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ON THE THERMAL ANALYSIS OF MINERAL COMPONENTS IN CLAYS

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The paper deals with the problem of the interactions of the mineral components in clay and argillite samples during the thermal analysis. It is shown that depending on the experimental conditions, the interaction of pyrite and carbonates may cause atypical course of DTA and TG curves. Also the common occurring of sylvine and halite shifts the temperature of their melting to a lower value and this phenomenon occurs in pure salts as well as in the great dilution to some percent in clays.

The relationship between the experimental conditions and results of thermal analysis is generally known. The influence of the heating rate, particle size and packing of the sample, inert material, furnace atmosphere, the shape and material of the sample holder are all described in the literature. The connection between the mineral composition of the sample and experimental conditions is less well known, and very often cannot be foreseen, and causes many difficulties in the interpretation of the thermal curves obtained for samples of unknown mineral composition. Some remarks on this problem have been mentioned by the author in previous papers [1, 2]. Examples showing some of these connections and observations concerning the thermal investigations carried out by means of a derivatograph, a Paulik – Paulik – Erdey GYEM Hungarian apparatus, will be given in the present paper. This apparatus makes it possible to obtain four thermal curves simultaneously: T (temperature), DTA (differential thermal analytical), TG (thermogravimetric, quantitatively in mg) and DTG (derivative thermogravimetric). This apparatus makes it possible to determine the temperature in the sample as well as in the inert substance. All the figures concern analyses carried out by measuring the temperature in the sample. This problem of temperature measurement is very important because the temperature of the reactions differs by several degrees depending on whether the measurement is made in the sample or in the inert substance. Thus, if the temperature is measured in the sample, the maximum corresponding to an endothermic reaction appears at some degrees lower than when measured in the inert substance, while the situation is reversed with exothermic reactions. All derivatograms reproduced have been made with the same DTA, DTG, TG sensitivity, and heating rate was 10°/min. The weight of sample was approx. 1 g.

Many complications arise from the presence of considerable amounts of pyrite and carbonates in the sample, particularly if the thermal analysis is carried out in a non-oxidizing atmosphere. The observation was made on the Silurian graptolite shales, investigated in a nitrogen atmosphere. As shown by Fig. 1, there is no visible endothermic effect of carbonates on the DTA curve. However, an apparent exothermic effect occurs in the temperature region above 800°. At the same time the TG curve shows a characteristic increase of weight above 890°. The presence of carbonates can be determined on the basis of the DTG curve alone, but only a few types of thermal apparatus enable this to be done. Graf [3] has also described earlier the influence of hydromica on the DTA effects of carbonates in sedimentary rocks. The phenomenon shown in Fig. 1 can be explained as follows: iron (II) present in pyrite which decomposes in the temperature region 400 to 500° cannot be oxidized in a nitrogen atmosphere and exists in the sample up to

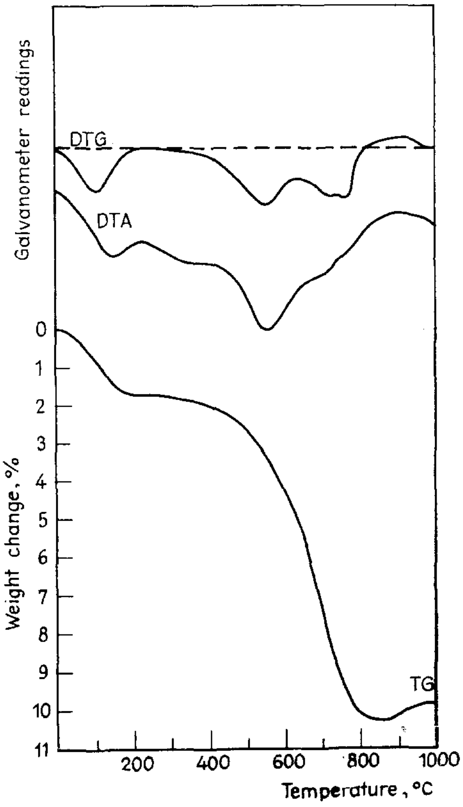

Fig. 1. Silurian graptolite shale, bore hole Bytów. Nitrogen atmosphere

the temperature region above 800° when the thermal decomposition of carbonates begins. The loss of CO_2 is indicated by the TG and DTG curves as the loss of weight in the sample. CO_2 going into the furnace atmosphere is decomposed at this temperature and produces oxygen which binds iron(II) and "returns" into the sample. This process is recorded as an increase of weight, and the exothermic effect of oxidation, overlapping the endothermic reaction of carbonates. The effect of the decomposition of carbonates has been observed only when their amount is greater than about 7% in this type of sample. This value is apparently influenced by the pyrite content, too.

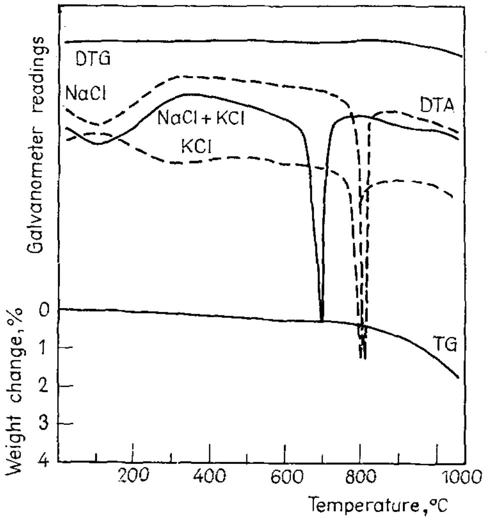

Fig. 2. Artificial KCl–NaCl (1 : 1) mixture

If the lack of the endothermic effect of carbonates is connected with the occurrence of an exothermic reaction (e.g. some minerals of the serpentine group or of the products of their weathering) in the same temperature region, the characteristic break of the TG curve connected with the characteristic kinetics of the thermal decomposition of carbonates proves the presence of these minerals. This break of the TG curve allows carbonates to be detected in other kinds of sample, in spite of the lack of an adequate DTA peak, e.g. in concretes.

The presence of soluble salts may also cause many complications due to the interactions between the rock components [3–5]. This problem needs further investigation, e.g. attention should be paid to the case when there is a mixture of chlorides, e.g. NaCl and KCl, in the sample. It has been confirmed [6] that although each of these chlorides separately gives an endothermic peak at about 800° (NaCl – 801°, KCl – 776°), in a 1 : 1 mixture they yield a common endothermic effect at a temperature almost 100° lower than do the minerals separately (Fig. 2). This is caused by the melting of both chlorides at a lower temperature.

In clays and argillites where the concentration of chlorides is small, e.g. 3% in illite clay, no chloride peak is observed (Fig. 3). A greater concentration of chlorides (e.g. 10%) gives rise to a peak at 700° which is analogous to the results obtained for pure chlorides. Thus, the common melting of both chlorides already occurs at a concentration of the order of a few percent. This DTA peak is broad, so that without TG and DTG curves it may be misinterpreted, for example, as a montmorillonite peak.

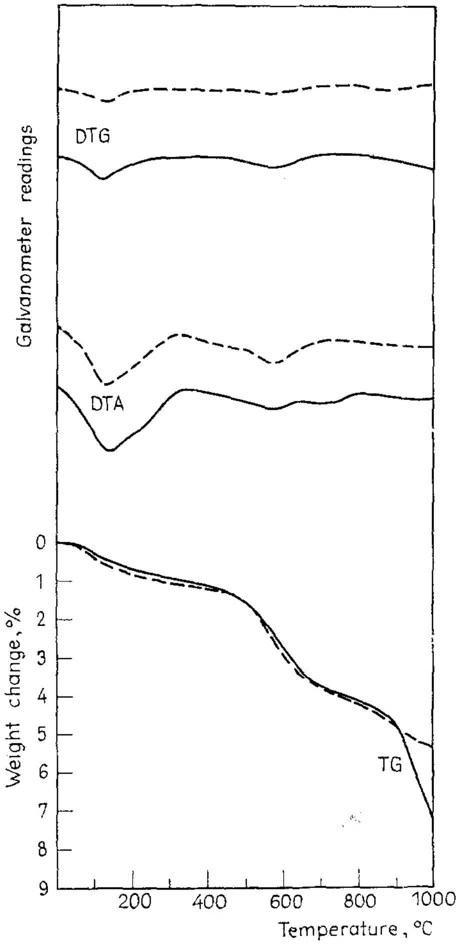

Fig. 3. Cambrian illite clay, bore hole Iwaniska-Zielonka with chlorides. Broken lines — sample with 3% NaCl + KCl (1 : 1), continuous lines — sample with 10% NaCl + KCl (1 : 1)

Some minerals yield an apparent endothermal effect caused by the different thermal properties of the sample and inert substance, e.g. iron carbonates and oxides with Al_2O_3 as inert, without there being any endothermic reaction within the sample (Fig. 4). In this case TG and DTG curves allow the nature of this peak to be determined, as now the effect of siderite at low temperatures is not connected with any loss of weight, so it is not caused by the loss of water.

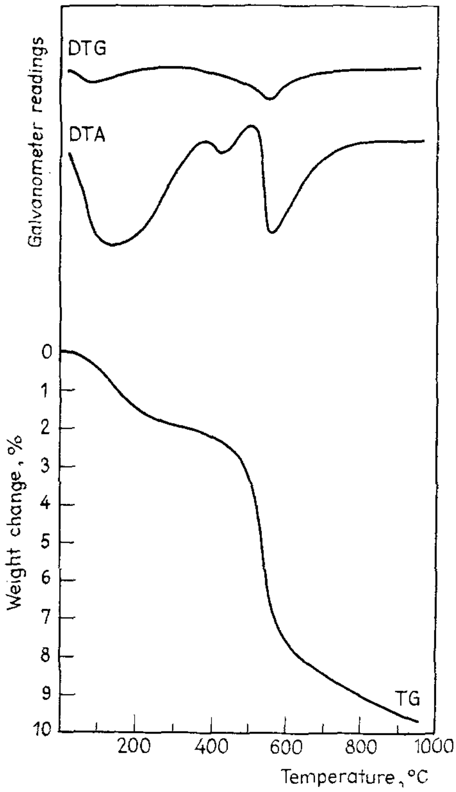

Fig. 4. Jurassic clay siderite, bore hole Rusinów

Generally, TG and DTG curves allow the kind of reaction to be determined (thermal dissociation with a loss of weight or recrystallization, intercomponent reaction, melting and polymorphous transformation) and in many cases permit a quantitative estimation of the mineral composition of the sample. Unfortunately, there are some difficulties if the sample contains amorphous minerals or organic matter. Then, the TG curve shows the continuous loss of weight without any distinct steps. This course of the TG curve makes it impossible to account for the amounts of mineral components (Fig. 1) which in another association may be estimated quantitatively. It is evident that only minerals showing loss of weight can be estimated quantitatively by means of TG curves, in contrast to minerals which do not suffer any thermal decomposition, such as quartz and other anhydrous oxides, felspars, anhydrous sulphates and chlorides, etc.

The importance of the TG curve also appears in the interpretation of thermal results of almost mono-mineral samples giving atypical differential thermal curves, e.g. montmorillonites Yavapai and Woburn, especially with respect to the nature of high temperature peaks.

In conclusion it may be said that the use of combined DTA, TG and DTG methods makes it possible to explain the nature of some thermal reactions, and frequently to estimate quantitatively the mineral composition of the sample, but its greatest importance lies in the possibility of the correct interpretation of differential thermal curves showing atypical shape owing to mineral interactions. These phenomena occur more often than is noticed, and they cause many difficulties or errors in the interpretation of DTA results. They can be detected by a number of systematic investigations of natural samples as well as by the studies of artificial mixtures of minerals.

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Résumé. — Les interactions des constituants minéraux des échantillons d'argile et d'argilite pendant l'analyse thermique ont été examinées. Suivant les conditions expérimentales, l'interaction de la pyrite et des carbonates peut provoquer un tracé des courbes ATD et ATG qui s'écarte de l'allure type. La présence simultanée de sylvine et d'halite produit un abaissement de leur point de fusion et ce phénomène apparaít aussi bien avec les sels purs qu'avec ceux fortement dilués, à raison de quelques pour cent, dans les argiles.

Zusammenfassung — Es wird über Zwischenreaktionen der mineralischen Komponenten von Ton und Argillit während der thermischen Analyse berichtet. Von den Versuchsbedingungen abhängend produzieren die Zwischenreaktionen von Pyrit und Karbonat DTA und TG Kurven deren Verlauf nicht charakteristisch ist. Das gemeinsame Vorkommen von Sylvin und Halit verschiebt ihren Schmelzpunkt in Richtung der niedrigen Temperaturen in reinen Salzen ebenso wie bei großer Verdünnung von einigen Prozenten in Ton.

Резюме. — Изучено взаимодействие, имеющее место при термическом анализе минеральных компонентов, встречающихся в образцах глины и глинистого сланца.
Показано, что в зависимости от условий эксперимента взаимодействе между пиритом и карбонатами может обусловить характерный ход термогравиметрической кривой (ТГ) и кривой дифференциального термического анализа (ДТА).
Совместное присутствие сильвина и галита снижает температуру плавления каждого компонента в отдельности. Это явление наблюдалось как в случае чистых солей, так и в случае глины при значительной степени разбавления.