THERMAL DECOMPOSITION OF RHOMBOHEDRAL DOUBLE CARBONATES OF DOLOMITE TYPE

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DTA and TG studies in air were carried out for hydrothermally prepared rhombohedral double carbonates of dolomite type, $CaMg(CO_3)_2$, $CaMn(CO_3)_2$, $CdMg(CO_3)_2$, $CdMn(CO_3)_2$ and $CdZn(CO_3)_2$. The solid decomposition products in air have been compared to those obtained under hydrothermal conditions with CO_2 pressure. The dolomite [$CaMg(CO_3)_2$] decomposes in two stages both in air as well as under high CO_2 pressure. The other carbonates studied, follow a single stage decomposition in air and a two stage decomposition under hydrothermal condition. In air, the manganese containing carbonates $CaMn(CO_3)_2$ and $CdMn(CO_3)_2$, decompose to form mixed oxides of $CaMnO_3$ and $CdMnO_3$ respectively, while $CdMg(CO_3)_2$ and $CdZn(CO_3)_2$ decompose to their respective two mono oxides.

## Introduction

Thermal decomposition of dolomite, $CaMg(CO_3)_2$ is apparently straight forward but, has still been studied by several workers because of considerable contraversy with respect to the decomposition mechanism of dolomite in air as well as CO_2 atmosphere [1−4]. The studies were reviewed in detail by Otsuka [5] and again re-studied by Engler *et al.* [6]. The latter used non-isothermal insitu XRD analysis of dolomite decomposition both in air and CO_2. They proposed a single stage decomposition for dolomite in air indicated by a single asymmetric peak on the DTA curve. But even in this single stage of decomposition, they found the reaction in the initial stage to be:

$$2CaMg(CO_3)_2 \rightarrow CaCO_3 + CaO + 2MgO + 3CO_2$$
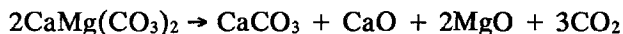
The $CaCO_3$ which crystallised along with CaO + MgO in early stages began to decompose at slightly higher temperature during the late stage of

the single decomposition peak. In CO_2 atmosphere, two stage decomposition was clear with two endothermic peaks pertaining to reactions:

1st stage $CaMg(CO_3)_2 \rightarrow CaCO_3 + MgO + CO_2$,

2nd stage $CaCO_3 \rightarrow CaO + CO_2$
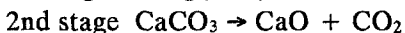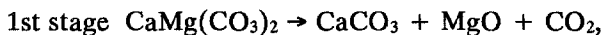
respectively.

We know that there are a few more rhombohedral double carbonates which are comparable to dolomite. The natural ones are Kutnahorite $(CaMn(CO_3)_2)$ and Minrecordite $(CaZn(CO_3)_2)$. The synthetic analogues are $CdMg(CO_3)_2$, $CdMn(CO_3)_2$, and $CdZn(CO_3)_2$. Although other combinations of Ca, Cd with transition metals Fe, Ni, Cu, Co are considered theoretical possible, could not hitherto been synthesized. The authors have been studying the hydrothermal decomposition of rhombohedral double carbonates on a P-T plane under P_{CO_2} of upto 3 Kbar in order to determine the equilibrium decomposition curve for these carbonates and use them for retrieval of the thermodynamic data for the double carbonates. The double carbonates so obtained in the hydrothermal studies were used for the decomposition studies in air. In this paper we intend to report the DTA and TG studies in air on the five synthetically prepared dolomite and dolomite type carbonates and compare their decomposition characteristics to those obtained under high CO_2 pressure.

Experimental

Five synthetic rhombohedral double carbonates namely $CaMg(CO_3)_2$ (dolomite), $CaMn(CO_3)_2$ (Kutnahorite), $CdMg(CO_3)_2$, $CdMn(CO_3)_2$, $CdZn(CO_3)_2$ have been used for the decomposition studies. The Minrecordite $CaZn(CO_3)_2$, could not be synthesized. While the complete phase diagrams for these double carbonates on P_{CO_2} $-T$ plane will be published elsewhere, we give here the pressures and temperatures of syntheses of these carbonates (Table 1). All syntheses have been done in cold seal Tuttle reactors. The starting material were the two carbonates (for instance, $CaCO_3 + MgCO_3$ in 1:1 mole ratios for dolomite synthesis) charged in crimped platinum capsules and placed in these reactors. The pressurising gas was dry CO_2, pumped into the vessels which were externally heated.

The ratio of Ca and Cd and the other combining cations have been determined by measuring the d_{104} spacing which shows a linear correlation [7] for solid solutions in rhombohedral carbonates. The products which were confirmed by X-ray powder diffraction as double carbonate were used for DTA.

Table 1 Experimental conditions for synthesis of rhombohedral double carbonates under CO_2 pressure

Double carbonates M'M''$(CO_3)_2$	$T/$ °C	Pres./ bars	Duration/ h	$d_{(104)}$ of the product
CaMg$(CO_3)_2$	650	1000	77	2.875
CaMn$(CO_3)_2$	700	1240	68	2.940
CdMg$(CO_3)_2$	650	1500	68	2.855
CdMn$(CO_3)_2$	550	1100	72	2.892
CdZn$(CO_3)_2$	400	2000	68	2.848

The simultaneous DTA and TG unit Netzsch Geratebau STA 409 (Pt 10 Rh-Pt thermocouple and alumina sample holders) was used. The heating rate was 10 deg/min and the temperature limit was 1000°C.

In each sample after a first run of DTA over the entire temperature range, it was repeated again with a fresh sample in order to arrest the reaction at different stages and identify the products at different stages of heating.

Results and discussion

Table 2 gives the details of DTA and TG runs for the five rhombohedral double carbonates. The corresponding DTA-TG traces are given in Fig. 1. An examination of these peaks show both single stage and two stage decomposition, though all the runs were done in air. The decomposition stages and the products were also not the same in all these carbonates. Earlier workers [6] while studying the natural dolomite sample with composition $Ca_{1.0}$, $Mg_{0.9}$ $Fe_{0.1}(CO_3)_2$ reported that the two stage decomposition existed only in the presence of CO_2 atmosphere which otherwise was a single stage decomposition. But in our synthetic samples with ordered dolomite structure, the two stages are distinct. The first stage $CaCO_3$(ss) forms alongwith MgO evolving CO_2. A substitution of upto 10% of Mg was noticed in $CaCO_3$. The second stage of decomposition involved the dissociation of $CaCO_3$ to CaO and CO_2. In all the rest of the double carbonates studied in air we found a single stage decomposition irrespective of the product, except in the case of CdMn$(CO_3)_2$, where a minor second endothermic peak occurs but with negligible weight loss. Both CdMg$(CO_3)_2$, and CdZn$(CO_3)_2$, directly decompose to their two monoxides, but the Mn containing carbonates CaMn$(CO_3)_2$, and CdMn$(CO_3)_2$, result in $CaMnO_3$ and $CdMnO_3$ as the final products of
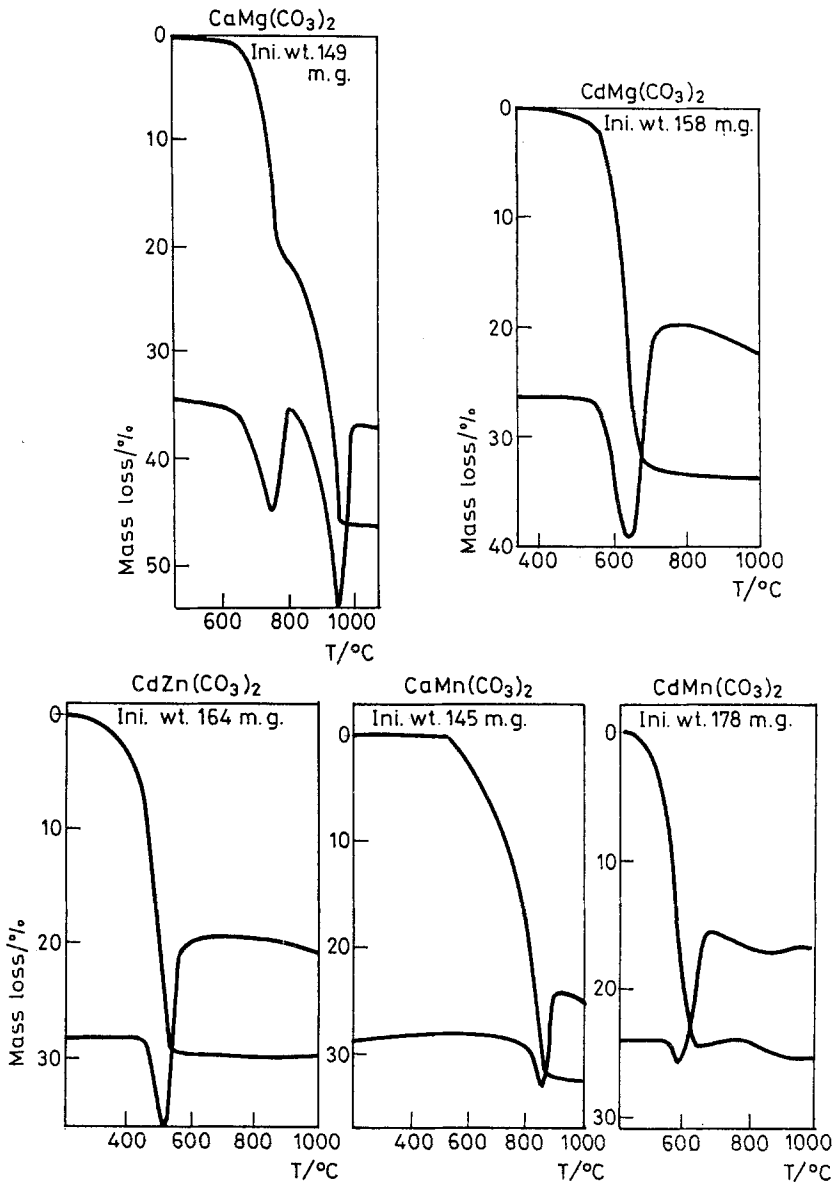
Fig. 1 DTA and TG curves for the five rhombohedral double carbonates in air. Note the two stage decomposition in CaMg(CO3)2

decomposition. While in Kutnahorite the CaMnO3 phase was directly formed as a result of the single decomposition reaction, in the CdMn(CO3)2 the formation of CdMnO3 was through an intermediate stage where CdO +

Table 2 Peak temperature of decomposition reactions in the rhombohedral double carbonates $M'M''(CO_3)_2$ from the DTA in air and the associated weight loss at different stages due to decomposition (rate of heating 10 deg/min)

Double carbonate $M'M''(CO_3)_2$	Peak I Temp./°C	Peak I loss wt.%	Peak II Temp./°C	Peak II loss wt.%	Total weight loss/%	Theoretical weight loss/%	Decomposition reaction
$CaMg(CO_3)_2$	735	20.8	942	25.5	46.3	47.7	$CaMg(CO_3)_2 \rightarrow CaCO_3(SS)+MgO+CO_2$ $\rightarrow CaO+MgO+2CO_2$
$CaMn(CO_3)_2$	862	33	–	–	33	38.1	$CaMn(CO_3)_2+O_2 \rightarrow CaMnO_3+2CO_2$
$CdMg(CO_3)_2$	630	32.3	–	–	32.3	34.2	$CdMg(CO_3)_2 \rightarrow CdO+MgO+2CO_2$
$CdMn(CO_3)_2$	595	24.1	837	1.6	25.7	29.01	$3CdMn(CO_3)_2+O_2 \rightarrow CdO+Cd_2Mn_3O_8+6CO_2$ $\rightarrow 3CdMnO_3+6CO_2$
$CdZn(CO_3)_2$	520	29.3	–	–	29.3	29.5	$CdZn(CO_3)_2 \rightarrow CdO+ZnO+2CO_2$

$Cd_2Mn_3O_8$ crystallized, which on further heating react to form $CdMnO_3$ at higher temperature. A small second endothermic peak with minor weight loss (1.6%) observed in the $CdMn(CO_3)_2$ decomposition may be due to some non detectable phase remaining but has to be ignored since this could not be reproduced. The theoretical weight loss along with the observed weight loss from TG curves is also given in Table 2. The weight losses agree well except in the Mn containing carbonates, where some complexity exists in the mechanism of decomposition. The formation of CaMnO phase by decomposition of $(CaMn)CO_3$ under vacuum was reported earlier [8], wherein the entire range of solid solution phases of CaO-MnO were prepared. In order to compare the decomposition in air with those under CO_2 pressure, selected experimental run products at 1 Kbar CO_2 pressure are given in Table 3 along with the temperature of decomposition of double carbonates.

Table 3 Equilibrium decomposition temperatures and pressures of rhombohedral double carbonates under CO_2 pressure of 1000 bars

Double carbonates	Pressure of CO_2/ bars	Temp. of decomposition/ ^{6}C	Solid decomposition product (1st stage decomposition)
$CaMg(CO_3)_2$	1000	825	$CaCO_3(ss) + MgO$
$CaMn(CO_3)_2$	1000	730	$CaCO_3 + MnO$
$CdMg(CO_3)_2$	1000	715	$MgCO_3 + CdO$
$CdMn(CO_3)_2$	1000	600	$MnCO_3 + CdO$
$CdZn(CO_3)_2$	1000	420	$CdCO_3 + ZnO$

Note: The products shown in the last column are only the decomposition product, though at equilibrium, the reactant (double carbonate) is also present

It is interesting to note that the single stage decomposition of dolomite in air reported by earlier workers [6], was not observed with synthetic ordered dolomite presently studied. The decomposition product has been identical in both air and CO_2 for dolomite. But for other rhombohedral carbonates, the presence of CO_2 made a significant difference. The low oxygen fugacity intrinsically generated in steel reactors retained manganese in divalent state and hence the formation of $CaMnO_3$ and $CdMnO_3$ as products noticed when their corresponding carbonates decompose in air was not noticed under CO_2 pressures. Though the higher stages of decomposition in the carbonates under CO_2 pressure were not investigated because of limitations of instrument tolerance for high temperature, it is quite clear that the distinct stages will appear at different temperatures until all carbonate components decompose to their respective oxides. Thus under CO_2 pressure, a single stage

decomposition is absent for all dolomite type double carbonates. Secondly mixed oxides such as $CaMnO_3$ and $CdMnO_3$ do not form when the decomposition is under CO_2 pressure. Finally the decomposition of dolomite is in two stages, even in air, unlike the previous report.

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Zusammenfassung — An den hydrothermisch präparierten rhomboedrischen Doppelcarbonaten vom Dolomittyp $CaMg(CO_3)_2$, $CaMn(CO_3)_2$, $CdMg(CO_3)_2$, $CdMn(CO_3)_2$ und $CdZn(CO_3)_2$ wurden in Luft DTA- und TG-Untersuchungen durchgeführt. Die in Luft erhaltenen festen Zersetzungsprodukte wurden mit denjenigen verglichen, die man unter hydrothermischen Bedingungen unter CO_2-Druck erhalten hatte. Dolomit [$CaMg(CO_3)_2$] zersetzt sich sowohl in Luft als auch unter CO_2-Druck in zwei Schritten. Die anderen untersuchten Carbonate folgen in Luft einer einstufigen Zersetzung, unter hydrothermischen Bedingungen einer zweistufigen. In Luft zersetzen sich die manganhaltigen Carbonate $CaMn(CO_3)_2$ und $CdMn(CO_3)_2$ unter Bildung der Mischoxide $CaMnO_3$ bzw. $CdMnO_3$, während $CdMg(CO_3)_2$ und $CdZn(CO_3)_2$ bei der Zersetzung die beiden entsprechenden Monoxide bilden.