, carbonates, phosphates, silicates); the determination of the degree of disorder of minerals formed in sedimentary environments by using the dehydration or inversion peak temperature and peak shape-dependence on the defect character of these crystal structures (clay minerals, quartz, cristobalite, hydroxides); the subdivision of mineral groups by using the interrelation of crystal chemistry and dehydration behaviour (zeolites, mixed-layer clay minerals); the characterization of ferromagnetic minerals by studying the Curie temperatures as a function of the chemical composition; the development of a DTA method to measure the degree of weathering of granitic rocks, etc. Data of 150 minerals are given.

The principles of differential thermal analysis (DTA) have been described in detail many times, e.g. by Lehmann *et al.* [1], Wendlandt [2], Mazieres [3], Garn [4], Paulik *et al.* [5], Smothers and Chiang [6], Berg and Egunov [7], Mackenzie [8, 9] and Heide [10]. Theoretical details are to be found in the papers of Arens [11], Eriksson [12], Boersma [13] and Deeg [14]. As regards the DTA of minerals and rocks, there exist numerous publications and some textbooks (for references see Lippmann [15], Földvári-Vogl [16], Todor [17], Mackenzie [8]

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* Plenary lecture

and [9] and Smykatz-Kloss [18]). However it is surprising that – in spite of these and other publications – this excellent method has been used so little in geoscience lately. DTA was originally a mineralogical method, and in the 1930's more than 80% of all publications concerning DTA dealt with mineralogical subjects. Today the number of DTA publications relating to the earth sciences is down to 5–7% (e.g. compare the lists of papers given at the ICTA-III to VI). The reason for this decline is in my opinion that many geoscientists do not bother to obtain information about the special qualities, advantages and disadvantages of DTA. They use (if they use the method at all) DTA in the same way as they use X-ray diffraction or infrared spectroscopy, and so they obtain their DTA diagrams without proper control of the experimental conditions. Then they are very surprised that they cannot get the wanted answers to their problems from the available textbooks and tables on DTA, as they are used to getting them in the case of X-ray or IR spectroscopy.

With luck their DTA diagrams may be quite similar to some diagrams in the literature, but they fail to obtain detailed information from this method. Thus, they publish their curves without the proper information regarding the experimental conditions, which means that the curves are of little or no value, or merely provide some statement such as: "DTA has not proved to be very suitable for the problems under investigation."

What is the reason for this state of affairs? Generally, most of these investigators forget that DTA is a dynamic method, a method where the results depend much more on the experimental conditions than in any other physical method of mineral identification and investigation.

One example of this is illustrated in Fig. 1. The most prominent feature of DTA effects is the peak temperature (point *C* in Fig. 1), which can be measured very accurately. Therefore, everybody takes the peak temperature as the most characteristic feature of a DTA effect. But the temperature that is really important is the initial temperature, the onset (Fig. 1, point *A*) of a reaction, because thermodynamically this is more correct. However this cannot be measured so accurately. The peak temperature depends on several factors relating to the apparatus and

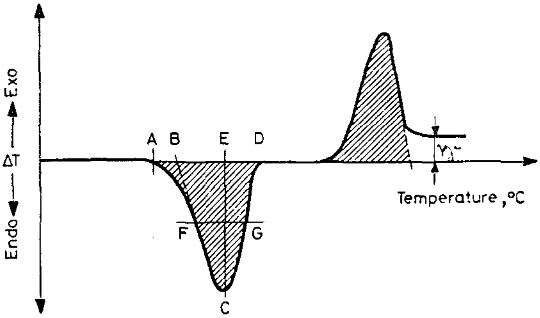

Fig. 1. Characteristics of a DTA curve

specimens, e.g. the construction of the sample holder, thermocouple location, heating rate, packing density and, for degassing processes, especially the amount of sample (Smykatz-Kloss [18], Lombardi [19], Warne [20]).

General remarks on the method

Let us recall what we can measure by DTA. In general, we can study all reactions and processes which include a change in energy during heating or cooling of a solid or liquid sample. For minerals and rocks, these are the following processes.

A. Endothermic reactions during heating

1. Dehydration: the release of water which may be bound to the structure of a mineral in three different ways:

a) by adsorption, i.e. bound to the surface of very fine-grained samples (clay minerals);

b) weakly bound by H-bonding and situated between the layers of a sheet structure (swelling clay minerals) or in structural channels (zeolites);

c) incorporated into the structure at fixed places (zeolites, sulfates)

2. dehydroxylation: the release of OH from a structure;
3. the decomposition of structures;
4. the transformation (inversion) of one structure into another (e.g. low-high quartz inversion);
5. magnetic changes (Curie points of ferromagnetic minerals);
6. the sintering and melting of substances (halides, sulfates, alumino-silicates);
7. the evaporation or sublimation of minerals.

B. Exothermic reactions during heating

1. Oxidations: burning of organic matter or sulfur, oxidation of Fe^{2+} to Fe^{3+};
2. the formation of a crystalline structure from any amorphous material.

Thousands of minerals exist in nature. More than 80% of these minerals exhibit at least one of these thermal effects. This means that DTA can be used to identify these minerals. Before we come to this possible application, some words should be said about the dependence of DTA on equipment factors. I will do this very briefly by referring to the above-mentioned literature. Three quantities can be measured in DTA diagrams:

the temperatures, the temperature difference (ΔT), and the peak areas.

These will be affected by: furnace atmosphere, arrangement and kind of sample holder and thermocouples, packing density and grain size of the sample, kind of inert material, heating rate, amount of sample, etc. For a complete list of factors, see Smykatz-Kloss [18], Lombardi [19] and Heide [10].

For the purpose of demonstration let us have a look at the two last-mentioned factors. A lot of work has been done, for instance, on studying the iron carbonate mineral siderite, $FeCO_3$, which exhibits great discrepancies in the published DTA

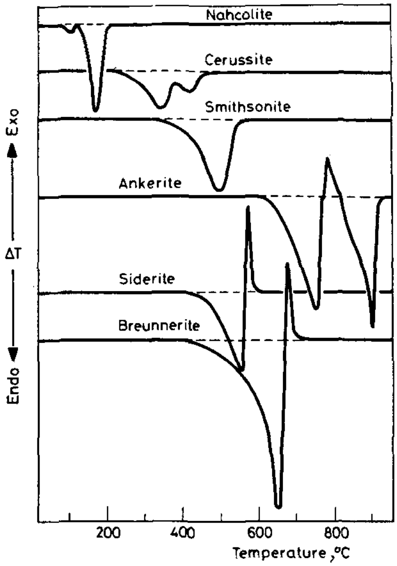

Fig. 2. DTA curves of some carbonate minerals including the iron minerals siderite, ankerite and breunnerite

curves (Fig. 2). The peak temperatures and the numbers of peaks differ, due to the different heating rates used. In the case of slow heating, only the strong exothermic peak will appear (mirroring the oxidation of Fe^{3+} to Fe^{4+}), showing increasing peak temperatures at increasing heating rates, until at a distinct heating rate the endothermic decomposition peak appears, too.

Still more striking is the dependence of peak temperatures on the amount of minerals which yield gaseous products. This means dehydration or dehydroxylation (the gaseous product = H_2O), and decomposition (e.g. of carbonates, gaseous product = CO_2). The endothermic dehydration or decomposition peak varies in an exponential manner with the partial pressure of the gaseous products. This influence is a major one, as can be seen from Table 1.

Table 1

Decomposition peak temperatures of different amounts of strontianite (locality: Loch Strontian, Scotland), $SrCO_3$; total weight of sample: 100 mg; standard conditions of anal.

mg $SrCO_3$	peak temp. ± 3°	mg $SrCO_3$	peak temp. ± 3°
1	910	20	1050
5	990	50	1100
10	1020	100	1150

In this case, the gaseous product (CO_2) is heavier than the furnace atmosphere (air), and will form a cover above the sample, thereby hindering the progress of the decomposition.

$$SrCO_3 \rightarrow SrO + CO_2 .$$

As shown in Fig. 3, the decomposition peak temperature as a function of the amount of strontianite in the sample is nearly a straight line in a linear/logarithmic plot. This means that the influence of the partial pressure on the decomposition is exponential in nature. Naturally, this straight line will appear only if all the factors affecting the thermal data are taken into account. Recently, Milodowski and Morgan [21] confirmed this interdependence by investigating small amounts of dolomites by evolved CO_2 analysis, while the studies of Warne [20] emphasize the care with which the constancy of DTA determination conditions must be maintained.

The general introduction given above can be summarized as follows: Comparable and reproducible results may be obtained from DTA performed under strictly standardized conditions or from the exact knowledge of the factors which will influence the results and the magnitude of the effects. The effect of the partial pressure of CO_2 or H_2O plotted against sample amount will yield PA-curves (Figs. 4–6) (from the German "Probenmengen-Abhängigkeit"), which can be used for semiquantitative evaluation of minerals provided the investigations are made under standardized conditions of analysis. The main factors used in obtaining the PA curves included in the Figures of this paper and the other DTA data are: reference

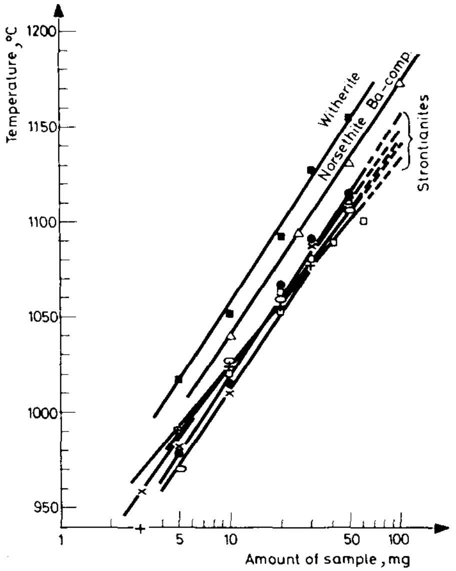

Fig. 3. PA-curves of strontianite, witherite and norsethite

material (inert): 150 mg annealed Al_2O_3; amount of sample: 100 mg; thermocouples: Pt-Pt_{90}/Rh_{10} in direct contact with the heated substance; furnace atmosphere: air, without any current or turbulence; sample holder: Pt crucibles with a diameter of 5 mm and a wall thickness of 0.1 mm; heating rate: 10°/min after 300°; for additional conditions, see Smykatz-Kloss [18].

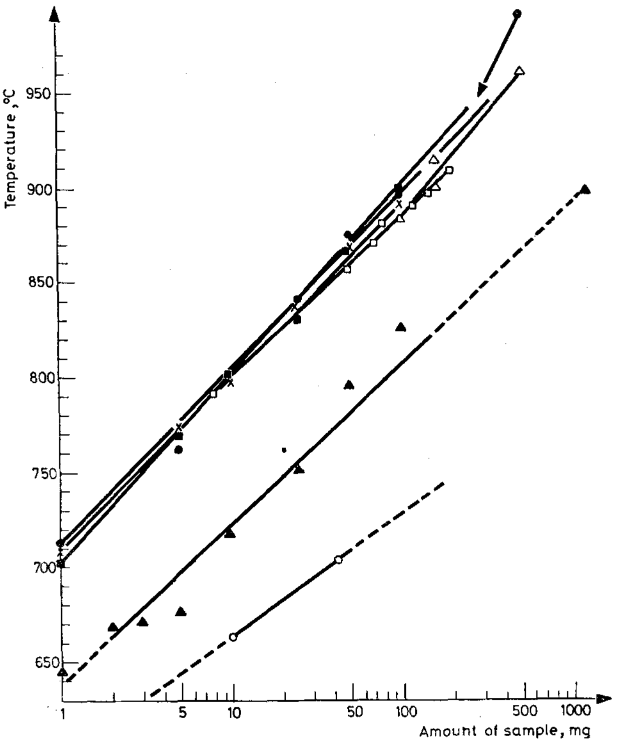

Fig. 4. PA-curves of calcite, $CaCO_3$, dolomite, $CaMg(CO_3)_2$, ankerite, $CaFe(CO_3)_2$, huntite $CaMg_3(CO_3)_4$, and zaratite, $Ni_3(OH)_4CO_3 \cdot 4 H_2O$. ■ Calcite (Andreasberg); ●● Double spar; × Plumbocalcite; △ Ankerite; □ Dolomite; ▲ Huntite; o Zaratite

Identification of minerals

As mentioned above, a DTA curve will yield three major items of information: the temperature of an effect, the ΔT value of this peak (i.e. the peak height) and the amount of heat (the peak area) emitted or consumed during the process. By making use of this third quantity, a DTA instrument can be used as a calorimeter (e.g. see Watson *et al.* [22]). This possibility is of great importance in petrological and technical mineralogical investigations, e.g. to gain data on the thermodynamics or reaction kinetics of minerals. This cannot be discussed in more detail here; a good theoretical discussion on this is given by Heide [10].

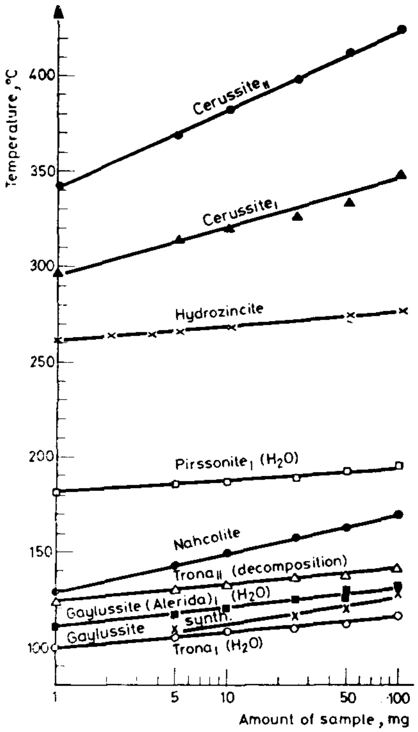

Fig. 5. PA-curves of some hydrated carbonates without other anions and of cerussite

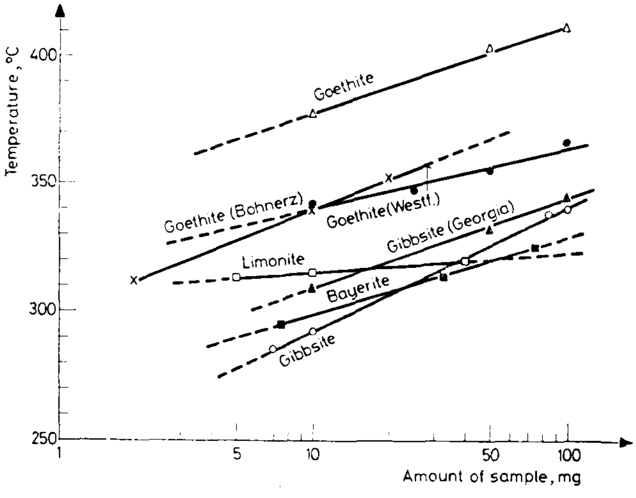

Fig. 6. PA-curves of some hydroxides

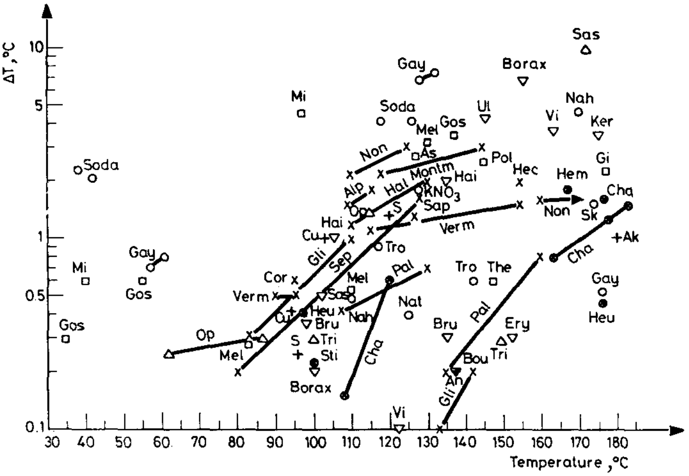

Fig. 7. Key diagram for the identification of minerals (endothermic effects between 40 and 180 °C)

For the purpose of identification and evaluation of minerals, the two most important properties, the peak temperature and the peak height (ΔT), must be obtained under highly standardized conditions of analysis. The first step in DTA curve analysis will be to compare the data of an unknown mineral with existing identification diagrams of known minerals, giving ΔT *versus* peak temperature, as shown in Fig. 7. Both parameters of this diagram are related to a mineral amount of 100 mg. If the sample studied contains less than 100 mg of any mineral (e.g. in a mixture of minerals) a difficulty arises, as the values for peak temperatures and ΔT will be somewhat different from those given in the standard diagrams for the same mineral. This problem may be solved by using the PA curves. But even then several difficulties may result, and consequently these identification diagrams may sometimes only be used as key diagrams and all data occurring around the measured values have to be looked at. Many minerals show more than one thermal effect, thereby offering a better possibility of identification, as illustrated in Figs 8–10. Another difficulty which may be the reason for varying data may be caused by structural defects, which generally lower the structural stability and hence the amount of energy needed for starting a thermal reaction. This means that in the key diagrams the plot of a mineral may vary from a point and may show a line due to crystal-physical defects occurring mainly in the case of minerals formed at low temperatures, e.g. in the sedimentary cycle.

Now let us have a short look at some groups and classes of minerals and their thermal behaviour, before discussing some special applications of DTA in the geosciences.

1. Among the elements which occur as natural materials (= minerals), some noble metals can be identified by their melting temperatures (e.g. silver: melting

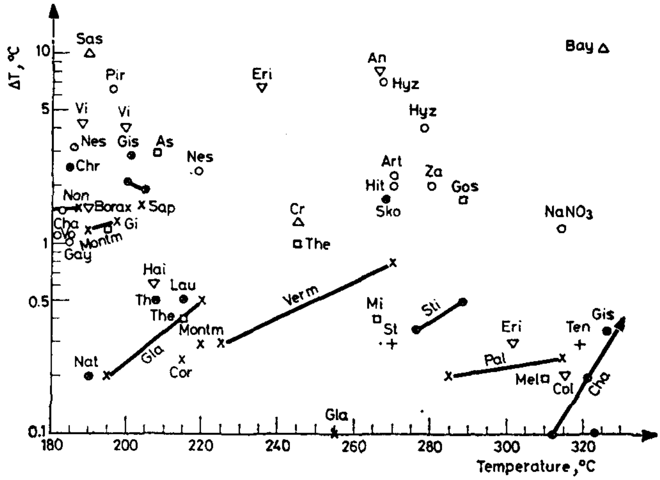

Fig. 8. Key diagram (endothermic effects between 180 and 320 °C)

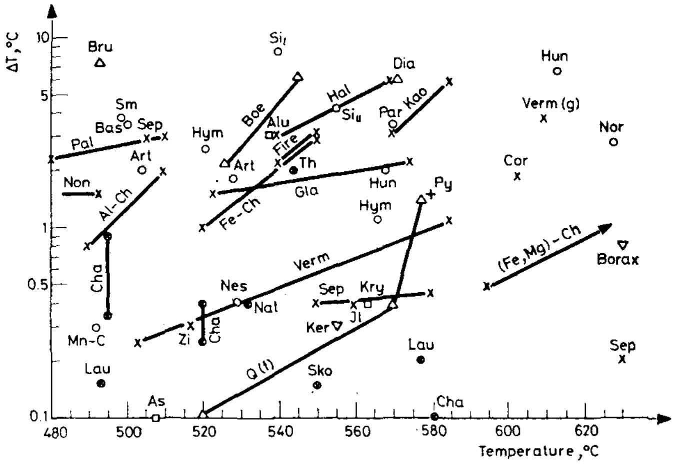

Fig. 9. Key diagram (endothermic effects between 480 and 640 °C)

point at 960°). Sulfur and graphite show very strong exothermic effects due to the oxidation of the elements to SO_3 or CO_2 (Fig. 11).

2. Strong exothermic effects also occur in the DTA diagrams of chalcogenides (sulfides, arsenides, antimonides, etc.). As shown in Figs 12 and 13 for iron, lead and zinc sulfides, the different chalcogenides can easily be distinguished, because of the different shapes, *ΔT*'s and temperatures of these exothermic peaks. However, one difficulty arises in the investigation of chalcogenides (or sulfur): the thermocouples and the crucible as well will be poisoned by the gaseous SO_3, SbO_3, etc;

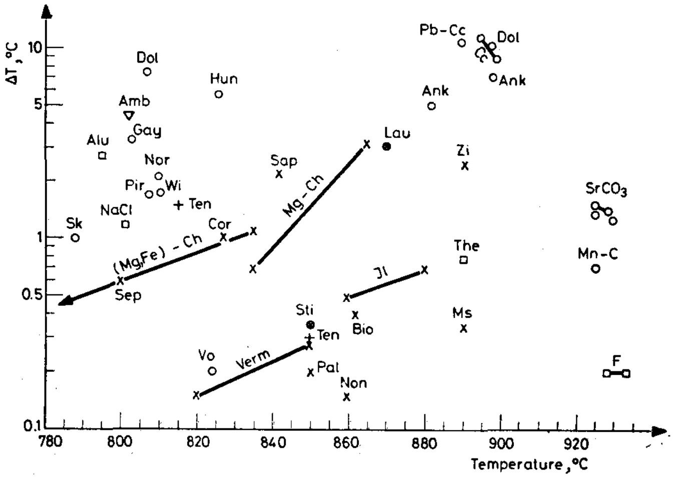

Fig. 10. Key diagram (endothermic effects between 780 and 940 °C)

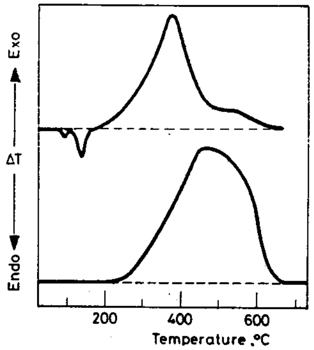

Fig. 11. DTA curves of 50 mg sulfur + 100 mg Al_2O_3 (above) and of 50 mg graphite + 50 mg Al_2O_3 (below)

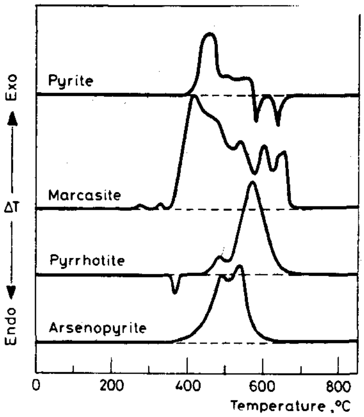

Fig. 12. DTA curves of iron sulfides

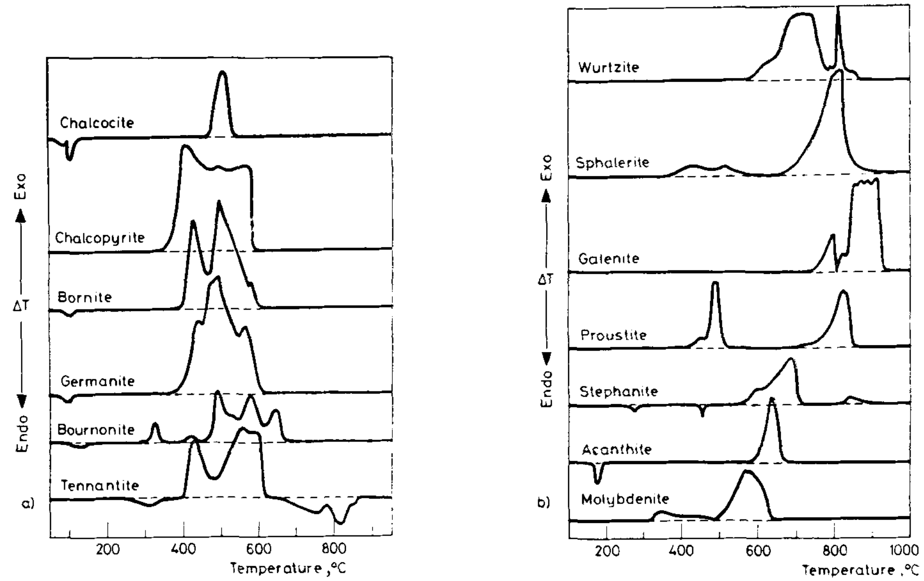

Fig. 13. a) DTA curves of copper sulfides, b) DTA curves of the sulfide minerals wurtzite (ZnS), sphalerite (ZnS), galenite (PbS), proustite (Ag_3AsS_3), stephanite ($5\ Ag_2S \cdot Sb_2S_3$), acanthite (Ag_2S), and molybdenite (MoS_2)

consequently, direct contact of the sample with the thermocouple should be avoided, and the crucible used should be made of ceramic material.

3. Halides and sulfates show typical melting and dehydration reactions (Fig. 14).
4. Hydroxides may be identified by their dehydroxylation effects (Fig. 15).
5. Among the oxides, only some display characteristic structural transformations (quartz, cristobalite) or Curie temperatures (Fe-oxides).
6. The large group of carbonates show very typical and strong decomposition effects (Fig. 16).
7. Borates, phosphates and arsenates can be identified by the dehydration effects (Fig. 17).
8. The large group of sheet silicates, including the clay minerals occurring in soils and sediments, constitutes the "classical field" of DTA. These minerals exhibit very specific dehydration, decomposition and recrystallization peaks; the shapes and temperatures of these fiield direct information about the type and degree of structural disorder and even about the possible technical use of clayish raw materials (Figs 18–19).
9. Some other groups of silicates can also be studied by DTA, provided the minerals incorporate some water or OH, show oxidation or melting behaviour, e.g. the zeolites (Figs 20a, b) or the amphiboles or tourmalines.
10. Some amorphous minerals, such as allophane, hisingerite or opal, display characteristic dehydration and recrystallization effects.

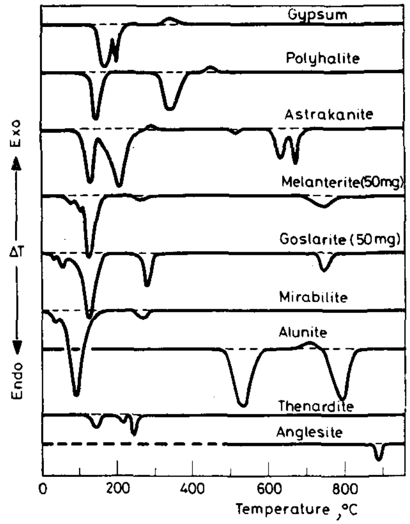

Fig. 14. DTA curves of the sulfate minerals gypsum, $CaSO_4 \cdot 2\,H_2O$, polyhalite, $K_2Ca_2Mg(SO_4)_2 \cdot 6\,H_2O$, astrakanite (bloedite), $Na_2Mg(SO_4)_2 \cdot 4\,H_2O$, melanterite, $FeSO_4 \cdot 7\,H_2O$, goslarite, $ZnSO_4 \cdot 7\,H_2O$, mirabilite, $Na_2SO_4 \cdot 10\,H_2O$, alunite, $KAl_3(OH)_6(SO_4)_2$, thenardite, Na_2SO_4, and anglesite, $PbSO_4$

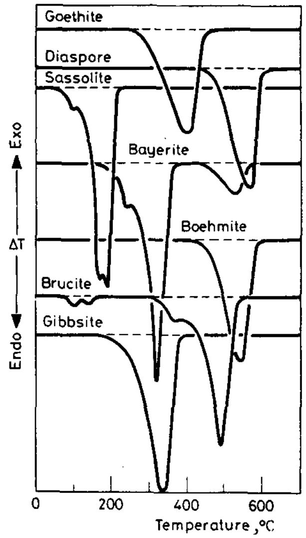

Fig. 15. DTA curves of the hydroxide minerals goethite, FeOOH, diaspore, α-AlOOH, sassolite, $B(OH)_3$, bayerite, α-$Al(OH)_3$, boehmite, γ-AlOOH, brucite, $Mg(OH)_2$, and gibbsite, γ-$Al(OH)_3$

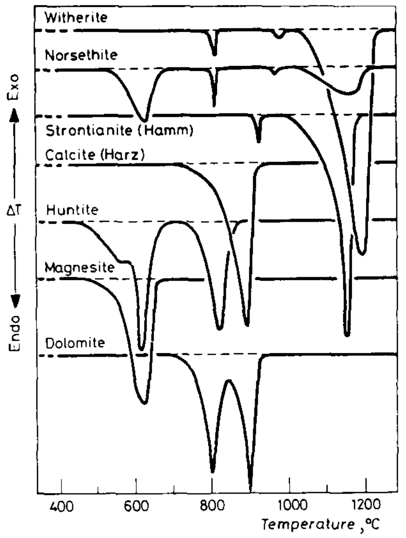

Fig. 16. DTA curves of the carbonate minerals witherite, $BaCO_3$, norsethite, $BaMg(CO_3)_2$, strontianite, $SrCO_3$, calcite, $CaCO_3$, huntite, $CaMg_3(CO_3)_4$, magnesite, $MgCO_3$, and dolomite, $CaMg(CO_3)_2$

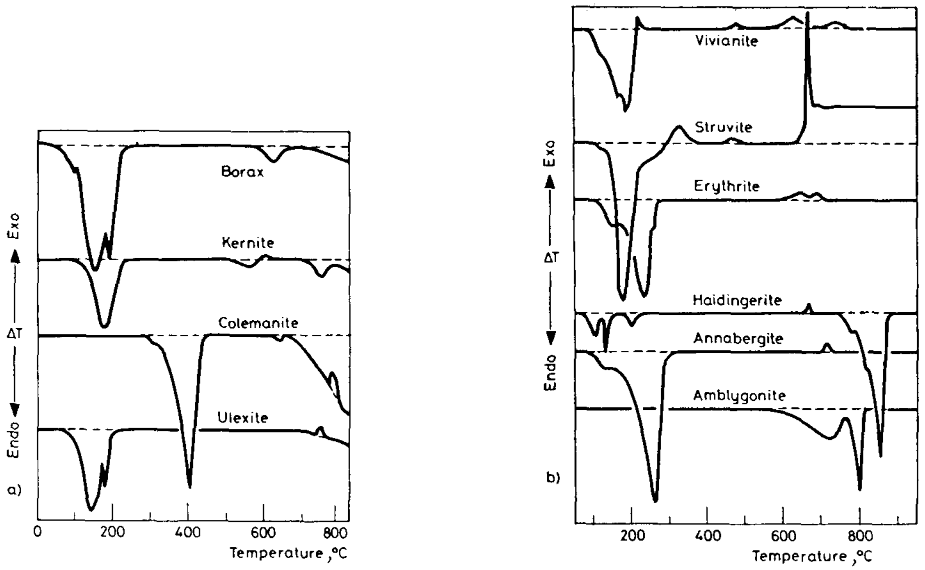

Fig. 17. a) DTA curves of the borate minerals borax, $Na_2B_4O_5(OH)_4 \cdot 8\ H_2O$, kernite, $Na_2B_4O_6(OH)_2 \cdot 3\ H_2O$, colemanite, $CaB_3O_4(OH)_3 \cdot H_2O$, and ulexite, $NaCaB_5O_6(OH)_6 \cdot$ $\cdot\ 5\ H_2O$; b) DTA curves of the phosphate and arsenite minerals vivianite, $Fe_3(PO_4)_2 \cdot 8\ H_2O$, struvite, $(NH_4)MgPO_4 \cdot 6\ H_2O$, erythrite, $Co(AsO_4)_2 \cdot 8\ H_2O$, haidingerite, $CaHAsO_4 \cdot H_2O$, annabergite, $Ni_3(AsO_4)_2 \cdot 8\ H_2O$, and amblygonite, $(Li, Na)Al\ (F, OH)PO_4$

To conclude this part, it can be stated that:

a) Many minerals exhibit characteristic thermal effects, and can be identified by means of these.

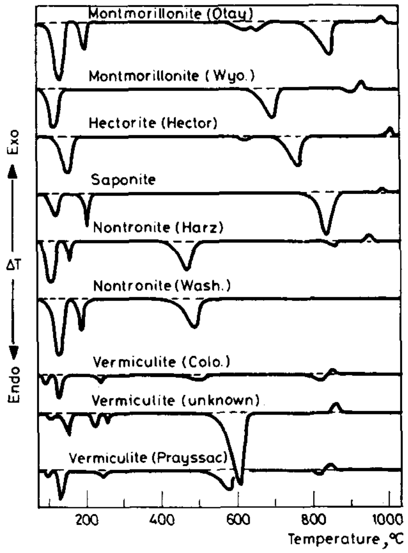

Fig. 18. DTA curves of some montmorillonites (smectites) and vermiculites

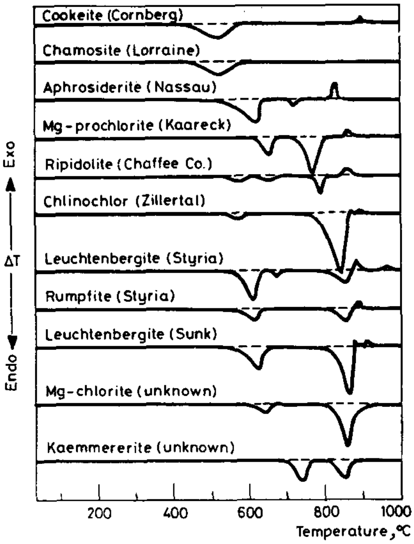

Fig. 19. DTA curves of some chlorites

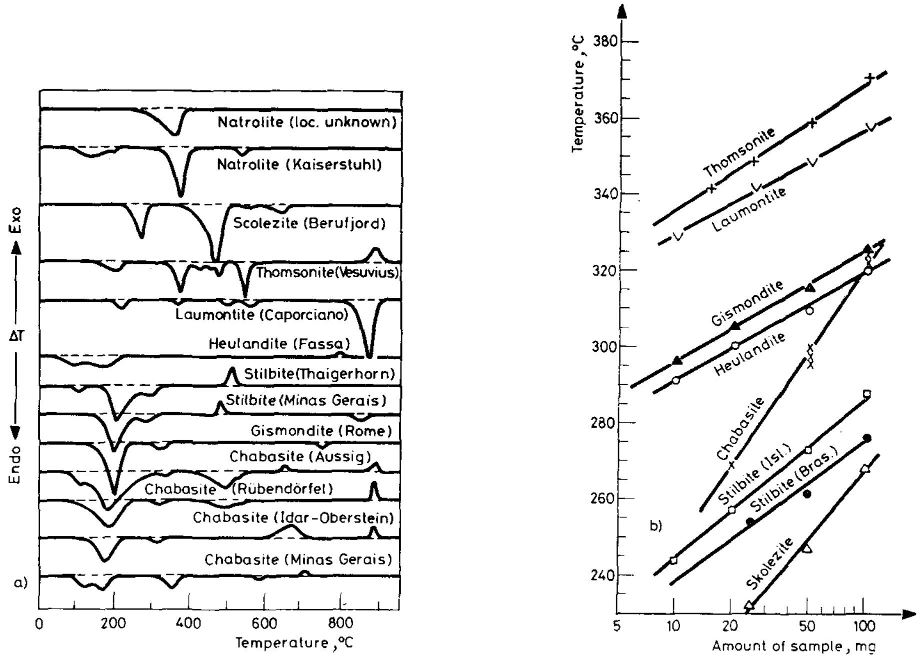

Fig. 20. a) DTA curves of the zeolite minerals natrolite, $Na_2Al_2Si_3O_{10} \cdot 2\ H_2O$, scolezite $CaAl_2Si_3O_{10} \cdot 3\ H_2O$, thomsonite, $NaCa_2Al_5Si_5O_{20} \cdot 6\ H_2O$, laumontite, $CaAl_2Si_4O_{12} \cdot 4\ H_2O$, stilbite, $CaAl_2Si_7O_{18} \cdot 7\ H_2O$, heulandite, $CaAl_2Si_7O_{18} \cdot 6\ H_2O$, gismondite, $CaAl_2Si_2O_8 \cdot 4\ H_2O$, and chabasite, $CaAl_2Si_4O_{12} \cdot 6\ H_2O$; b) PA-curves of some zeolites (dehydration reactions)

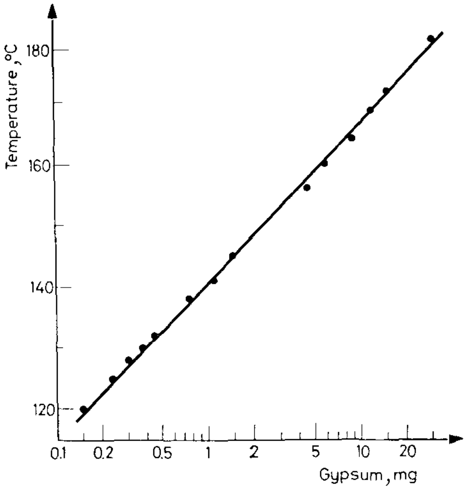

Fig. 21. PA-curve of gypsum

b) Compared to X-ray analysis, DTA has some advantages, as in identifying X-ray amorphous minerals, such as opal, etc., and in determining some strongly disordered minerals, such as sedimentary minerals, e.g. minerals from iron sediments or from clays.

c) In the case of minerals which exhibit very strong thermal effects (sulfides, carbonates), the sensitivity of detection is higher than for X-ray analysis. For instance, by DTA 0.1 mg of pyrite, FeS_2, may easily be identified in a soil sample of 100 mg (Linseis [23]) and as shown in Fig. 21, the same amount of gypsum, $CaSO_4 \cdot 2\,H_2O$, can also be identified from a DTA curve.

One should not be led to believe that DTA is always a better method for mineral identification than X-ray analysis. However, in the hands of an experienced DTA investigator the DTA method can be a valuable one to identify minerals or to control the suitability of raw materials.

Some special applications of DTA to mineralogy

Besides the identification and determination of minerals and rocks, DTA can be used in many cases for special mineralogical investigations. An important contribution is made by DTA to petrologic phase diagram studies (with and without pressure), e.g. by studying solid solutions by means of melting temperature (for instance see Eysel [24] and Heide [10]) or phase transformation determinations, Schwab [25], as well as Schwab and Jablonski [26].

Phase diagram studies by means of DTA are well known in chemical research, too, and therefore this important application of DTA will only be mentioned here. The following examples are dedicated to special mineralogical applications of DTA, namely to determine amorphous or poorly-crystalline material, chemical composition, degree of disorder or petrogenesis of minerals, or to check the technical application of minerals and rocks.

1. *Study of recent iron sediments*

Around the Greek island of Santorini, muddy iron sediments are to be found which have recently been formed by postvolcanic activity (fumaroles, hot springs) in a reducing environment. They consist of amorphous or nearly amorphous minerals rich in water, iron and sulfur. The geochemistry of these muddy sediments has been well investigated by Puchelt [27]. Mineralogically the sediments can only be studied by means of IR spectroscopy and DTA. Figure 22 includes the thermal effects of iron sulfides, opal, and amorphous Fe–Al-hydrosilicates (allophane, hisingerite) as well as some poorly-crystalline carbonates (siderite, ankerite).

2. *The influence of chemical composition on the decomposition temperatures of carbonates*

The decomposition upon heating of a pure, scarcely disordered crystal will occur very suddenly; the crystal structure will be stable until a sufficient amount of energy has been supplied, and then it breaks down at many places simultaneously.

This will be reflected in the DTA curve by a very sharp endothermic peak with relatively large ΔT.

However, if the crystal contains some impurities or crystal defects, the stability of the structure will be lower at these sites, and these disordered parts of the crystal need a lower amount of energy to be destroyed than other parts of the crystal do. Hence, the decomposition of the crystal will begin earlier, starting at these sites of lower structural energy. The resulting DTA curve will show an endothermic decomposition peak somewhat different from that of a comparable mineral without any disorder, i.e.:

the shape of the peak is broader,

the initial temperature is lower,

ΔT is lower,

sometimes a small additional endothermic effect due to the decomposition of the disordered parts of the crystal can be observed.

In the case of iron-containing dolomites, Ca(Mg, Fe)$(CO_3)_2$, this additional endothermic peak will appear even with very small amounts of iron substituting the magnesium in the dolomite structure (Fig. 23). By using the calibration diagram

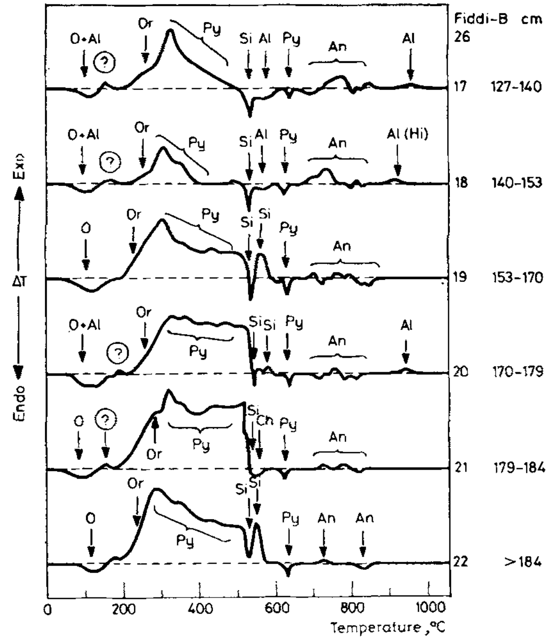

Fig. 22. DTA curves of some recent submarine iron sediments from Santorini, Greece (for providing the samples the author is grateful to Prof. Dr. H. Puchelt, Univ. of Karlsruhe); O = opal, Al = allophane, Or = Organic matter, Py = pyrite, An = ankerite, Hi = hisingerite, Si = siderite, Ch = chalcedony

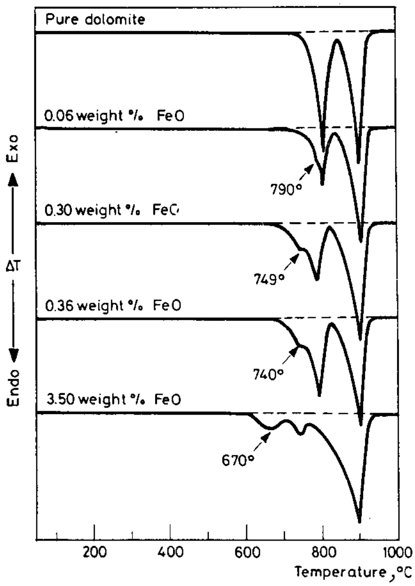

Fig. 23. DTA curves of some iron-bearing dolomites

given in Fig. 24, it is possible to estimate the iron content in dolomites. This determination of iron in dolomites is of some importance in petrographic investigations of sedimentary carbonates. From the physical chemistry of dolomite formation we know that primary dolomites do not incorporate iron into their structures (because the solutions from which these primary dolomites form are very poor in iron), but the secondary dolomites do, having been formed during diagenesis in older sedimentary rocks. Hence, this method offers a very quick distinction between primary and secondary dolomites, giving some petrologic information about the genesis and diagenesis of dolomite-bearing rocks. Similar observations were made by Otsuka *et al.* [28] for Korean Fe-dolomites and by Zawislak [29] for zinc-bearing dolomites from Zn-deposits in Poland.

In semi-arid environments (e.g. in the Djebel Nefusa, Libya, see Smykatz-Kloss [30]) dolomites free of iron or any other possible substituent occur which show very unusual decomposition behaviour (Fig. 25): the first endothermic effect, which is due to the decomposition of the $MgCO_3$ component of the dolomite, appears nearly 200° lower (earlier) than in the case of a "normal" dolomite. Evidently, the crystal structure shows some defects at the sites of the Mg, this lowering the decomposition temperature of the $MgCO_3$ without influencing the decomposition of the $CaCO_3$ component. Additional chemical and crystal-chemical investigations showed the dolomite to be a Mg-deficient type, with a lack of 5–8 % of the Mg compared with normal dolomites. The Mg-deficiency was caused by weathering processes. Thus, the DTA curve of dolomites may point to crystal-

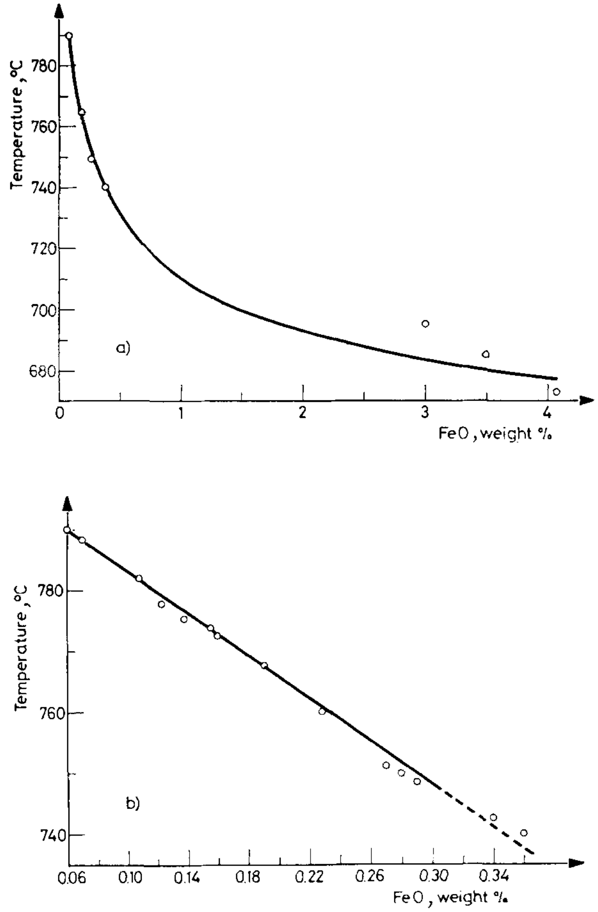

Fig. 24. Diagrams for determining Fe^{++} incorporated in dolomites; b: the magnified first part of the curve a

chemical variations. Similar observations can be made in the DTA curves of other carbonates, e.g. by studying solid solutions of Cu – Zn-carbonates or substitutions in aragonites (Smykatz-Kloss [18]).

3. *Contribution to the classification of chlorites*

The sheet silicates of the chlorite family are formed by sedimentary, hydrothermal or metamorphic processes. Chemically they are alumino-silicates, solid solutions mainly between an iron and a magnesium end-member; some other chemical types may occur, too (Cr-, Al- or Li-chlorites). The X-ray diagrams of all types are similar, and therefore the main mineralogical classification of chlorites is performed by the determination of crystal-optical properties which reflect their chem-

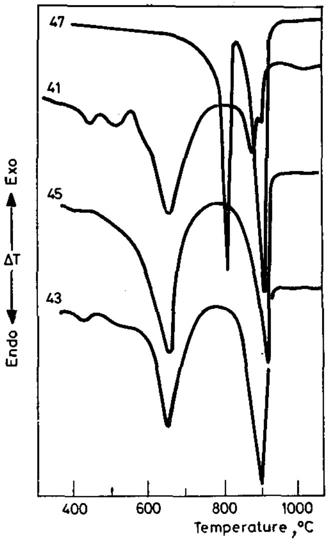

Fig. 25. DTA curves of three Mg-deficient dolomites and of one "normal" dolomite (sample 47) from the Djebel Nefusa, Tripolitania (NW-Libya); the four samples represent 20 m profile (43 = bottom, 47 = top)

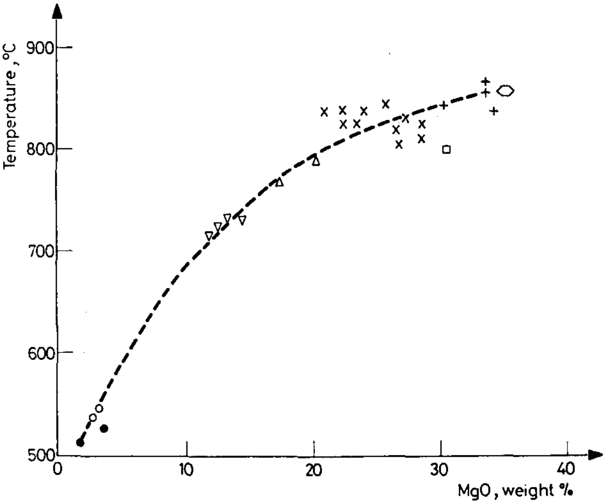

Fig. 26. Interdependence of decomposition temperature and MgO content of chlorites. ● Al-chlorite; ○ Fe-chlorite; ▽ Rhipidolite; + Clinochlor; × Pennine; ◇ Co'6'-chlorite; □ Cr'4'-chlorite

ical compositions. However, sometimes (e.g. in the case of sedimentary chlorites) the crystal size of chlorites is too small for optical studies. Figure 26 shows that the correlation of the decomposition peak temperature (the last endothermic effect in the DTA curves, see Fig. 19) with the magnesium content of chlorites may be a suitable criterion for the classification of chlorites, permitting even distinction between the two structurally different types of chromium chlorites (Lapham [31]).

4. *The influence of chemical composition on the temperature of structural transformations*

Many minerals exist in high- and low-temperature modifications, for instance the silica minerals quartz, cristobalite and tridymite, some carbonates and sulfates, and many silicates and chalcogenides. The sulfides, arsenides, antimonides, etc. of silver, copper, zinc and nickel can be recognized easily by such structural transformations, which are usually enantiotropic, i.e. true inversions. On heating the transformation will show up as a small endothermic effect, and on cooling again there will be an exothermic effect reflecting the structure of the mineral being inverted again. All these inversion temperatures depend strongly on the chemical compositions of the chalcogenides (the crystal defects can be neglected because nearly all minerals of this class have been formed at higher temperatures, so they do not display structural disorder). Figure 27 shows the dependence of the inversion temperatures of three different copper sulfides on the amount of iron present in the structures of these minerals. This clear dependence shows that DTA can be used in routine investigations of copper sulfides, or other chalcogenides (Kopp and Kerr [32–34] and Maurel [35]), in order to make quick estimates of impurities, which can be important from an economic point of view (e.g. silver in galenites, which lowers the transformation temperatures, too).

5. *The influence of chemical composition on the Curie temperatures of magnetites*

Results similar to those obtained from the temperatures of structural transformations, can be obtained from the Curie temperatures of ferromagnetic substances, such as the minerals magnetite, maghemite or pyrrhotite. (at the Curie point a substance loses its ferromagnetism.) This change of magnetic properties can be recognized in a DTA curve as a very slight but still sharp endothermic peak. As an example, the Curie temperatures of some 20 magnetites, from tertiary basalts of North Germany and from Scandinavian iron ores have been studied by means of standardized DTA (to suppress the strong exothermic oxidation peak the analyses were performed in an inert furnace atmosphere using argon). All the Curie temperatures of these samples lie between 490 and 586 ± 2°. In Fig. 28 the Curie temperature is plotted *versus* the amount of substituents for Fe^{2+} and Fe^{3+} in several magnetites. This shows that there is a strong linear dependence between the total amount of impurities in magnetites (Fe_3O_4), and the Curie temperature obtained by DTA.

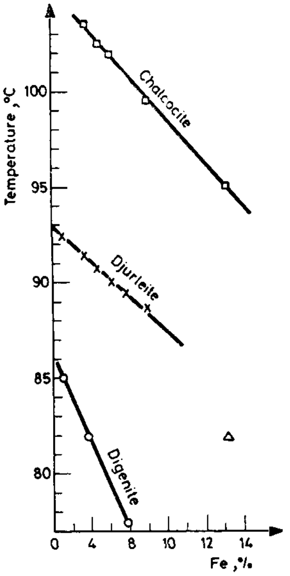

Fig. 27. Dependence of the transformation temperatures of the copper sulfides chalcocite (Cu_2S), djurleite ($Cu_{1,96}S$), and digenite (Cu_9S_5) on the iron content which is incorporated into the structures

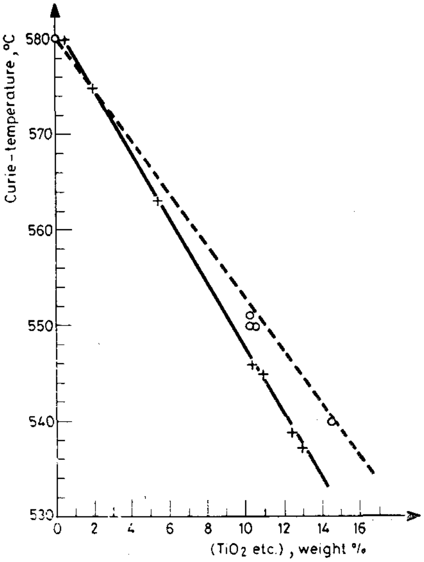

Fig. 28. Curie temperatures versus the contents of $Fe^{2+,3+}$ — substituents of some magnetites. — — — synthet. Ti-magnetites and chromites-magnetites; ——— natural Ti-magnetites

6. *Determination of the degree of disorder in kaolinites*

The burning (sintering) behaviour of kaolinites, $Al_2(OH)_4Si_2O_5$ (which are used as raw materials for china and pottery), depends strongly on the degree of disorder of these minerals. When the structural disorder increases, the sintering will start at lower temperatures (but – due to the inhomogeneities in the structure – at different spots and at different temperatures). The product will be pottery with different mechanical properties even in a single piece. Only kaolinites with a low degree of disorder will produce china or pottery with homogeneous and useful mechanical qualities. Therefore, a quick method for determining the degrees of disorder of such alumino-silicates will be of high value to ceramic engineers. As shown in Fig. 29, both the endothermic peak temperature and the ΔT value of kaolinites decrease with increasing structural disorder.

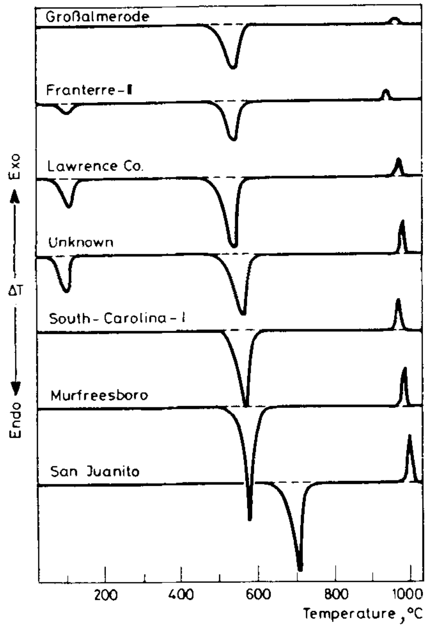

Fig. 29. DTA curves of some kaolinite minerals showing increasing degree of disorder from bottom to top (from the dickite from San Juanito to the "fireclay-mineral" of Großalmerode, Hesse)

This has been proved by extensive calibration by means of IR spectroscopy and X-ray analysis. On the basis of the corresponding values for this peak temperature and ΔT, it is possible to calculate an index of (dis-)order (Smykatz-Kloss [36]) Fig. 30 and the degree of (dis-)order. This can be checked by comparing with the temperature and ΔT of the exothermic peak around 950°, which are also lowered by increasing disorder. This gives a method for estimating the quality of any kaolinitic raw material.

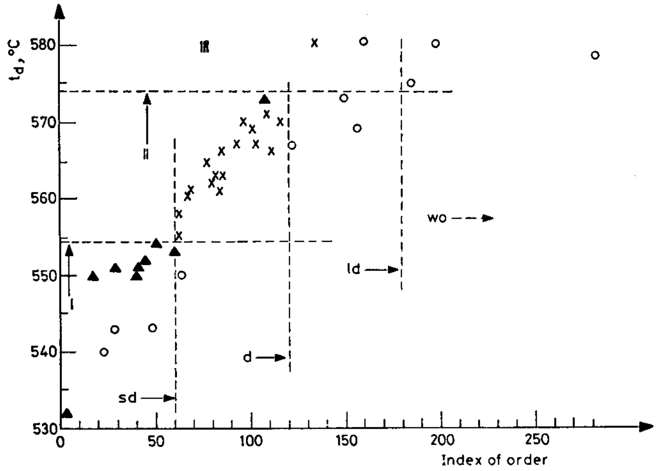

Fig. 30. Dehydroxylation temperatures *vs* index of order of kaolinites (from Smykatz-Kloss, 1976). ○ 11 kaolinites worldwide; kaolinites from Germany: × = Oberpfalz (Bavaria); ▲ = Westerwald (Rhineland); sd = strongly disordered; d = disordered; ld = little disordered; wo = well ordered

7. *The high-low-quartz inversion as a petrologic tool*

Since the research of Keith and Tuttle [37], who found certain differences in the temperature of the high-low quartz inversion, numerous papers have been published on this displacive transformation. The variations from the "textbook" value of 573°, the equilibrium temperature (1 atm) between the two quartz modifications, are explained by the defect character of the crystals: an increasing quantity of crystal-physical defects lowers the inversion temperature (Smykatz-Kloss [38]). For synthetic quartz crystals Sabatier and Wyart [39] pointed out that chemical environment has some influence on the inversion temperatures, too. Whether the low-high inversion temperature of natural quartz crystals occurs (I) spontaneously in one sudden step at 570–578 ± 1° (the accuracy of measurement may be improved by using K_2SO_4 as an internal standard, which exhibits an inversion at 583°) or (II) sluggishly in several steps at 500 to 573°, depends mainly on the number and kind of structural defects in these quartz crystals. It has been found that all studied quartz crystals of igneous origin and most crystals of metamorphic origin show the type (I) inversion (Fig. 32), whereas all studied samples formed during processes of weathering, sedimentation or diagenesis belong to the inversion type (II) (Fig. 31). Some quartz crystals of complex metamorphic origin exhibit the latter inversion type, too. Both types are distinctly different in their DTA curves, e.g. they show different peak temperatures, ΔT values and shapes of the inversion peaks. Lameyre *et al.* [40], Kresten [41] and Giret *et al.* [42] used the method for petrographic mapping of metamorphic regions (Fig. 32). Thus, the study of the inversion behaviour of quartz crystals by means of a highly standardized DTA technique may be used as a mineralogic and petrologic tool in

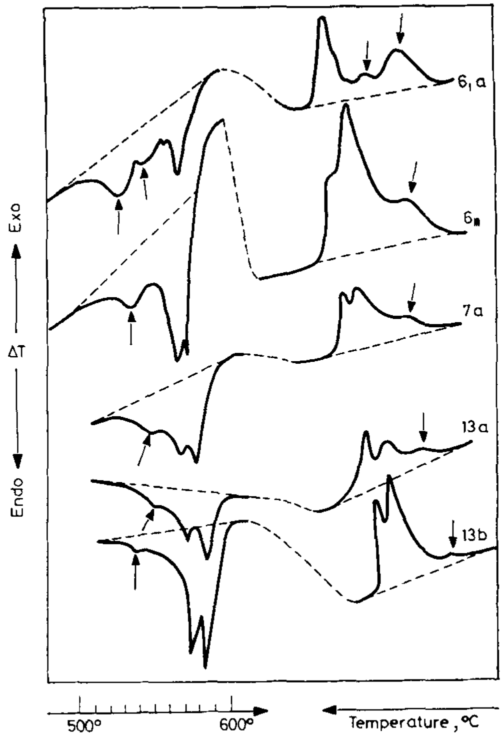

Fig. 31. DTA curves (first heating and cooling) of some quartz crystals which had formed by sedimentary processes; the endothermic effect which occurs at the highest temperature is due to the inversion of the internal standard K_2SO_4 (= 583 °C)

order to characterize the defect structure of the crystals, their possible origin, diagenetic or metamorphic recrystallization effects and their technical applicability.

8. *Determination of the degree of weathering of rocks*

The weathering of rocks means the destruction of primary material, mainly by the activity of water. This hydration of rock components results in the neoformation of hydroxides and/or hydrosilicates ("clay minerals") by precipitation from weathering solutions. Figure 33 shows the increasing amount of sheet silicates with increasing intensity of weathering of a granite.

From this correlation it emerges that DTA can be a suitable and quick method to characterize the degree of weathering of rocks (granites, basalts) by estimating the content of newly-formed sheet silicates (Fig. 34) and hydroxides. The determination of the degree of weathering of rocks is helpful and interesting in engineering-geological studies (Goebelbecker and Smykatz-Kloss [43]).

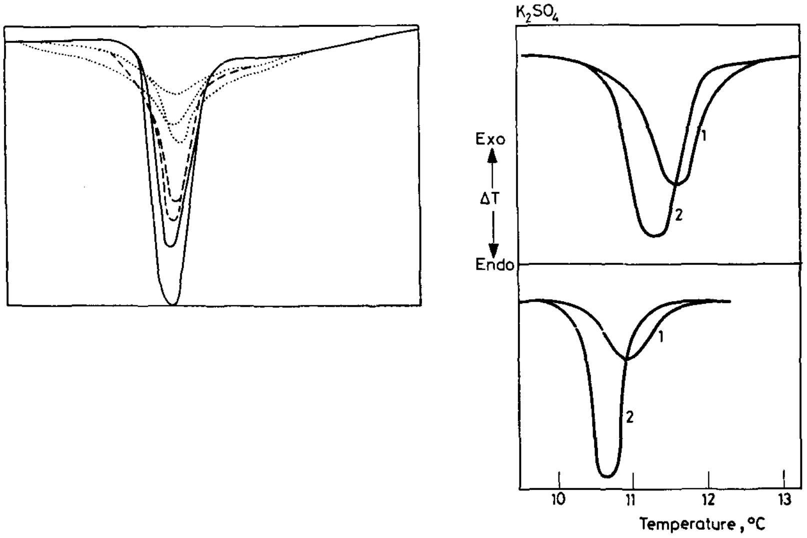

Fig. 32. DTA curves of the low-high quartz inversion; left: some quartz crystals from different specimens of the same granite massive (the samples contain different amounts of quartz); right: the comparison of the quartz from a (meta-) sedimentary rock (quartzite, arkose) with that from a contactmetamorphic hornfels of the same massive; the quartz crystals of both massives are clearly to be differentiated by means of their inversion temperatures (from Giret *et al.* [42])

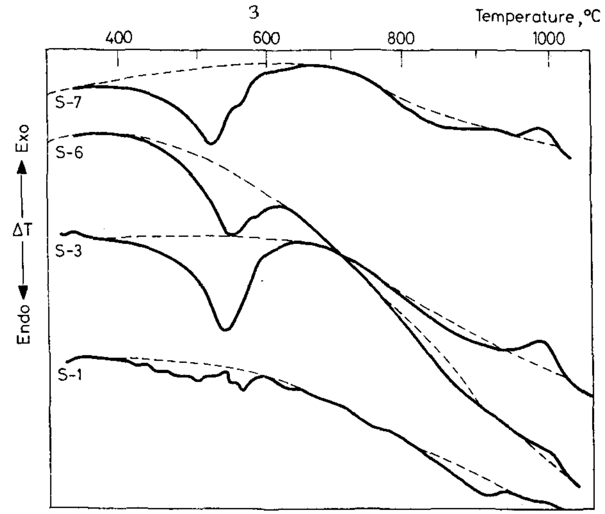

Fig. 33. Four DTA curves of a granite weathering profile: S-1 = fresh mother granite, S-3 = coarsely weathered material enriched in kaolinite, S-6 fine-grained weathering product, S-7 = soil

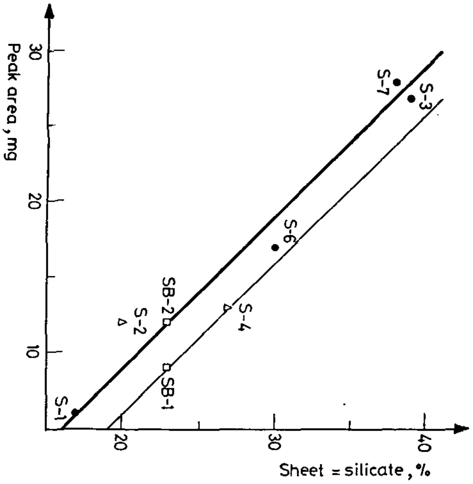

Fig. 34. Interdependence between the total amount of sheet silicates (determined by means of X-ray diffraction) and the total peak area of the dehydration and dehydroxylation effects of these minerals in DTA curves

Outlook

These eight examples may give an idea of the special applications of DTA as used in solving geoscientific problems. Of course, DTA can also be used to solve many more specific problems, especially when combined with some other methods of thermal analysis, e.g. with TG (Paulik *et al.* [5]), high pressure (Wyllie and Raynor [44]), TDA or mass-spectrometry (Wiedemann and Smykatz-Kloss [45]) and so on. In each case some work of calibration must be done, and done very exactly; standardized conditions of analysis are needed which make runs reproducible, and some concept of interpretation may be needed, based on a detailed knowledge of how DTA may be applied to geoscientific problems.

*

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Zusammenfassung — Die Differenz-Thermo-Analyse kann in der Mineralogie, allein oder mit anderen Methoden kombiniert, auf dreierlei Art angewandt werden:

1. für die qualitative Mineral-Identifikation und die (halb-) quantitative Bestimmung von Gesteins- und Bodenkomponenten,

2. für die Charakterisierung kristallchemischer und kristallphysikalischer Mineral-Eigenschaften, einschließlich kinetischer Parameter und der Bestimmung von thermodynamischen Daten, Phasen- und Reaktionsgleichgewichten,

3. für spezielle petrogenetische Untersuchungen, etwa den Zusammenhang zwischen mit der DTA gemessenen mineralogischen Eigenschaften und der Bildung, dem Zerfall oder der Rekristallisation von Mineralen.

Die präsentierten Ergebnisse wurden unter Einhaltung streng standardisierter und reproduzierbarer Analysenbedingungen erhalten und unter Anwendung kürzlich von dem Verfasser entwickelter Methoden. Im einzelnen werden widergegeben: neu konstruierte Schlüsseldiagramme ΔT gegen Peaktemperatur zur Bestimmung unbekannter Minerale; PA-Kurven, die den Zusammenhang zwischen Entwässerungs- und Zerfallsreaktionen und dem Partialdruck dabei entstehender gasförmiger Reaktionsprodukte widerspiegeln; die Bestimmung chemischer und kristallchemischer Mineralparameter durch den Zusammenhang zwischen Dehydroxylations-Peaktemperaturen und Zusammensetzung von Mischkristallen (Chlorite, Smektite); die Bestimmung des Zusammenhangs zwischen den Peaktemperaturen von Strukturumwandlungen und kristallchemischen Substitutionen (Sulfide, Carbonate, Phosphate, Silikate); die Bestimmung des Fehlordnungsgrades von Mineralen aus sedimentärem Bildungsmilieu durch die Messung der Abhängigkeit von Entwässerungs- oder Inversions-Peaktemperaturen und Peakflächen vom Defektcharakter dieser Mineralstrukturen (Tonminerale, Quarz, Cristobalit, Hydroxide); die Unterteilung von Mineralgruppen durch Nutzung des Zusammenhangs zwischen Kristallchemie und Entwässerungsverhalten (Zeolithe, Tonminerale mit Wechsellagerungsstrukturen); die Charakterisierung ferromagnetischer Minerale durch die Abhängigkeit der Curietemperaturen von der chemischen Zusammensetzung; die Entwicklung einer DTA-Methode zur Messung des Verwitterungsgrades von granitischen Gesteinen etc. Daten von 150 Mineralen werden angeführt.

Резюме — В минералогических исследования дифференциальный термический анализ используется как таковой или же как совмещенный метод для трех целей:

1. Для качественного определения минералов и полуколичественного определения компонентов в горных породах и почвах.

2. Для характеристики кристалло-физических и кристалло-химических свойств, включая изучение кинетики реакций и определения термодинамических данных, фазовых и реакционных равновесий.

3. Для специальных петрогенетических исследований, касающихся взаимосвязей минералогических свойств с образованием, разложением или рекристаллизацией минералов.

Представленные результаты были получены при строго стандартных и воспроизводимых условиях анализа и с помощью недавно разработных методов. Они включают построение ключевых диаграмм ΔT против температурных пиков с целью идентификации неизвестных минералов; установление зависимости температурных пиков дегидратации и разложения от парциального давления газообразных продуктов реакции (ПА-кривые); определение химических и кристалло-химических параметров минералов, используя зависимость температурных пиков дегидроксилирования твердого раствора (хлориты, смектиты)

или используя взаимосвязь между температурами структурных превращений и кристаллохимическими заместителями (сульфиды, карбонаты, фосфаты, силикаты); определение степени наружения минералов, образующихся в осадочных породах, используя температурные пики дегидратации или превращения и зависимость фирмы этого пика от характера нарушения этих кристаллических структур (глинистые минералы, кварц, кристобалит, гидроокиси); подразделение групп минералов, используя взаимосвязь между их кристаллохимией и отношением их к дегидратации (цеолиты, смешано-слоистые глаинистые минералы); характеристика ферромагнитных минералов, изучая их температуру Кюри в зависимости от химического состава; разработка метода ДТА для измерения степени выветривания гранитных пород и др. Представлены данные для 150 минералов.