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NEW ASPECTS OF TA APPLICATION FOR STUDIES OF Ca–Mg CARBONATE MINERALS EXEMPLIFIED BY UPPER PERMIAN ROCKS

S. Cebulak[1], *A. Langier-Kuźniarowa*[2*], *G. Czapowski*[2] *and*
G. Bzowska[1]

[1]Silesian University, Będzińska 60, 41-200 Sosnowiec, Poland
[2]Polish Geological Institute, Rakowiecka 4, 00-975 Warsaw, Poland

Abstract

The paper discusses the influence of variable experimental conditions on the thermal decomposition of carbonate minerals. This study was based on Ca–Mg carbonate minerals from Upper Permian dolomite and zuber rocks as well as on calcite and magnesite samples from geological formations of various ages. X-ray diffraction was applied for comparative purposes. Experimental conditions were chosen based on the authors' experience related to studies of both fossil and contemporary organic matters as well as various materials of geological provenience.

Since the main factor in thermal analysis of carbonates is the appropriate choice of experimental conditions for outflow of gaseous reaction products, the thermal analyses were carried out with various sample holders, various sample masses and varied thickness of sample layers in holders, using also a dynamic atmosphere.

The results obtained indicated that different experimental conditions produced extremely different TA data, e.g. the traditional analysis in crucible sample holders with a thick sample layer (great sample mass) showed well expressed double thermal effects of dolomite. For thin sample layer both peaks of thermal decomposition of carbonate components occurred in very close or almost identical temperatures.

The presented results enabled to devise a detailed procedure referring to the choice of experimental conditions and interpretation possibilities as well as to recommend specific TA instruments design and sample holders types.

Keywords: carbonate minerals, thermal analysis

Introduction

The many years' experience of the present authors in application of thermal methods to the studies of organic matter [1, 2] and their natural mixtures of geologic origin revealed the inadequacy of classical procedures of thermal techniques for this purpose. Recent work carried out on the natural mixtures of many minerals of sulphide, chlo-

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[*] Author for correspondence: E-mail: tzych@pgi.waw.pl

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ride, sulphate and carbonate groups allowed to broaden earlier observations. Preliminary results of investigations here presented reveal some aspects of the problem exemplified by TA of Ca–Mg carbonate minerals. They show the great significance of experimental conditions and the need of their very careful choice. Correctly chosen experimental conditions may even enable the differentiation of carbonate samples sometimes not obtainable by X-ray method.

Sampling

A set of 48 samples of carbonate minerals from Polish Upper Permian rock complexes, including single Ca-carbonates (calcites), Mg-carbonates (magnesites) as well as dolomites (Ca–Mg-carbonates) differing in chemical composition was used for the investigation.

The final selection of samples was done from samples showing remarkable differences in the course of thermal curves but no differences in their X-ray characteristics.

Methods

Thermal analysis was carried out by means of thermal analysis apparatus derivatograph developed by Paulik–Paulik–Erdey (modified). Five different manners of sample arrangement in the sample holders were used in order to obtain different conditions of CO_2 removal from carbonate particles. The following versions of experimental conditions were applied:

1. the Pt-crucible 18 mm in diameter and 20 mm in height, loosely filled up with a 2000 mg sample,
2. the Pt-crucible 13 mm in diameter and 16 mm in height, loosely filled up with a 400 mg sample,
3. the multiplate holder of 10 Pt-plates, 19 mm in diameter, loosely filled up with a 2000 mg sample,
4. the multiplate holder as above, but filled up with a 1000 mg sample,
5. the multiplate holder as above, but filled up with a 400 mg sample,
6. the multiplate holder of 2 plates, 14 mm in diameter, loosely filled up with 20 mg sample.

The samples were ground by hand during 20 min to obtain very fine granulation for free removal of CO_2. The dynamic atmosphere with suction about 2 L min^{-1} was used.

Discussion

The presented thermal results of carbonate minerals indicate that TA methods used so far take no account of one very important factor – the arrangement of sample in the apparatus. Figures 1 and 2 show that thermal analyses conducted under a totally free escape of gaseous decomposition products are much more effective for carbonate minerals dissociation.

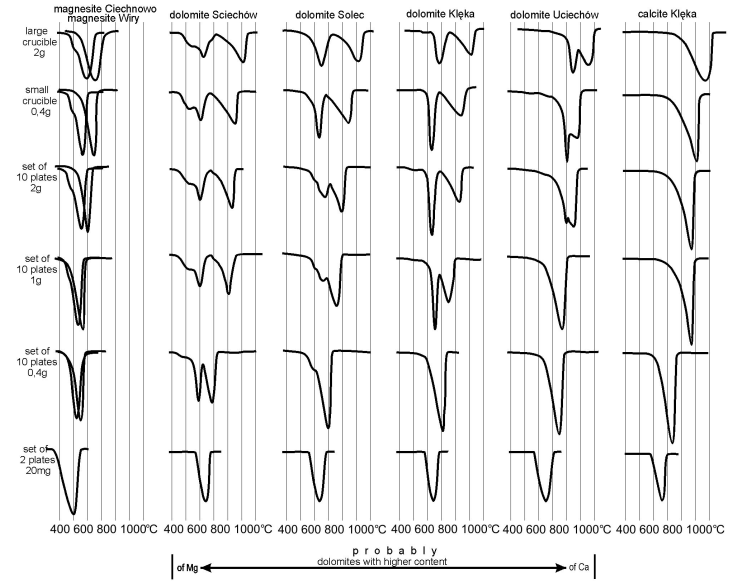

Fig. 1 The effect of different manners of sample arrangement on the course of thermal decomposition exemplified by some of Ca–Mg carbonate minerals

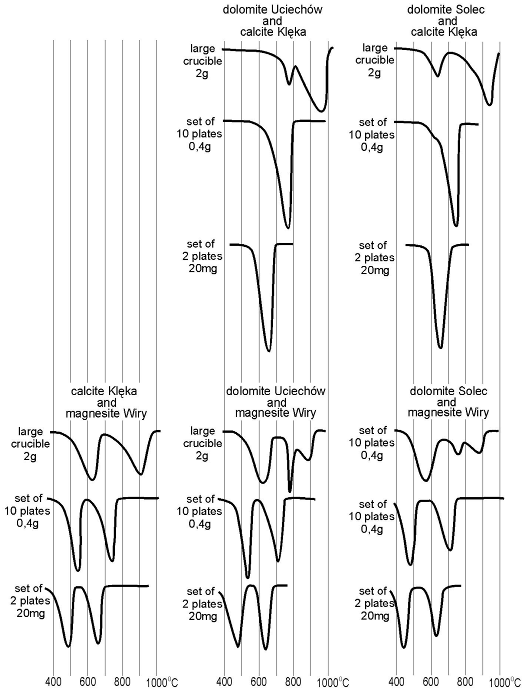

Fig. 2 The effect of different manners of sample arrangement on the course of thermal decomposition exemplified by some mixtures of Ca–Mg carbonate minerals

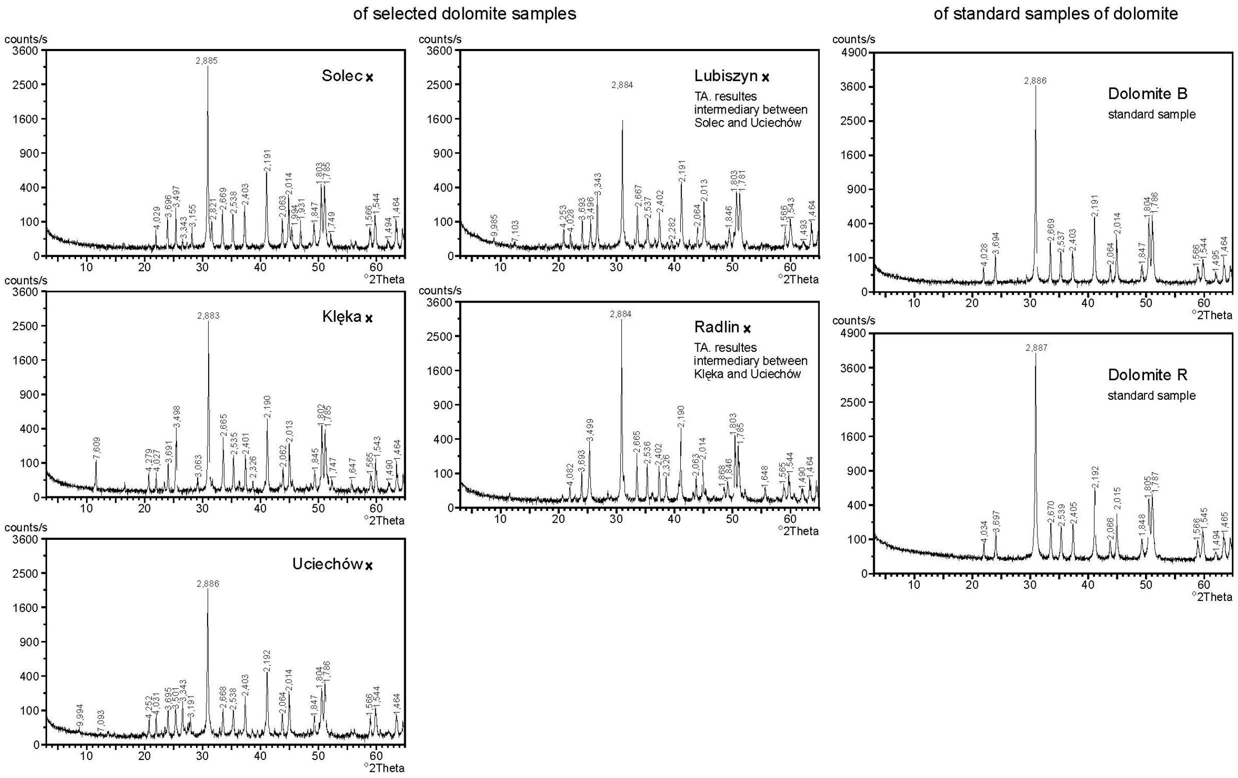

Fig. 3 X-ray patterns of Ca-Mg carbonate. *x* in all samples small content of clay minerals or other silicate minerals

They also show clearly the differentiation of the courses of this reaction dependent on the arrangement of the sample in the TA apparatus.

The effect of CO_2 pressure in the furnace atmosphere as well as of some other factors on the shape of carbonate thermal curves has been known for over 50 years [e.g. 3–16]. The observations dealing with the remarkable differentiation of the course of thermal decomposition of carbonate minerals have been mentioned in many papers, monographs and handbooks dealing with TA [e.g. 17, 18]. Its reason was defined correctly with indication of the need of applying the experimental conditions required by Clausius–Clapeyron equation. But it has not been considered either in the thermal procedures or in the constructional designs (with the exception of Paulik, Paulik and Erdey equipment) of equipment of DTA, TG, simultaneous methods or DSC. Noteworthy is that this problem concerns not only carbonates, but all materials releasing gaseous products in the reaction processes [1, 2]. Interesting, that usually thermoanalysts as well TA devices constructors have neglected these factors influencing the correct performing thermal analyses process (Clausius–Clapeyron equation, the Le Châtelier–Braun principle and others), besides using only very small amounts of sample and developing DSC method because of the lack of repeatability of traditional thermal analysis results.

The presented thermal curves (Fig. 1) illustrate the effect of carbonate samples arrangement on the course of thermal decomposition, with calcites, magnesites, dolomites and their mixtures used as examples (Fig. 2). The selection of an appropriate thermal environment can thus provide essential information. The presented thermal curves show that the lack of repeatability of TA results has been appearing from a very different arrangement of the sample and neglecting enough careful choice of experimental conditions required by thermal decomposition thermodynamic principles. Nevertheless, it should be emphasized that a free release of volatile products is controlled also by other factors, for example grain size, dynamic atmosphere in the furnace and heating rate.

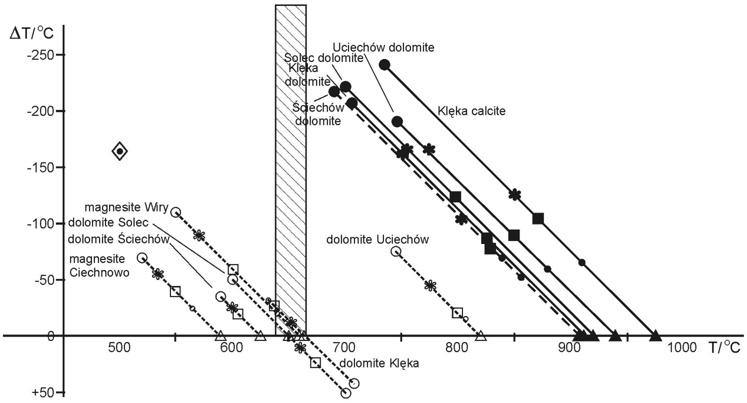

Fig. 4 The diagram of the temperatures variability of maximum CO_2 release due to thermal decomposition of different Ca–Mg carbonate minerals dependent on different manner of sample arrangement

The results here presented show clearly expressed regularities. The Ca–Mg carbonates thermal analysis carried out according to thermodynamic requirements is an effective method for the determination of their composition. The recognition of the influence of varying factors of analysis process on the results is the essential one for the verification of our method of carbonate minerals identification. The adequate choice of experimental conditions for decomposition reactions is the fundamental factor for correct leading of TA investigations.

Probably the greatest role for the elaboration of a correct TA procedure will play a good recognition of the influence of the different conditions also on thermal dissociation of CO_2, i.e. gaseous product of carbonates decomposition [e.g. 19]. It seems that the principle of Le Châtelier–Braun very well explains the extremely differentiated TA curves of the decomposition reactions under extremely different experimental conditions as well as the appearance of different (twofold) decomposition reactions of Ca–Mg carbonates analysed on thick and thin layer, i.e. with difficult CO_2 removal on thick layer and of one joint decomposition with CO_2 dissociation to CO and 1/2 O_2 under its free removal. The CO_2 presence (not the products of its dissociation – CO and 1/2 O_2) better explains the tendency for calcite formation in a thick layer and its lack in thin layers. The considerations presented may serve as the basis for further improvement of TA experimental conditions. Nevertheless our opinion is that the solving of this problem needs further investigations for a final elaboration of TA procedures as well as requirements for TA instruments designers.

The comparison of thermal (Figs 1 and 2) and X-ray results (Fig. 3) shows that, under a free release of volatile products, TA can be a useful source of information enabling to differentiate samples with respect to features non-detectable by X-ray method. In the case of some dolomites the detailed interpretation of temperature differentiation of the thermal maxima (Fig. 4) can imply different bonding energies in the carbonate structures as well as crystallochemical differences. Probably the difference of CO_3^{2-} arrangement in calcite structure due to Ca^{2-} replacement by Mg^{2-} is not revealed in X-ray results.

Final conclusions resulting from our experiments:

1. The need to introduce methodological modifications in TA both for carbonates and other materials releasing volatile products during thermal reactions and apply these modifications in the construction of thermal equipment (e.g. sample holders).
2. Possibility to expand TA application in studies of composition and structure of carbonates and other materials releasing volatile products during the thermal reactions processes by a careful choice of experimental conditions.

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