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*Dedicated to Professor Ferenc Paulik on the occasion of his 75th birthday*

# PHASE TRANSFORMATIONS IN MIXTURES OF CALCITE AND DOLOMITE WITH CONDENSED PHOSPHATES OF CALCIUM DURING HEATING

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## Abstract

The thermal interactions of dolomite and calcite with calcium polyphosphates up to 1000°C were studied by thermal (dynamic heating and isobaric conditions) and X-ray diffraction methods. It was found that in mixtures with Ca–polyphosphates less than half of the carbonates reacted before decomposition to oxides with the phosphates. The rates of the reactions of phosphates with MgO were much lower than those with CaO. The scheme of the main crystalline phase transformations was constructed.

**Keywords:** calcite, calcium polyphosphates, dolomite, phase transformation, TG, X-ray

## Introduction

Calcite (CA) and dolomite (DO) are minerals widely used as sources of calcium and magnesium in synthesis or for the processing of various thermophosphates [1–3]. From technological and theoretical points of view, it is important to know how the interactions with phosphates take place. This paper presents the main results of an investigation of reactions between carbonates and $Ca_2P_2O_7$ as the first member, and $[Ca(PO_3)_2]_n$ as the last member of the Ca–polyphosphate series. The temperatures and rates of the thermal decompositions of CA and DO are well known to depend strongly on the partial pressure of $CO_2$ [4]. Therefore, the performance of many experiments under the same conditions is complicated. In this context, Paulik devised several original thermoanalytical procedures [4] which formed a strong basis for other investigations in this field. In the current work, the key to obtaining scientifically valuable results was the usage of a labyrinth crucible and a reference thermocouple not placed on the balances.

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## Experimental

All experiments were carried out with a derivatograph (Hungarian Optical Works, Budapest) and a labyrinth crucible under dynamic conditions. Heated samples were investigated by quantitative X-ray phase analysis, using a DRON-3M diffractometer ('Burevestnik', Russia). Quartz or $AlF_3$ was used as internal standard. Dolomite (DO) (98.2% $CaMg(CO_3)_2$) from the Kaarma deposit (Estonia) and calcite (CA) (98.6% $CaCO_3$) from the Carrara deposit (Italy) were used as source materials. $Ca_2P_2O_7$ was prepared from $CaHPO_4 \cdot 2H_2O$, and $[Ca(PO_3)_2]_n$ from $Ca(H_2PO_4)_2 \cdot H_2O$. Samples of powdered mixtures (particle size less than 5 μ) of DO:$[Ca(PO_3)_2]_n$=1:1 (molar ratio), CA:$[Ca(PO_3)_2]_n$=2:1, DO:$Ca_2P_2O_7$=1:2 and CA:$Ca_2P_2O_7$=1:1 were heated at a rate of 10 deg $min^{-1}$. The number of moles of $CO_2$ was calculated to be equal in all samples heated. All experiments were

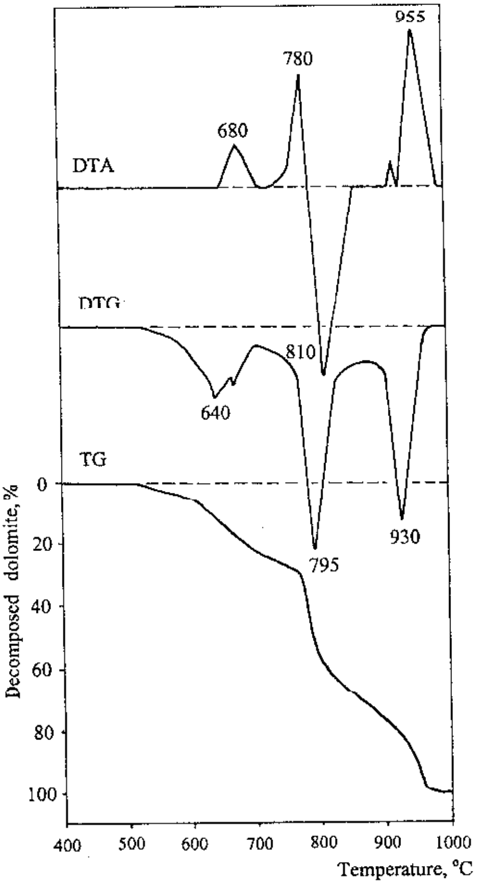

**Fig. 1** Thermal curves of 1:1 mixture of DO and $[Ca(PO_3)_2]_n$

performed under the same conditions and the results were comparable with each other.

Investigations were started by examining all mixtures with simultaneous TG, DTG and DTA up to 1000°C. For elimination of endothermic peaks of decomposition of DO and CA from the DTA curve, the same mass of DO or CA as in the sample diluted with the inert material as reference material was used. From the TG, DTG and DTA curves, characteristic points for the following experiments, in which samples of mixtures were heated to a certain temperature or mass loss, were determined. After the termination of heating, samples were cooled at 20–30°C $\min^{-1}$. In the products, the phase composition was determined by X-ray analysis.

## Results and discussion

The TG curve for the mixture DO:$[Ca(PO_3)_2]_n=1:1$ (Fig. 1) reveals that $CO_2$ was liberated in 5 steps (510–610, 610–770, 770–800, 800–920 and 920–970°C),

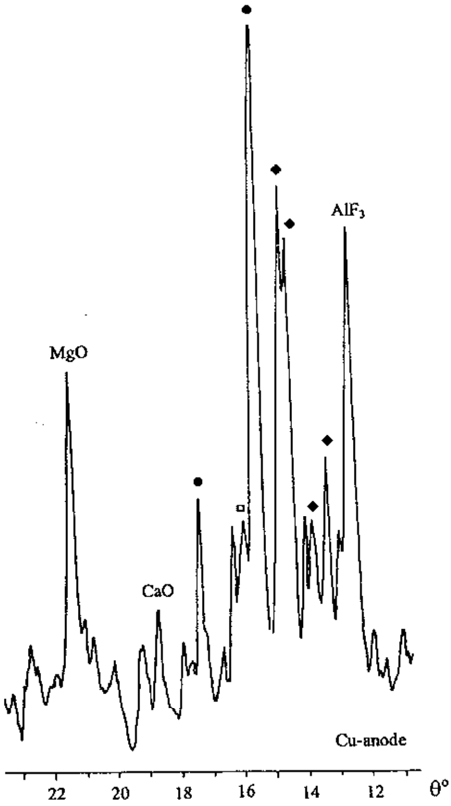

**Fig. 2** X-ray diffraction pattern of mixture of DO and $[Ca(PO_3)_2]_n$, heated up to 1000°C, with addition of $AlF_3$(20%); ● – $(Ca,Mg)_3(PO_4)_2$, ◆ – $(Ca,Mg)_2P_2O_7$, □ – $(Ca,Mg)_4P_2O_9$

with an exo- or endothermic peak for each step. It can be proposed that reactions between DO and Ca–phosphates take place from 510°C.

For the X-ray analysis, the mixture was heated up to the liberation of 21 (sample No. 1), 30 (No. 2), 62 (No. 3) or 79% (No. 4) of the total $CO_2$, or to a temperature of 1000°C (No. 5). In the X-ray diffraction patterns of samples No. 1 and 2, the peaks of MgO and CaO were missing. This shows that reactions between phosphates and DO or oxides have taken place. Samples No. 3 and 4 contained very small amounts of CaO and much more MgO. In sample No. 5, the content of MgO was 8.4% and that of CaO was 3.1% (Fig. 2). This means that 84% of the total CaO and 38% of the MgO reacted with phosphates. In addition to CaO and MgO, $(Ca,Mg)_3(PO_4)_2$, $(Ca,Mg)_2P_2O_7$ and $(Ca,Mg)_4P_2O_9$ were present in the sample [5, 6].

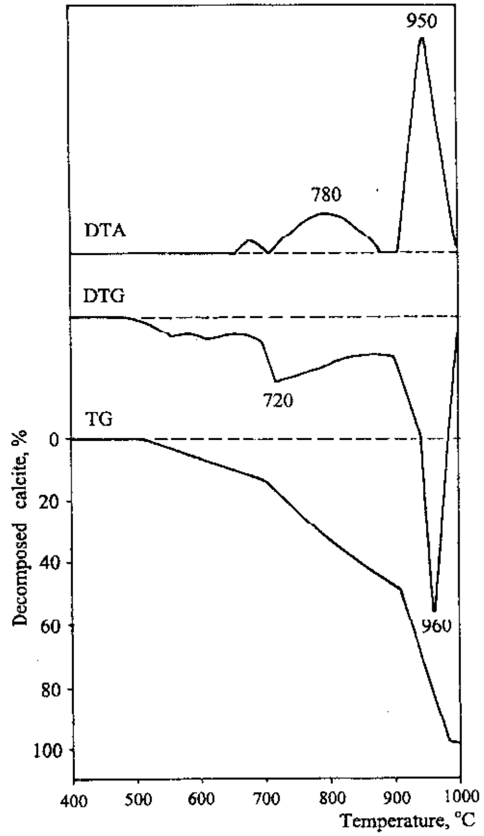

**Fig. 3** Thermal curves of 2:1 mixture of CA and $[Ca(PO_3)_2]_n$

From the mixture CA:$[Ca(PO_3)_2]_n$=2:1, $CO_2$ was liberated in 3 steps (500–700, 700–905 and 905–990°C) (Fig. 3), an exothermic peak being associ-

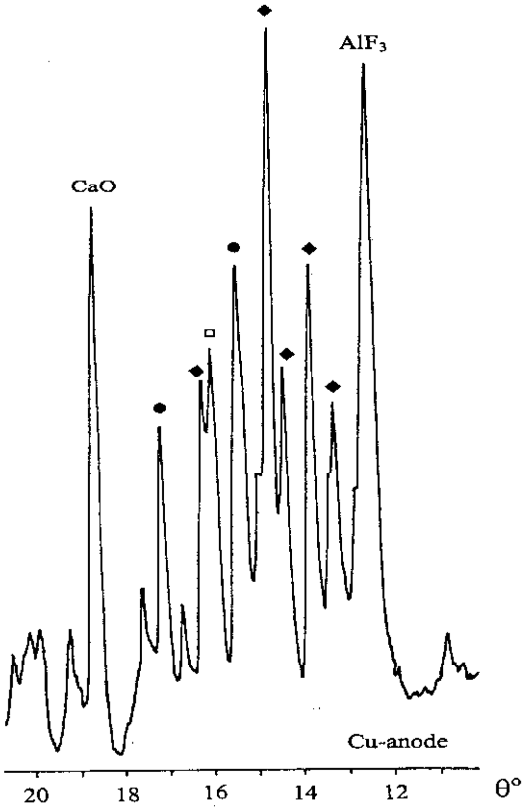

**Fig. 4** X-ray diffraction pattern of mixture of CA and $[Ca(PO_3)_2]_n$, heated up to 1000°C, with addition of $AlF_3$ (20%); ● – $Ca_3(PO_4)_2$, ◆ – β-$Ca_2P_2O_7$, □ – $Ca_4P_2O_9$

ated with each step. For X-ray analysis, the mixture was heated up to evolving 12 (sample No. 6) or 50% (No. 7) of the total $CO_2$, or to a temperature of 1000°C (No. 8). In the X-ray diffraction pattern of sample No. 6, the peak of CaO was missing, and in the pattern of sample No. 7, the corresponding peak was low. Sample No. 8 (Fig. 4) contained 11.9% CaO. This means that 67% of the total CaO had reacted with phosphates. In the last sample, β-$Ca_3(PO_4)_2$, β-$Ca_2P_2O_7$ and $Ca_4P_2O_9$ were identified.

On the basis of the results of the investigations of the mixtures DO–$[Ca(PO_3)_2]_n$ and CA–$[Ca(PO_3)_2]_n$ it may be stated that the carbonates partly reacted directly with the phosphates, while they were partly decomposed, and the phosphates reacted with MgO and CaO.

Mixtures of DO–$Ca_2P_2O_7$ and CA–$Ca_2P_2O_7$ were investigated by the same procedures, and the results were similar to those for mixtures with $[Ca(PO_3)_2]_n$.

## Conclusions

It was found that at a heating rate of 10°C $\mathrm{min}^{-1}$, 52% of calcite and 30% of dolomite reacted with Ca–polyphosphate, while 20% of calcite reacted with Ca–diphosphate. Nonreacted carbonates decomposed to oxides and those reacted with phosphates. As the decomposition rates of the carbonates exceeded the reaction rates of the oxides, the heating products after complete decomposition of dolomite and calcite contained oxides. In conclusion, the interactions between the condensed phosphates and Ca–Mg–carbonates could be described by the following scheme:

$$\begin{array}{ll} \mathrm{CaCO_3} & \searrow \\ \quad \Downarrow 48\% & +[\mathrm{Ca(PO_3)_2}]_n \rightarrow \mathrm{Ca_2P_2O_7} \rightarrow \mathrm{Ca_4P_2O_9} \rightarrow \mathrm{Ca_3(PO_4)_2} \\ \mathrm{CaO} & \nearrow \end{array}$$

$$\begin{array}{ll} \mathrm{CaMg(CO_3)_2} & \searrow \\ \quad \Downarrow 70\% & +[\mathrm{Ca(PO_3)_2}]_n \rightarrow \mathrm{(Ca,Mg)_2P_2O_7} \rightarrow \mathrm{(Ca,Mg)_4P_2O_9} \rightarrow \\ \mathrm{MgO + CaO} & \nearrow \qquad\qquad\qquad\qquad\qquad \rightarrow \mathrm{(Ca,Mg)_3(PO_4)_2} \end{array}$$

$$\begin{array}{ll} \mathrm{CaCO_3} & \searrow \\ \quad \Downarrow 80\% & +\mathrm{Ca_2P_2O_7} \rightarrow \mathrm{Ca_4P_2O_9} \rightarrow \mathrm{Ca_3(PO_4)_2} \\ \mathrm{CaO} & \nearrow \end{array}$$

$$\begin{array}{ll} \mathrm{CaMg(CO_3)_2} & \searrow \\ \quad \Downarrow 100\% & +\mathrm{Ca_2P_2O_7} \rightarrow \mathrm{(Ca,Mg)_4P_2O_9} \rightarrow \mathrm{(Ca,Mg)_3(PO_4)_2} \\ \mathrm{MgO + CaO} & \nearrow \end{array}$$

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