*Thermochimica Acta*, 121 (1987) 479–485
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

# NOTE ON THE THERMAL DECOMPOSITION OF DOLOMITE *

H.-G. WIEDEMANN

*Mettler Instrumente AG, 8606 Greifensee (Switzerland)*

G. BAYER

*Institut für Kristallographie und Petrographie, ETH-Zürich, 8092 Zürich (Switzerland)*

(Received 4 November 1986)

Like calcite the thermal decomposition of dolomite has been studied extensively by various thermoanalytical methods [1–6]. Whereas the decomposition of calcite is a one-step reaction giving the solid and gaseous reaction products CaO and $CO_2$, the reaction is more complex for dolomite, $CaMg(CO_3)_2$. Although dolomite is recognized as an independent mineral species rather than a mixture of $CaCO_3$ and $MgCO_3$, the thermal decomposition curves show two endothermic peaks in the DSC, or two weight steps in TG. It has been argued that the first peak, which begins at ~ 600–650 ° C, corresponds to a decomposition of dolomite to MgO and $CaCO_3$, whereas the second peak, starting at ~ 700 ° C, is due to the decomposition of $CaCO_3$ [7]. This is obviously true when the experiments are carried out in air, whereby these two peaks (or two steps) show considerable overlapping and are difficult to resolve. Comparison of these DSC curves with those of magnesite and calcite proves that the first endothermic peak for dolomite occurs at a much higher temperature than the magnesite decomposition.

More systematic studies of the thermal decomposition of dolomite in different atmospheres definitely proved that the type of solid decomposition products depends on the partial pressure of $CO_2$ in the atmosphere [8]. In DTG runs carried out at < 50 Torr the reaction is $CaMg(CO_3)_2 \rightarrow CaO + MgO + 2CO_2$, whereas at $CO_2$ pressures greater than 50 Torr, the decomposition occurs in two steps, with the first step: $CaMg(CO_3)_2 \rightarrow CaCO_3 + MgO + CO_2$. The $CaCO_3$ formed in this reaction is then decomposed at even higher temperatures to CaO. Both the MgO and CaO formed during these decompositions are poorly crystallized and highly reactive. Therefore, one may assume that in a $CO_2$-free atmosphere, dolomite decomposes in one step to the mixture of the oxides.

---

* Dedicated to Professor W.W. Wendlandt on the occasion of his 60th birthday.

0040-6031/87/$03.50

Whenever $CO_2$ is present in small amounts in the atmosphere or generated as the decomposition of dolomite begins, the highly reactive CaO becomes recarbonated to $CaCO_3$. All this depends not only on the $CO_2$ partial pressure, but also on the amount and shape of the sample, on the crucible form and on the heating rate. In our experiments we found that with a heating rate of 0.5 °C $min^{-1}$ and a sample weight of ~ 10 mg, the recarbonation does not take place when the partial pressure of $CO_2$ is less than 3 Torr [9]. The results of these investigations will be described and briefly discussed below. These results add to the understanding of the decomposition behavior of dolomite and clarify some of the questions which still exist.

## EXPERIMENTAL

### *Instruments*

The TG and DTG curves were recorded with Mettler Thermoanalyzer TA1 in atmospheres with $CO_2$ partial pressures from 10 to 700 Torr and with the Mettler Thermosystem TA 3000/TG 50 in air and in nitrogen. The heating rates were 0.5, 6 and 10 °C $min^{-1}$, respectively. The starting and decomposition products were analyzed by X-ray powder techniques (Guinier de-Wolff camera with $CuK_\alpha$ radiation). The SEM pictures were taken with a Cambridge electron microscope.

### *Materials*

The minerals used in these experiments were magnesite from Radenthein, Austria, calcite from Gonzen, Switzerland and coarse crystalline "sugar-dolomite" from Binntal, Switzerland. All these materials were ground to fine powders of $< 20$ $\mu$m in a sapphire mortar.

## RESULTS AND DISCUSSION

Typical DTG curves of the dolomite decomposition in atmospheres with different $CO_2$ partial pressures are shown in Fig. 1. The DTG single peak which was recorded for the decomposition of dolomite in high vacuum ($< 10^{-5}$ Torr) at about 450 °C is not shown in this figure. However, this one-step decomposition of dolomite leads directly to the mixture MgO + CaO and can be seen clearly in a heating X-ray photograph of dolomite (Fig. 2) which was also taken in high vacuum ($< 10^{-5}$ Torr). This photograph proves the poor crystallinity of MgO and CaO and their subsequent recrystallization with increasing temperatures.

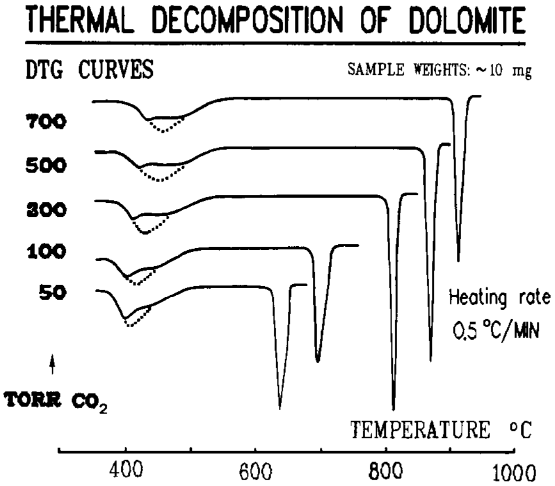

Fig. 1. DTG curves of the thermal decomposition of dolomite in atmospheres with different $CO_2$ partial pressure.

The poorly crystallized CaO, which is formed during thermal decomposition of dolomite either in high vacuum or in an inert atmosphere ($N_2$), reacts immediately with any trace of $CO_2$ present in the atmosphere. However, the small amount of $CaCO_3$ which is formed in such a reaction is not observable in heating X-ray photographs. The quantitative recarbonation of CaO to $CaCO_3$ can be shown by increasing the $CO_2$ pressure. This may be seen in Fig. 3 where dolomite was decomposed first in dynamic, pure $N_2$ atmosphere to the mixture MgO/CaO. At 760 °C the nitrogen atmosphere was

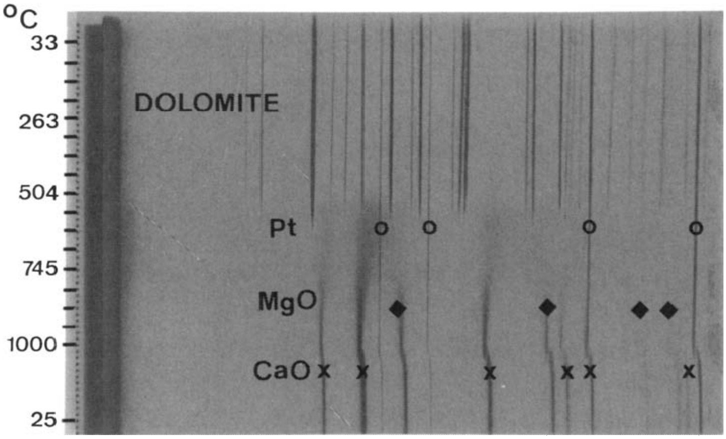

Fig. 2. Heating X-ray photograph of dolomite in high vacuum (1–$10^{-5}$ Torr), heating rate 1 °C $min^{-1}$. Diffraction lines are indicated by the following symbols: (○) Pt, (◆) MgO and (×) CaO.

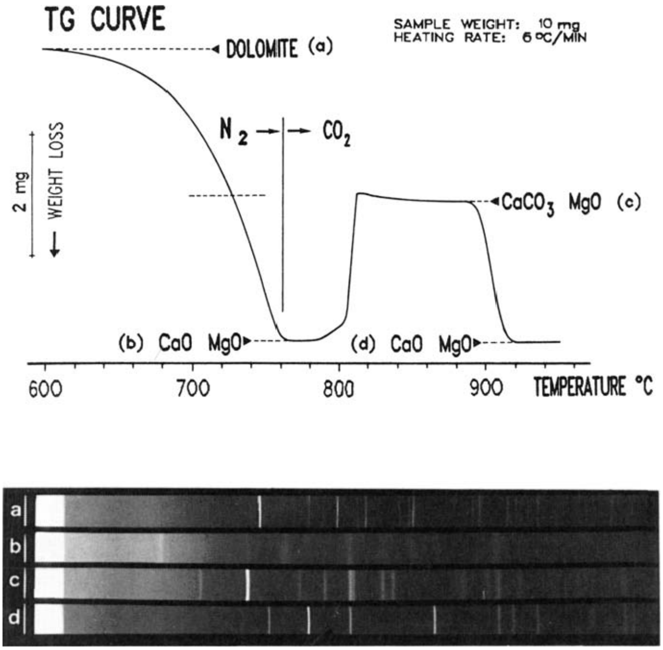

Fig. 3. TG curve of dolomite heated in dynamic $N_2$ atmosphere to 760 °C followed by further heating in dynamic $CO_2$ atmosphere to 960 °C. Heating rate, 6 °C $min^{-1}$; flow rate of $N_2$ and $CO_2$, 50 $cm^3$ $min^{-1}$, sample weight, 10 mg. The X-ray patterns correspond to the reaction products formed at the various weight steps a, b, c and d, respectively.

switched to pure $CO_2$, which led to carbonation of the CaO to $CaCO_3$ in the region of ~ 780–800 °C. The weight steps and the corresponding phases were identified by X-ray diffraction and confirmed the postulated reaction mechanism:

$$CaMg(CO_3)_2 \xrightarrow[N_2]{< 760\,^\circ C} CaO + MgO + 2CO_2$$

$$CaO + MgO \xrightarrow[CO_2]{> 760\,^\circ C} CaCO_3 + MgO$$

$$CaCO_3 + MgO \xrightarrow[CO_2]{890\,^\circ C} CaO + MgO + CO_2$$

The DTG curves in Fig. 1 show the strong effect of the $CO_2$ partial pressure on the position of the $CaCO_3$ decomposition peaks. These DTG peaks decrease in magnitude and are shifted to lower temperatures with decreasing $p_{CO_2}$. The first DTG peak is less affected in terms of temperature, but more so in terms of its shape and magnitude. The assymetrical, distorted shape of these DTG peaks, especially at $p_{CO_2} > 100$ Torr, is caused by the simultaneous recarbonation of CaO. This CaO is initially formed due to the complete breakdown of the dolomite structure but reacts immediately with the $CO_2$ to form $CaCO_3$. The dotted line indicates the peak shape without this recombination reaction. With decreasing $CO_2$ partial pressure the two

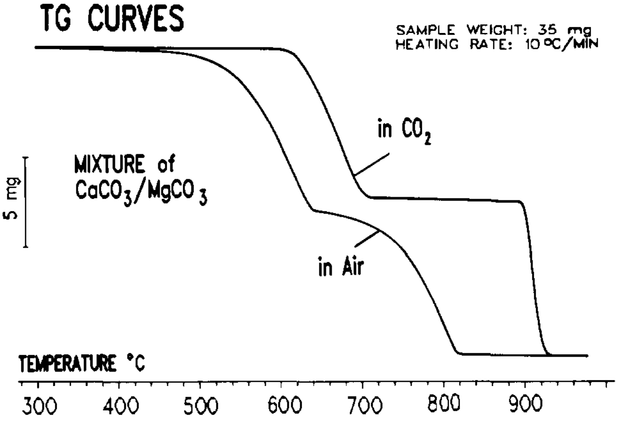

Fig. 4. TG curves of stoichiometric mixtures 1 $CaCO_3$/1 $MgCO_3$ heated in dynamic air and in $CO_2$.

DTG decomposition peaks approach each other more and more and merge to one peak at $p_{CO_2} < 3$ Torr.

For comparison and to prove that dolomite shows a characteristic, individual decomposition behavior, TG/DTG runs were carried out with stoichiometric mixtures of $CaCO_3$ and $MgCO_3$ in different atmospheres. Figure 4 shows TG curves of $CaCO_3$/$MgCO_3$ samples heated in dynamic air and in $CO_2$. As expected, two decomposition steps were found at the same temperatures as for the individual carbonates (which were shifted to higher temperatures in pure $CO_2$). A sample of dolomite which was run under identical conditions shows a distinctly different decomposition behavior (Fig. 5). The TG curves show a one-step reaction in air, whereas two decomposition steps are found with a $CO_2$ atmosphere. The first decomposi-

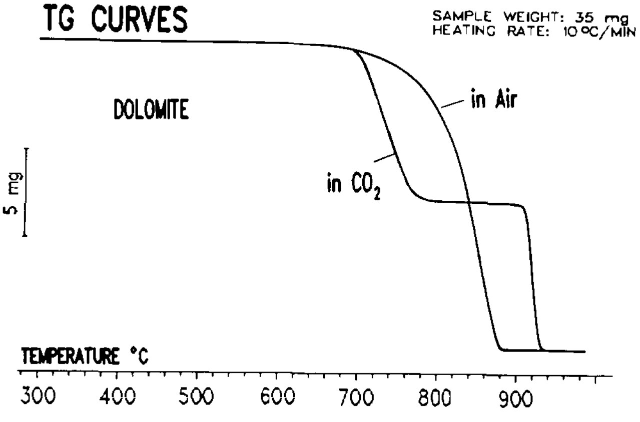

Fig. 5. TG curves of dolomite heated in dynamic air and in $CO_2$.

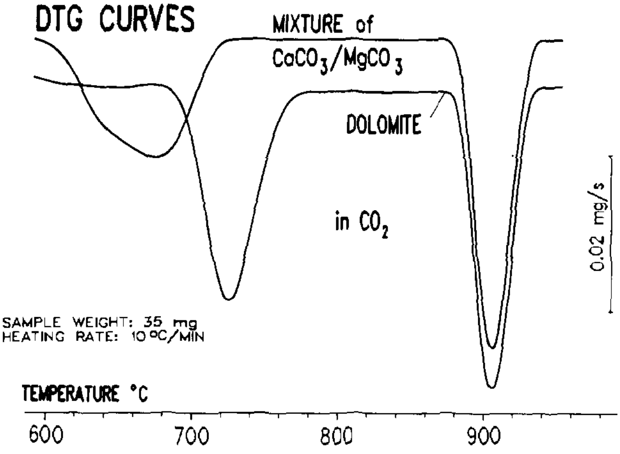

Fig. 6. DTG curves of dolomite and of 1 $CaCO_3$/1 $MgCO_3$ heated in dynamic $CO_2$.

tion step with a $CO_2$ atmosphere is a result of the decomposition of dolomite. The second step, at a higher temperature, is the decomposition of the $CaCO_3$ formed by the immediate recarbonation of the initially formed CaO. The different decomposition behavior of dolomite as compared to a mixture 1 $CaCO_3$/1 $MgCO_3$ is also clearly demonstrated by the DTG curves of such samples when heated in $CO_2$ (Fig. 6). Magnesite decomposes at a much lower temperature than dolomite.

Figure 7 shows SEM photographs of (a) undecomposed dolomite; (b) dolomite which is 0.5% decomposed; and (c) dolomite which is 1% thermally decomposed. The surface becomes corrugated and bloated due to the evolution of $CO_2$. After cooling to room temperature the $CO_2$ in the

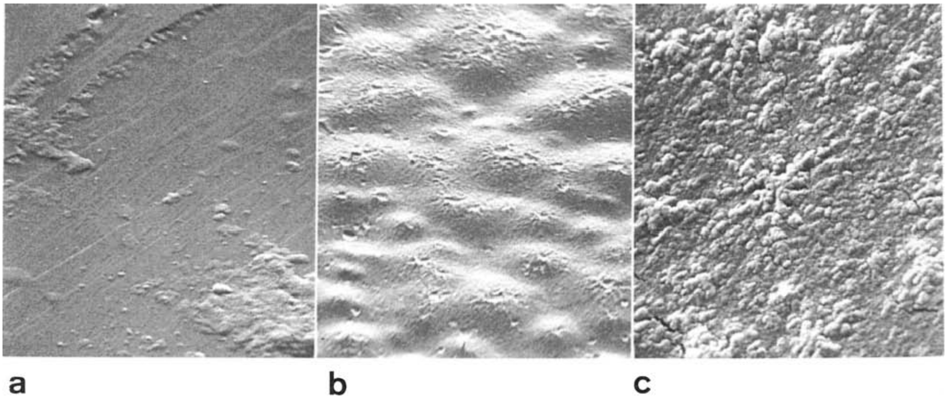

Fig. 7. SEM photographs of (a) a dolomite surface, (b) after heating with initial decomposition and (c) after cooling to room temperature with recarbonation of CaO to $CaCO_3$ (1500×).

atmosphere causes a recarbonation of the initially formed CaO to $CaCO_3$ as shown in Fig. 7c.

In conclusion, these thermoanalytical investigations proved that dolomite shows complete decomposition to the oxide mixture MgO and CaO in one step when the partial pressure of $CO_2$ is less than 3 Torr. This temperature is definitely much higher than the decomposition temperature of magnesite. At higher $CO_2$ pressures, $CaCO_3$ is formed as an intermediate reaction product due to recarbonation of the CaO which is generated during breakdown of the dolomite structure.

## REFERENCES

1 J.W. Smith, Proc. 3rd ICTA, Davos, 1971, Vol. 3, Birkhäuser-Verlag, Basel, 1972, pp. 605–635.
2 A.E. Milodowski and D.J. Morgan, 2nd ESTA Conf., Aberdeen, U.K., 1981, pp. 468–471.
3 J.W. Smith, D.R. Johnson and M. Müller-Vonmoos, Thermochim. Acta, 8 (1974) 45.
4 S.St.J. Warne, Nature (London), 269 (1977) 678.
5 R. Otsuka, Thermochim. Acta, 100 (1986) 69.
6 W.R. Bandi and G. Krapf, Thermochim. Acta, 14 (1976) 221.
7 N.G. Dave and I. Masood, Proc. 4th ICTA, Budapest, 1974, Vol. 2, Akademiai Kiado, Budapest, 1975, pp. 685–694.
8 E.K. Powell and A.W. Searcy, J. Am. Ceram. Soc., 61 (1978) 216.
9 H.G. Wiedemann and G. Bayer, Topics of Current Chemistry, Vol. 77, Springer-Verlag, Berlin, 1978, p. 126ff.