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STUDY OF THE REACTION MECHANISM AND COMPOSITION ANALYSIS OF MULTIPLE-COMPONENT MIXED MINERALS

DTA/T/EGD/GC on-line coupled simultaneous technique

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Abstract

An established DTA/T/EGD/GC on-line coupled simultaneous technique and relevant equipment were applied to identify the micro impurity minerals – pyrite and siderite in two kinds of dolomite in air and N_2. The proportional five-component mixed minerals (siderite, kaolinite, dolomite, calcite and quartz) and the proportional six-component mixed minerals (pyrite and the above five minerals) were detected in N_2 and in air/CO_2 (1:1) separately by applying DTA/EGD/GC and DTA/GC. The experimental results provide the basis for demonstration of the reaction mechanism of thermal decomposition of various gas–solid-phase minerals in N_2 and air/CO_2. The compositions of six-component mixed minerals can be distinguished individually from the DTA/GC curves; reliable results are obtained.

Keywords: calcite, differential thermal analysis, dolomite, gas chromatography, kaolinite, pyrite, siderite

Introdution

With the development and progress of thermal analysis techniques and various modern EGA coupled simultaneous techniques, the wide future of applications in the field of mineralogy study has been demonstrated [1–3].

The author has established a DTA/T/EGD/GC on-line coupled simultaneous technique and relevant equipment since 1980 [4, 5]. The essence of this thermal analysis equipment is as follows: the EGD curve traces the variation in the DTA curve. The features of the thermal effect can reveal directly whether it is due to a physical process or a chemical reaction. According to the variation in the DTA/EGD curves, the relevant reaction gases evolved at any temperature can be collected for GC analysis. The information and data from four aspects of DTA/T/EGD/GC can be obtained by detection on samples at the milligram level. A reliable basis for demonstration of the reaction process of thermal decomposition of gas–solid-phase in various gas atmospheres and for study of the reaction mechanism is provided. This article is written on the basis of previous

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work [6, 7]. It is a study for identifying micro impurities in minerals, for establishment of the reaction mechanism, and for composition analysis of multiple-unit mixed minerals in various gas atmospheres.

Experimental

Each mineral was finely ground to about 100 mesh in an agate mortar, and stored separately in sample bottles. Each mineral was tested with the DTA/T/EGD/GC on-line coupled simultaneous equipment. The results were as follows: siderite contains a trace amount of kaolinite [7]; kaolinite contains a trace amount of siderite [7]; and dolomite(1) and dolomite(2) contain trace amounts of pyrite and siderite, respectively, as shown in Figs 1 and 2. Pyrite and calcite are minerals of high purity, as shown in [6] and Fig 3. The composition and wt% contents of proportional five-component and six-component mixed minerals are shown in Table 1

Table 1 Compositions of proportional five-component and six-component mixed minerals

Mixed	Contents /wt%						
mineral	Pyrite	Siderite	Kaolinite	Dolomite(1)	Dolomite(2)	Calcite	Quartz
five-component	–	14.3	28.5	–	14.3	28.5	14.3
six-component	10	10	20	10	20	20	10

Equipment

The DTA/T/EGD/GC on-line coupled simultaneous equipment was constructed with a differential thermal analyser and an EGD/GC unit with a binary flow and binary thermal conduction detection system [TCD(1), TCD(2)] connected by a specially designed gas conduit and other accessories. With such a system, on-line coupled simultaneous application can be undertaken [4, 5]. The model CRY-1 differential thermal analyser was made by the Tian Ping Instrumental Factory, Shanghai, P.R. China. The operating temperature range was from ambient temperature to 1200°C. The sample crucible: aluminum cell, 5x3 mm. The DTA/EGD/GC testing conditions are shown in the Figures. In these Figures, TCD(1) and TCD(2) represent the response values of the peak height on the vertical coordinate of the EGD curve and the GC curve, respectively. The chromatographic column was filled with the 401 organic support. The length of the column was 2 m and the carrier gas was N_2. Under the specified testing conditions, the peak directions for H_2, O_2 and H_2O were contrary to those for CO_2 and SO_2. The relative retention times were 0.85 min, 0.9 min, >2.5 min (tail peak), 1.7 min and 2.5 min successively [8].

Results and discussion

Identifying trace pyrite in dolomite(1)

DTA/EGA/GC coupled simultaneous curves of dolomite(1) in air are shown in Fig. 1. The EGD curve traces the variation in the DTA curve. Four peaks occur due to the chemical reaction. In association with the two strong endothermic peaks (810 and 890°C), abundant CO_2 was detected at 830 and 920°C in the GC-gram. The two strong endothermic peaks are due to CO_2 release in two steps during the thermal decomposition of dolomite(1). In association with two lower-temperature, small, sharp exothermic peaks (500 and 565°C), at 505 and 575°C trace SO_2 was detected in the GC gram, and the O_2 peak heights decreased. (Note the dashed line in Fig. 1.) This conforms to previous experimental results [6]. Accordingly, trace pyrite in dolomite(1) was identified.

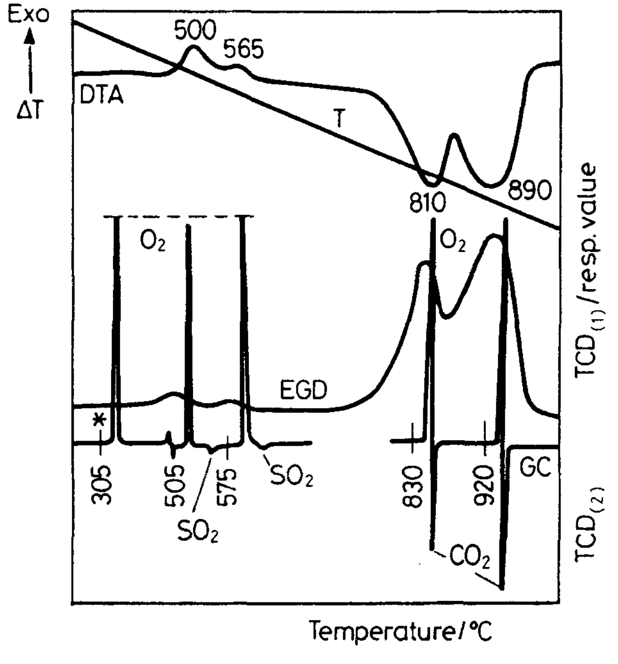


Fig. 1 DTA/EGC/GC curves of dolomite(1) (47.13 mg) containing trace pyrite.
DTA ±100μV, 20 deg/min, air: 25 ml/min. Other test conditions as in Fig. 4.
*Nominal height of O_2 peak detected by GC shown as dashed line

Identifying trace siderite in dolomite(2)

DTA/GC coupled simultaneous curves of dolomite(2) in N_2 are shown in Fig. 2. The temperatures of the endothermic peaks (805 and 860°C) with a shoulder in the DTA curve relate to the temperature range in the GC gram. CO_2 is detected at 720, 750, 780, 810, 840, 870 and 910°C. Evidently, the endother-

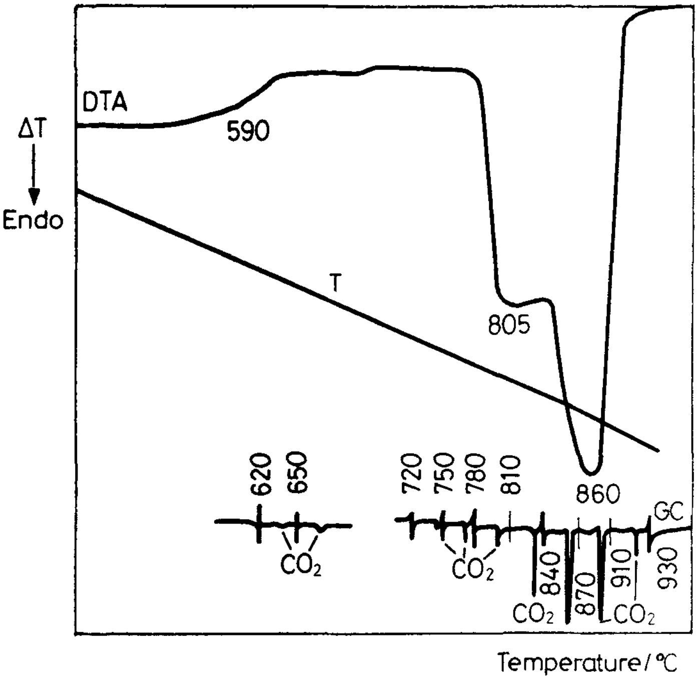


Fig. 2 DTA/GC curves of dolomite(2) (38.16 mg) containing trace siderite. DTA ±100μV, 20 deg/min, N_2: 25 ml/min. Other test conditions as in Fig. 4

mic peak with a shoulder is the same as that for dolomite(1). It is due to CO_2 release in two steps during the thermal decomposition. In the GC-gram, at temperatures corresponding to a wide but weak endothermic peak in the DTA curve, CO_2 is detected at 620 and 650°C. A comparison with previous experimental results [7] reveals that trace siderite is present in the tested dolomite(2).

Determination of purity of calcite

DTA/EGD/GC coupled simultaneous curves of calcite in air are shown in Fig. 3. In the DTA curve relating to the EGD curve, a wide and unsymmetric endothermic peak (840°C) appears. At temperatures of 755, 790, 820 and 850°C in the GC-gram, the only product detected is CO_2. The percentage (wt.%) of the residue is 57.93%, which is near the theoretical value of 56.03%. Accordingly, the tested calcite is $CaCO_3$ of high purity.

Composition analysis of five-component mixed minerals

Figure 4 depicts DTA/EGC/GC coupled simultaneous curves of proportional five-component mixed minerals of siderite, kaolinite, dolomite, calcite

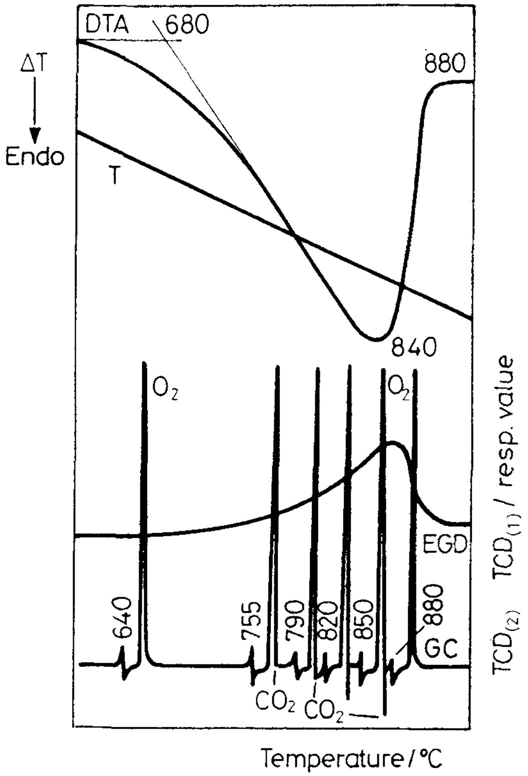
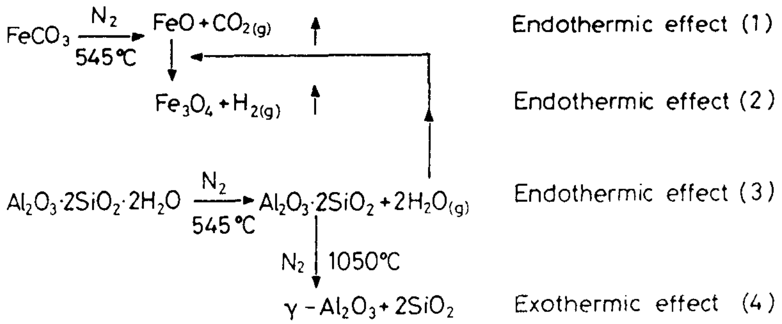


Fig. 3 DTA/EGD/GC curves of calcite (15.89 mg). DTA ±100μV, 20 deg/min; N_2: 30 ml/min. Other test conditions as in Fig. 4

and quartz. In the GC-grams (a) and (b), in the temperature range relating to the first broad endothermic peak (545°C) in the DTA curve, CO_2, H_2 and H_2O peaks with tails (GC-gram (a), 540 and 860°C) are detected at 520, 540, 570, 620 and 680°C. Evidently, CO_2 and H_2O are released in the endothermic reactions of thermal decomposition of siderite and kaolinite, respectively. However, a large amount of H_2 was detected in the evolved gas, and it was found that some of the remaining pellets are magnetic. According to the results of a previous article [7], this is a result of the gas–solid-phase reaction of FeO, the primary product of thermal decomposition and OH groups from the thermal decomposition of $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$. In the EGD curve relating to the small exothermic peak (1050°C) in the DTA curve, there is a horizontal line, because of no release of evolved gas. The small exothermic peak is due to a polymorphous transformation of metakaolin to γ-Al_2O_3 at high temperature [7]. According to the information provided by the DTA/EGD/GC curves, the equations for the gas–solid-phase reaction of siderite and kaolinite in the 5-component mixed minerals in N_2 are as follows:



It is seen in the GC-gram (a) that a H_2O peak with a tail was detected at 860°C. This indicates that kaolinite does not release H_2O from the structural OH groups until very high temperature [7].

The endothermic effect of polymorphous transformation of quartz in mixed minerals under programmed heating is normally concealed by the strong endothermic effects of siderite and kaolinite in N_2. After the reaction, programmed cooling was applied to the residue. A small exothermic effect (Fig. 4, top right corner, DTA curve) appears at 580°C in the DTA curve. This is due to the reversible polymorphous transformation of quartz in the residue, (Fig. 5). The reaction equation is as follows:

$$\beta\text{-SiO}_2 \overset{578^\circ\text{C}}{\leftrightarrow} \alpha\text{-SiO}_2 \qquad (5)$$

In GC-grams (a) and (b), in association with the second broad endothermic peak (850°C) in the DTA curve, CO_2 peaks are detected at 750, 790, 830, 860, and 890°C. The experimental results indicate that in the case of smaller quantities of sample in N_2 (or air), CO_2 is released in the thermal decompositions of dolomite and calcite. Three peaks of endothermic effects almost overlap with each other to form a broad and unsymmetric endothermic peak, and can not be distinguished from each other. However, if an appropriate quantity of CO_2 is added to the flowing atmosphere, the result is different (Fig. 5).

Composition analysis of six-component mixed minerals

Proportional mixed minerals of pyrite, siderite, kaolinite, dolomite, calcite and quartz were tested in a mixed atmosphere of air/CO_2 (1:1); the resultant DTA/GC curves are shown in Fig. 5. In the GC–gram relating to the temperature range of the two strong exothermic peaks at 485 and 540°C in the DTA curve, it is found that at 370, 490 and 570°C, the CO_2 peak increases gradually, the O_2 peak decreases continuously and a SO_2 peak is identified. At 640°C, the

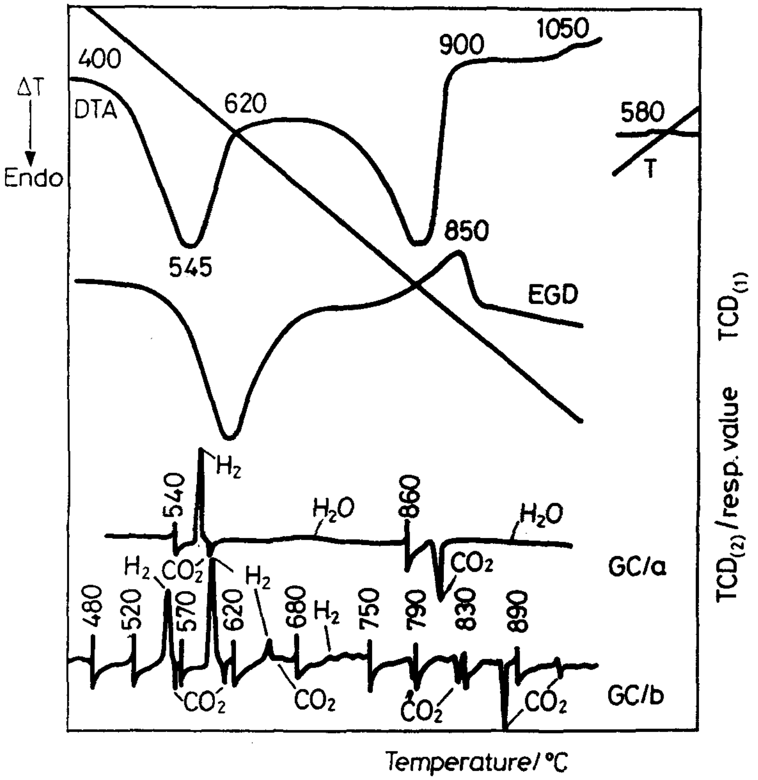
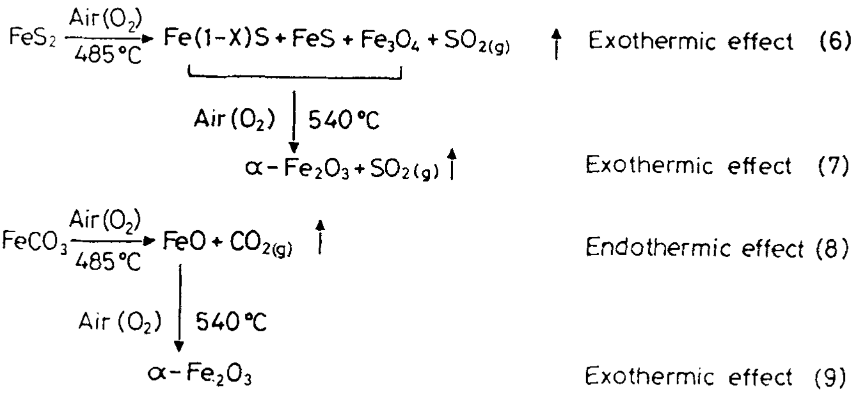
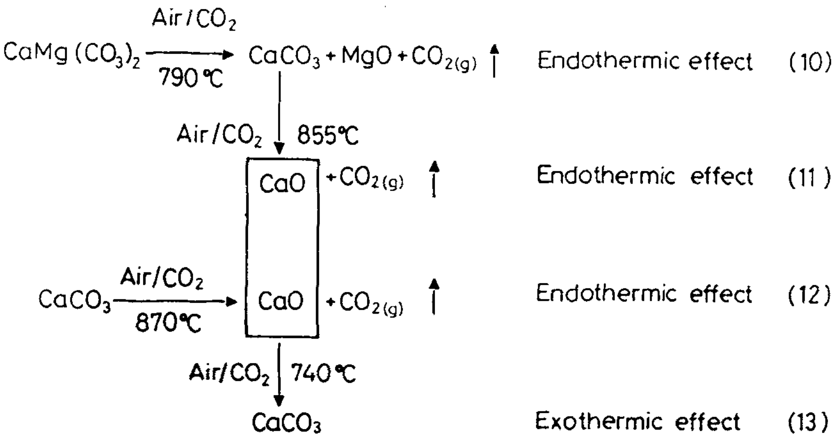


Fig. 4 DTA/EGD/GC curves of the proportional five-component mixed minerals (a - 22.33 mg, b - 22.68 mg): $FeCO_3 + Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O + CaMg(CO_3)_2 + CaCO_3 + SiO_2$. DTA ±100μV, 20 deg/min, N_2: 30 ml/min, EGD/TCD (1): 100 deg/120 mA; GC/TCD (2): 110 deg/140 mA, column: 401 organic support, carrier gas N_2: 30 ml/min

reaction approaches an end and the CO_2 and O_2 peaks return to their normal heights (note the dashed lines in Fig. 5). The information provided by the DTA/GC curves suggests that pyrite present in the mixed minerals participates in a strongly exothermic oxidizing reaction in air. In the oxygen-consuming process releasing SO_2, not only are the endothermic decompositions of siderite and kaolinite concealed, but also a strongly exothermic oxidizing reaction takes place due to FeO, the primary decomposition product of siderite, reacting with the oxygen in the air. The resultant product is Fe_2O_3. Two strong exothermic peaks in the DTA curve are due to the large amounts of pyrite and siderite present in the tested mixed minerals. With reference to previous articles [6, 7], the reaction processes are expressed by Eqs (6–9):



In the temperature range of the endothermic peak at 790°C and the strong endothermic peaks with shoulders at 855 and 870°C in the DTA curve, at 740, 790 and 850°C in the GC-gram, the heights of the CO_2 peaks increase gradually. Because of the pressure sharing of CO_2 in air/CO_2 mixed gases, the release of CO_2 in the two-step thermal decomposition of dolomite yields two separate endothermic peaks (790 and 855°C), producing MgO and CaO, and CO_2 release in the thermal decomposition of calcite produces an endothermic peak (870°C), with CaO as residue. Both peaks are 15 deg different from those in the DTA curve. Thus, it can be considered that the tested mixed minerals contain large amounts of $CaMg(CO_3)_2$ and $CaCO_3$. At 970°C, the height of the CO_2 peak is equal to its nominal height (end of the reaction). However, in the GC gram at 730°C, on programmed cooling, the height of the CO_2 peak decreases below the nominal height. In the DTA curve, a strong exothermic peak (740°C) appears due to the reversible reaction of CO_2 in the flowing mixed gases with CaO (the product of the thermal decomposition of dolomite and calcite). With reference to a previous article [6], the reaction processes can be expressed by Eqs (10–13):



In the DTA curve, a small exothermic peak appears at 1020°C, due to the γ-Al_2O_3 polymorphic transformation of metakaolin at high temperature. The reaction equation is shown in Eq. (4). In the DTA curve of programmed heating and cooling processes, the relevant endothermic peak and exothermic peak appear near 570°C, due to the reversible polymorphic transformation of quartz. The reaction equation is shown in Eq. (5).

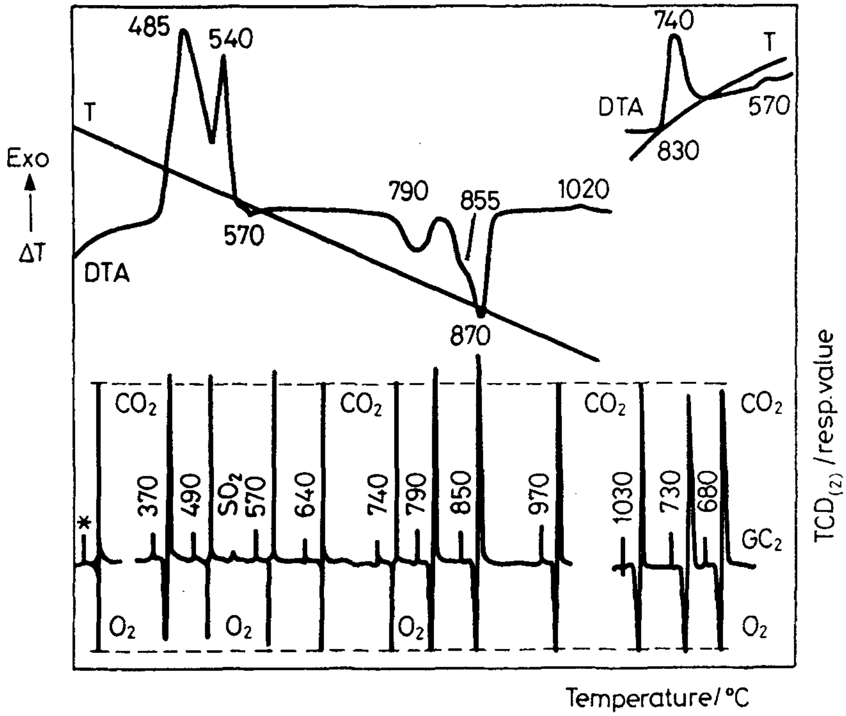


Fig. 5 DTA/GC curves of the proportional six-component mixed minerals (20.04 mg): FeS_2+$FeCO_3$ +$Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$ +$CaMg(CO_3)_2$ +$CaCO_3$ +SiO_2. DTA ±100μV, 20 deg/min, air/CO_2 (1:1): 30 ml/min, other test conditions as in Fig. 4.
*Nominal heights of O_2 and CO_2 tested by GC shown as dashed lines

From the information provided by Fig. 5, with application of the DTA/GC on-line coupled simultaneous technique and the testing of proportional six-component mixed minerals in air/CO_2 (1:1), the compositions of six-component mixed minerals can be identified individually from the tested DTA/GC curves; reliable results are obtained.

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Zusammenfassung — Zur Identifizierung der Mikroverunreinigungsminerale Pyrit und Siderit in zwei Arten von Dolomit wurde in Luft und Stickstoff eine on-line gekoppelte DTA/T/EGD/GC-Simultantechnik und die relevante Ausrüstung verwendet. Die proportionalen fünfkomponentigen Mischminerale (Siderit, Kaolinit, Dolomit, Kalzit und Quarz) und die proportionalen sechskomponentigen Mischminerale (Pyrit und die obigen fünf Minerale) wurden in Stickstoff und in einem Luft/CO_2 (1:1) Gemisch jeweils separat unter Einsatz von DTA/EGD/GC und DTA/GC detektiert. Die experimentellen Versuche liefern die Grundlage für die Demonstration des Reaktionsmechanismus der thermischen Zersetzung verschiedener Gas-Feststoffphasen-Minerale in Stickstoff und in Luft/CO_2. Die Zusammensetzung von sechskomponentigen Mischmineralen kann anhand der DTA/GC-Kurven individuell unterschieden werden; zuverlässige Ergebnisse wurden erhalten.