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THERMAL CHARACTERIZATION OF DOLOMITES

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Abstract

The decomposition behaviour of dolomite samples has been carried out by simultaneous DTA-TG experiments. Dolomite samples could be classified broadly into two categories as regular and iron-bearing dolomites based on DTA decomposition temperatures. The mass% FeO of all the dolomite samples was identified by DTA and the results are confirmed by atomic absorption spectrophotometer experiments.

Keywords: differential thermal analysis, dolomite, thermogravimetry

Introduction

Thermo-analytical methods have been among the standard methods of mineralogy. From reactions which occur in a mineral or other chemical substance during thermal treatment (heating or cooling), the mass and energy changes can be identified and measured very clearly. Mass loss, which, for example, occurs during dehydration, or loss of CO_2, SO_3 etc., can be determined with thermogravimetry (TG). In differential thermal analysis (DTA), temperature differences relative to a thermally inert material are measured during heating or cooling of a sample. The study of clays and silicate minerals played an important role in propagation of the thermal analysis techniques. Clay minerals constitute to be important industrial raw materials and are used in the manufacture of structural clay products, as filler in the paper and polymer industries, and as an additive in paints and inks. Organo-clays find extensive use as oil drilling fluids and have been the subject of many studies because of their potential use as stereo-specific catalysts.

Dolomite is a double salt of calcium and magnesium carbonate and is one of the two forms of limestone. The thermal decomposition of dolomite shows peculiar characteristics depending on the atmosphere in which the experiments are carried out. In an atmosphere of carbon dioxide the decomposition occurs via a two-stage process. This is peculiar to dolomite and can be used in the identification of dolomite in samples of unknown composition. The same decomposition process occurs in a single stage in an inert atmosphere of nitrogen. The partial pressure of carbon dioxide

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causes the decomposition to split into a two-stage process. The effect of procedural variables such as flow rate of the purge gas, grain size, sample size and heating rate was investigated in detail. It was found that for performing decrepitation studies on dolomite, experiments in carbon dioxide give better information as compared to experiments carried out in other atmosphere [1–7].

Ortega *et al.* [8] studied the thermal decomposition of dolomite and showed that the 'rate-jump' results are independent of both sample mass and the nature of the $f(\alpha)$ function, regardless of the range of temperature used. Khan *et al.* [9] have shown that, for a given particle size, calcite decomposes at lower rate compared to limestone in spite of the fact that calcite heats up more rapidly when equal masses of samples are introduced into a furnace set at a predetermined temperature. Mako and Juhász [10] determined the structural changes caused by mechanical forces of dolomites by thermal analysis and XRD. In situ high temperature XRD was applied to study the thermal decomposition of mechanically treated dolomite. In the case of original dolomite a simultaneous formation of $CaCO_3$, CaO and MgO indicates the dolomite decomposition at 700°C. The ground dolomite decomposes directly to $CaCO_3$, accompanied by the formation of MgO at 580°C. Dollimore *et al.* [11] showed that TG reveals the extent of the hydration product portlandite $Ca(OH)_2$ in the sample, the amount of $CaCO_3$ present and the amount of dolomite. XRD studies confirm the presence of these materials. Mako and Juhász [12] studied the crystal structure deformation of dolomite caused by intensive grinding by XRD and thermal analysis. Structurally deformed dolomite crystallites developed due to the mechanical treatment decomposes in two steps at a higher and lower CO_2 partial pressure as well. Deformed dolomite decomposes directly to calcite and periclase accompanied by the formation of CO_2 between 500 and 600°C. The proportion of structurally distorted dolomite increases with the grinding time. Shoval *et al.* [13] studied the infrared spectra of different kaolinite by curve fitting. These spectra generally exhibit four hydroxyl-stretching bands. The fifth OH band is also observed in transmission IR spectra of hydrothermal and authigenic kaolinites, which have a high degree of crystallinity. This additional band is weak or undetectable for kaolinites with a low degree of crystallinity.

Experimental

The local dolomite samples used in this research were collected from different geological formations. Lump samples were ground and size fraction <60 mesh collected for experiments. All samples were dried at 120°C and kept in desiccators prior to use.

Simultaneous DTA and TG experiments were carried out using Netzsch thermal analyser (STA 409 EP). Simultaneous DTA and TG experimental procedure involves placing sample (100 mg) setting the heating and gas flow rate, then commencing the experiment. All experiments were performed at a linear heating rate of 10°C min^{-1} over the temperature range of ambient to 1200°C. Prior to experiments simultaneous DTA and TG equipment was calibrated and experiments were performed twice for repeatability. X-ray diffraction (XRD) patterns were recorded on a Philips diffractometer, using Ni-filtered CuK_α radiation. Mg, Mn and Fe analyses were performed by atomic absorption spectrophotometer.

Results and discussion

The decomposition of a pure, scarcely disordered crystal by means of pressure or heat will occur very spontaneously. The crystal structure will keep stable until a sufficient amount of energy has been supplied, then will break down at many spots 'simultaneously'. This will be reflected in the DTA curve by a very sharp endothermic peak with relatively large temperature difference. However, if the crystal contains some impurities or crystal physical defects, at these spots of disorder the stability of the structure is decreased. That means that the decomposition of the crystal will begin earlier, starting at these spots of disorder being reflected in the DTA curve at a lower initial temperature and a lower value of ΔT. Compared with the sharp decomposition peak of a pure crystal, the DTA curve of the same mineral that is impure or disordered only shows a broad deflection of lower intensity without a distinct endothermic minimum. The shape of a decomposition peak therefore indicates if substitutions or crystal physical defects are present or absent in a crystal structure. This statement will be possible if there is no coincidence [14].

In this research, based on the XRD results, samples were divided into two groups: regular and iron bearing dolomites. Figures 1a–g show representative DTA-TG curves of the dolomite samples studied. DTA curve of regular dolomite (Fig. 1a) shows large endothermic effects at 790–890°C. In DTA curves of iron bearing dolomites a third endothermic effect before the first decomposition peak of dolomites can be observed, forming a shoulder hardly visible in the curves of low-iron dolomites or a separate peak in the curves of dolomites rich in iron. In the case of dolomites containing remarkable amounts of Fe^{++} and Mn^{++}, both peaks due to

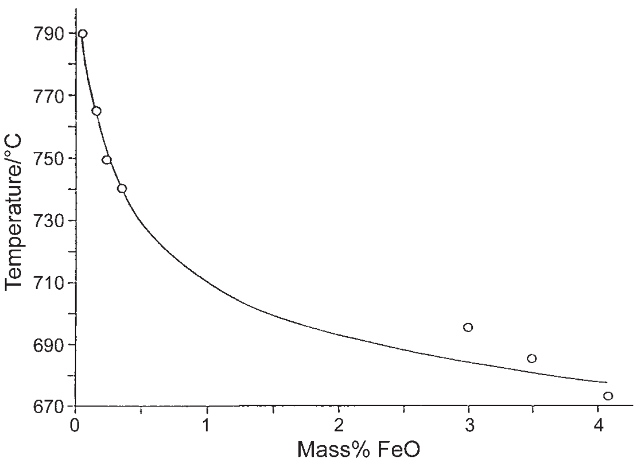

Fig. 1a Diagrams for determining Fe^{++} incorporated in dolomites

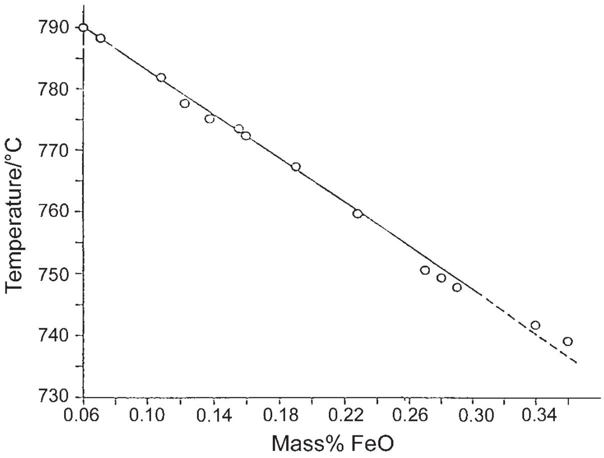

Fig. 1b Diagrams for determining Fe^{++} incorporated in dolomites [14]

the decomposition of the Fe and Mn component disturb each other, but dolomites free of Mn^{++}, which incorporate only the substituent Fe^{++}, can be investigated by DTA in order to determine the Fe content. In the dolomite samples studied (samples b–g), third endothermic effect before the first decomposition peak is observed (Table 1).

Table 1 Decomposition temperatures of the dolomite samples

Sample	Decomp. peak (I)/°C	Decomp. peak (II)/°C	Decomp. peak (III)/°C
Sample-a	–	790	890
Sample-b	730	750	850
Sample-c	705	775	880
Sample-d	725	795	880
Sample-e	730	760	850
Sample-f	740	800	880
Sample-g	640	720	830

In the case of dolomites containing remarkable amounts of Fe^{++} and Mn^{++}, both peaks due to the decomposition of the Fe and Mn component disturb each other, but dolomites free of Mn^{++} which incorporate only the substituent Fe^{++}, can be investigated by DTA in order to determine the Fe content. Figure 2a represents the decomposition temperature (DTA) *vs.* mass% FeO incorporated in the dolomite for determining Fe-contents lying between 0.1 and 0.5 mass% FeO. Fe-contents higher than 0.5 mass% FeO can also be determined (Fig. 2b). Decomposition temperatures and the corresponding mass-% FeO of the samples studied are given in Table 2.

Table 2 Decomposition temperatures and the corresponding mass% FeO (DTA and AAS)

Sample	Decomp. temp./°C	Mass% FeO	
		DTA	AAS
Sample-a	–	–	–
Sample-b	730	0.55	0.858
Sample-c	705	1.20	1.892
Sample-d	725	0.70	1.052
Sample-e	730	0.55	0.858
Sample-f	740	0.40	0.674
Sample-g	640	–	–

In order to correlate the mass% FeO values obtained from DTA curves, experiments were carried out by atomic absorption spectrophotometer and it was observed that the values are close to each other (Table 2).

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