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RECENT STUDIES ON THE DECOMPOSITION OF THE DOLOMITE GROUP BY THERMAL ANALYSIS

R. OTSUKA

Department of Mineral Industry, School of Science and Engineering, Waseda University, 4-1, Okubo 3 Chome, Shinjuku-ku, Tokyo 160 (Japan)

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ABSTRACT

Recent thermoanalytical investigations of the decomposition of the dolomite group are reviewed.

Dolomite shows two DTA endotherms in CO_2 due to a two-step decomposition. It is well established that the higher decomposition temperature is very sensitive to atmospheric CO_2 partial pressure. However, there has been much discussion on whether or not the lower decomposition temperature depends on CO_2 pressure. Recent studies confirm that the lower decomposition temperature is shifted to a lower temperature on increasing CO_2 pressure, so that the lower and higher decomposition temperatures are shifted in opposite directions with changing CO_2 pressure. Regarding the mechanism of formation from dolomite in CO_2, a direct formation theory is supported.

The decomposition mechanisms of ferroandolomite-ankerite and kutnahorite are much discussed. Recent studies indicate that these minerals decompose in two steps in a similar manner to dolomite itself in the atmosphere, in which the O_2 partial pressure is sufficiently low to maintain both Mn and Fe as bivalent cations.

In addition, recent investigations on the effects on salts on the decomposition mechanism of dolomite are briefly reviewed.

INTRODUCTION

The history of the thermal analysis of carbonate minerals goes way back to 1780, when Higgins measured weight losses of chalk and limestone at various temperatures to improve the quality of quick lime [1]. Since then up to the present time, the thermoanalytical investigation of carbonate minerals has been very actively carried out by various methods. For example, papers relating to carbonate minerals have been presented at all ICTA and ESTA conferences. In addition, original papers on these minerals have very often been published in both Thermochimica Acta and the Journal of Thermal Analysis. In particular, both calcite and dolomite have been extensively studied. This is because these minerals, showing a widespread occurrence in

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nature, are most important industrial minerals. Above all, regarding the dolomite group, the following three problems remain to be solved.

(1) Decomposition of dolomite and formation mechanism of $CaCO_3$.

(2) Decomposition of ferroandolomite-ankerite and kutnahorite.

(3) Effects of salts on the mechanism of decomposition of dolomite.

In this paper, the recent studies on these problems are briefly reviewed.

DECOMPOSITION OF DOLOMITE AND FORMATION OF $CaCO_3$

The important works of the decomposition of dolomite were published by Haul and co-workers [2–7] and Kulp et al. [8] at the beginning of the 1950s. Above all, Haul and co-workers carried out extensive studies by DTA, X-ray and carbon isotope (C^{13}) techniques. They obtained DTA curves under different CO_2 pressures as shown in Fig. 1. They indicate that in the CO_2 pressure range from 100 to 760 mm-Hg, dolomite decomposes in two steps, as follows:

First peak: $$CaMg(CO_3)_2 \rightarrow CaCO_3 + MgO + CO_2 \qquad (1)$$

Second peak: $$CaCO_3 \rightarrow CaO + CO_2 \qquad (2)$$

At CO_2 pressures lower than 100 mmHg, the decomposition proceeds in one step:

$$CaMg(CO_3)_2 \rightarrow CaO + MgO + 2\ CO_2 \qquad (3)$$

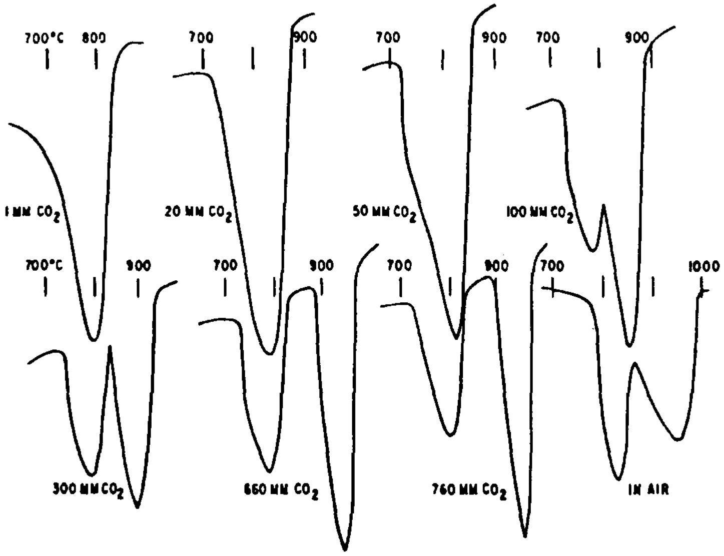


Fig. 1. DTA curves of dolomite at different CO_2 pressures (Haul and Heystek [6]).

As shown in Fig. 1, the first endotherm is not affected by CO_2 pressure, while the second endotherm is shifted to a lower temperature with decreasing CO_2 pressure. Consequently, the second peak gradually merges with the first peak.

At present, in the two-step decomposition of dolomite in CO_2, it is well established that the second peak represents the reversible reaction of the $CaCO_3$ formed (eqn. 2), and its decompositoin temperature strongly depends on the partial pressure of CO_2 in the atmosphere. However, many different interpretations have been expressed on the mechanism of the first endotherm and its dependence on CO_2 pressure [4,6,9,10].

Further, the mechanism of the one-step decomposition (eqn. 3) remains to be extensively discussed. To elucidate these problems, it will be necessary to perform DTA on a small amount of sample under a strictly controlled CO_2 atmosphere.

The mechanism of the first endotherm in CO_2

Recently, Bandi and Krapf [11] carried out a detailed investigation of the mechanism of dolomite decomposition with a specially designed DTA apparatus. The measurement was performed on approximately 1 mg of sample in a dynamic atmosphere. The gas flow rate was controlled to less than 1 ml min^{-1}. Figure 2 illustrates one of the results in a mixed gas flow of CO_2 and O_2 obtained by them. Curve 1 shows two endotherms at 775 and 870°C, representing the two-step decomposition already described. With the decrease of CO_2 partial pressure, the first endotherm is clearly shifted to a higher temperature, and it merges with the second endotherm at pressures lower than 260 mmHg. This indicates that the first decomposition temperature is very sensitive to CO_2 pressure and the first and second decomposition temperatures are shifted in opposite directions to each other. Hashimoto [12] and Hashimoto et al. [13] obtained similar results. Otsuka et al. [14] also observed a shift of the first endotherm to higher temperature with decreasing CO_2 partial pressure in a mixed gas flow of CO_2 and N_2 using a small amount (5 mg) of well-crystallized, nearly stoichiometric Korean dolomite in the CO_2 pressure range from 20 to 100 mmHg. These recent results reveal that the mechanism of the first decomposition is a complex and not straightforward decomposition reaction [11]. Garn [10] suggests that another mechanism of decomposition occurs, involving the exchange of CO_2 between the sample and the atmosphere. Haul et al. [2] showed the exchange of CO_2 between $CaCO_3$ and the CO_2 atmosphere. Hashimoto [12] considers that adsorbed CO_2 on the surface of dolomite promotes the diffusion of cations, consequently, increasing CO_2 pressure lowers the decomposition temperature.

The mechanism of the partial decomposition of dolomite in CO_2 and of

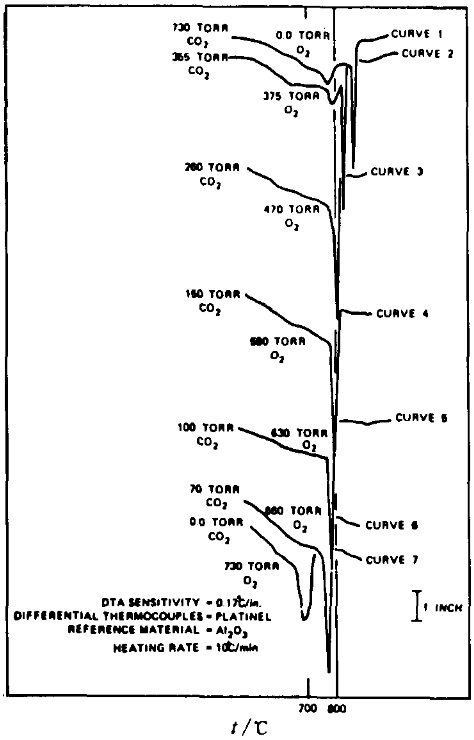


Fig. 2. Effect of partial pressure of CO_2 on decomposition of 1 mg NBS No. 88 standard dolomite (Bandi and Krapf [11]).

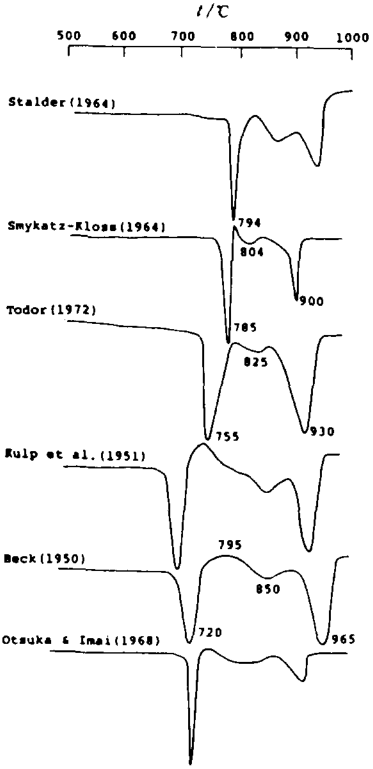


Fig. 3. Some DTA curves of ferroandolomite (Iwafuchi et al. [25]).

the formation of $CaCO_3$ have been summarized by Lange and Roesky [15] in the following three groups:

(1) Formation of the solid solution of the carbonate.

$$n\ MgCa(CO_3)_2 \rightarrow (n-1)\ MgO + n\ CaCO_3MgCO_3 + (n-1)\ CO_2 \qquad (4)$$

(2) Primary dissociation into two carbonates, followed by the decomposition of $MgCO_3$.

$$MgCa(CO_3)_2 \rightarrow MgCO_3 + CaCO_3 \rightarrow MgO + CaCO_3 + CO_2 \qquad (5)$$

(3a) Primary dissociation into oxides and successive exchange reaction.

$$CaO + MgCa(CO_3)_2 \rightarrow MgO + 2\ CaCO_3 \qquad (6)$$

(3b) Primary dissociation into oxides and recarbonization.

$$MgCa(CO_3)_2 \rightarrow MgO + CaO + 2\ CO_2 \rightarrow CaCO_3 + MgO + CO_2 \qquad (7)$$

These four processes are divided into two categories, i.e. direct formation of $CaCO_3$ (eqns. 4 and 5) and recarbonization (eqns. 6 and 7).

Recently, Hashimoto et al. [16] investigated the decomposition of dolomite into $CaCO_3$ and MgO in CO_2 by isothermal kinetic measurements, X-ray diffraction and electron diffraction techniques and reexamined the above classical theories. As a result of their work, they suggest the direct formation of $CaCO_3$. Further, they consider the mechanism of the formation of MgO and $CaCO_3$ from dolomite as follows:

At the beginning of decomposition, CO_2 is easily released at defects on the surface of dolomite, leaving O^{2-}. Then, Mg ions in the neighboring domains may move to the vicinities of O^{2-}, with Ca ions migrating in the opposite direction. The migration or diffusion of these ions occurs in the interfacial zone. $CaCO_3$ is formed in this zone coherently to the surface of the dolomite lattice, mainly by a topotactic process. The lattice constant, a, of the $CaCO_3$, is between 4.93 and 4.97 Å, being smaller than that of normal $CaCO_3$ (Calcite, 4.99 Å). This means that the $CaCO_3$ is in the form of magnesian calcite. MgO may be formed at first in an amorphous state and then gradually crystallize. The above mentioned mechanism may be expressed as:

$$MgCa(CO_3)_2 \rightarrow CaCO_3(1-n)\ MgCO_3 + n\ MgO + n\ CO_2 \qquad (8)$$

n increases from 0 to 1 with time. This equation corresponds with eqn. (4). Calcite is formed as magnesian calcite at the initial stage of the decomposition, and Mg ion is gradually released with time from the calcite lattice. Hashimoto et al. [16] concluded that the evolution of CO_2 instead of the dissociation into two carbonates as in eqn. (5) initiates decomposition.

The mechanism of the one step decomposition

As already mentioned, dolomite decomposes in a single step at low CO_2 pressure (eqn. 3). The single DTA endotherm is also observed in both vacuum and dynamic N_2 [12,17]. Bandi and Krapf [11] showed that the rapid single step decomposition of dolomite to MgO and CaO occurs at CO_2 pressures of less than 150 mmHg (curves 4, 5 and 6 in Fig. 2). Assuming that the initial step involves formation of CO_2 and oxide ion, they indicated that the rate-controlling factor in this decomposition may be the formation of CaO or a simultaneous indiscriminate formation of CaO and MgO rather than preferential formation of MgO. At very low CO_2 partial pressures of less than 5 mmHg, the single step decomposition proceeds slowly at a lower temperature, showing a broad endotherm (curve 7 in Fig. 2). The curve is very similar to the endotherm of calcite decomposition at 0 mmHg CO_2.

Bandi and Krapf [11] consider that in this slow single decomposition, decomposition of the $MgCO_3$ part of the dolomite may be the rate-controlling factors. According to Iwafuchi [18], at very low CO_2 partial pressures, Co_3^{2-} easily dissociates into O^{2-} and CO_2 and an intermediate oxide solid solution, (Ca, Mg)O, is formed, which ex-solutes rapidly into CaO and

MgO. Therefore, the dissociation of CO_3^{2-} will be the rate-determining process in this one step decomposition. Powell and Searcy [19] studied the decomposition of dolomite at 750–900 K in vacuum by the torsion–effusion and torsion–Langmuir methods. They consider that dolomite and CO_2 are at equilibrium with a glass-like solid having the chemical composition $CaO \cdot MgO$ at the early stages of decomposition.

DECOMPOSITION OF FERROANDOLOMITE-ANKERITE AND KUTNAHORITE

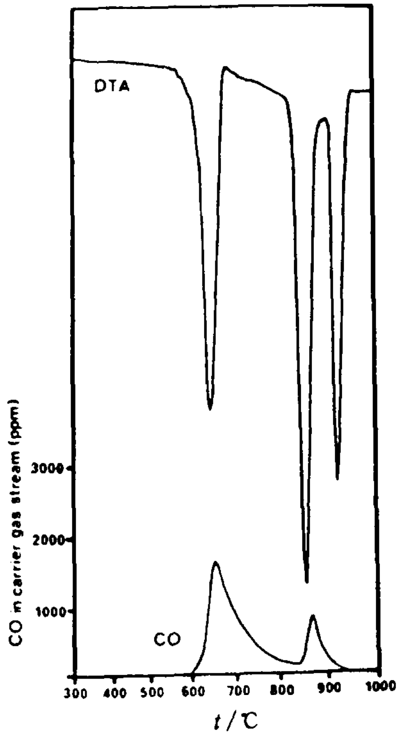
The dolomite group includes dolomite, $CaMg(CO_3)_2$, ankerite, $CaFe(CO_3)_2$ and kutnahorite, $CaMn(CO_3)_2$. A continuous solid solution series exists in the system $CaMg(CO_3)_2$–$CaFe(CO_3)_2$ and with increasing Fe^{2+} content substituting Mg^{2+}, it is called ferroandolomite-ankerite. However, natural occurrence of ankerite having the composition of the end member, $CaFe(CO_3)_2$, is not reported yet, and the solid solution series ends at approximately 70 mol% of $FeCO_3$. Furthermore, immiscibility gaps exist in a wide intermediate field in the system $CaMg(CO_3)_2$–$CaMn(CO_3)_2$ and over the whole area in the system $CaMn(CO_3)_2$–$CaFe(CO_3)_2$.

Ferroandolomite-ankerite

In the case of ferroandolomite-ankerite, many works have been carried out by thermal analysis [8,20–24]. They all recognized three endotherms accompanied by weight loss and an exotherm immediately succeeding to the first endotherm in air as shown in Fig. 3 [25]. In addition, it was reported that with increasing Fe content, the peak temperature of the first endotherm lowers and the peak area of the second endotherm increases. Therefore, it is suggested that Fe contents in minerals of the dolomite–ferroandolomite–ankerite series can be estimated by DTA results. From this viewpoint, Warne et al. [26] recorded the DTA curves of the nine samples in this series whose Fe contents range from 0.35 to 26.3% (expressed as weight % of $FeCO_3$). The measurements were carried out on 1.0 g samples in flowing CO_2, with a heating rate of 15°C min^{-1}. From these results, they recognized that with increasing Fe content the peak temperature of the first endotherm decreases remarkably from 800 to 665°C, and the peak area of the second endotherm increases. Based on the second endotherm, the detection limit of Fe was of the order of 1% $FeCO_3$. They concluded:

> DTA using a flowing CO_2 furnace atmosphere provides a suitable method for Fe content evaluation of members of the dolomite–ferroandolomite–ankerite series. Amounts equivalent to 1 wt% of the $FeCO_3$ component in the dolomite structure can be detected and distinguished from $FeCO_3$ occurring as the discrete mineral siderite.

The DTA curves obtained by various workers have similar patterns,



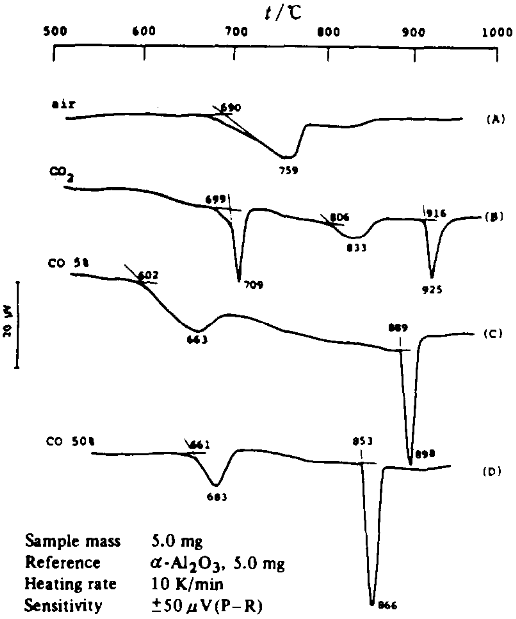


Fig. 4. DTG–EGA curves of ankerite from Erzberg, Austria (Milodowski and Morgan [27]). 100-mg sample, heating rate 15°C min^{-1}, atmosphere, flowing CO_2 at 300 cm^3 min^{-1}.

Fig. 5. DTA curves of ferromanganoan-dolomite from Budo mine, Niigata Pref., Japan under four kinds of atmosphere (Iwafuchi et al. [25]).

however, they are interpreted differently [8,20–24]. Recently, Milodowski and Morgan [27] obtained simultaneous TG–DTG and DTA–EGA curves of ankerite from Erzberg, Austria ($Ca_{1.025}Mg_{0.329}Fe_{0.588}Mn_{0.060}(CO_3)_2$) in flowing CO_2. The latter curves are reproduced in Fig. 4, indicating that CO is evolved during the first and second endotherms. They attribute the first endotherm to the decomposition of $FeCO_3$ and $MgCO_3$ components, which produces $CaCO_3$, MgO and $FeO \cdot Fe_2O_3$ by oxidation of FeO. Further, they suggest that $FeO \cdot Fe_2O_3$ subsequently reacts with MgO to form $MgO \cdot Fe_2O_3$, and that CO evolution during the first endotherm results from the oxidation of FeO by CO_2 to form $FeO \cdot Fe_2O_3$. According to their interpretation, the second endotherm is caused by the reaction of $MgO \cdot Fe_2O_3$ with $CaCO_3$ to form $2\ CaO \cdot Fe_2O_3$ and MgO. The second CO peak may be ascribed to the oxidation of the remaining Fe^{2+} after the first endotherm by CO_2 released during the second reaction. The third endotherm is due to the decomposition of unreacted $CaCO_3$. The two-step evolution of CO is also recognized in N_2 atmosphere.

Very recently, Iwafuchi et al. [25] recorded DTA curves of ferromanganoan dolomite (abbreviated as FeMn-dolomite) from the Budo mine, Niigata Prefecture, Japan ($Ca_{1.015}(Mg_{0.515}Fe_{0.225}Mn_{0.245})(CO_3)_2$) in atmospheres of (1) static air, (2) flowing CO_2, (3) a mixed gas flow of CO_2 and CO (5% CO), and (4) a mixed gas flow of CO_2 and CO (50% CO) (Fig. 5). The total gas flow rate was 100 ml min^{-1} in every case. The DTA curve in air (A) has a single asymmetric endotherm, showing a remarkable difference from any of the other curves in Fig. 3. Iwafuchi et al. [25] suggested that this may be due to the negligible effect of the self-generated CO_2 [28]. The DTA curve in CO_2 (Fig. 5B) indicates three discrete endotherms accompanied by a very weak exothermic hump immediately after the first peak. This curve is very similar to those in Fig. 3 obtained in air. From the X-ray analysis of the products, they consider that the first endotherm is due to the decomposition of $MgCO_3$, $FeCO_3$ and $MnCO_3$ components, to give $CaCO_3$, $(Fe, Mn)_3O_4$ and MgO. The second endotherm may be ascribed to the reaction of $CaCO_3$ with $(Fe, Mn)_3O_4$ to form $CaMnO_3$ and $CaFe_2O_4$. Further, they confirm that the third endotherm is due to decomposition of the unreacted $CaCO_3$, because of giving a reverse exotherm in the cooling process. The results in CO_2 indicate that the Fe and Mn existing as bivalent cations in the unheated sample have been oxidized. It is well established that CO_2 dissociates into CO and O_2. Based on the basic dissociation reaction, $2\ CO_2 \rightleftharpoons 2\ CO + O_2$, Iwafuchi et al. [25] estimated the equilibrium O_2 partial pressure in CO_2 flow as approximately 10^{-10} atm at 800 K. Then, they tried to introduce CO into CO_2 to decrease the O_2 partial pressure of the atmosphere. In a mixed gas flow of CO_2 + CO (5% CO), the estimated O_2 partial pressure decreases to approximately 10^{-25} atm at 800 K. The DTA curve in CO_2 + CO (5% CO) (Fig. 5C) indicates two endotherms corresponding to a two step decomposition. They consider that the first endotherm is due to the decomposition of $MgCO_3$, $FeCO_3$ and $MnCO_3$ components to give $CaCO_3$, $(Mg, Mn)\underline{O}$ and Fe_2O_3, the second endotherm is ascribed to the reaction of $CaCO_3$ with $(Mg, Mn)\underline{O}$ and Fe_2O_3 to form (Ca, Mn)O, $(Mg, Mn)\overline{O}$ and $Ca_2MgFe_2O_6$. Further, they suggest that the decrease in the lattice parameter, along with the increase in Mg/Mn ratio [29] from $(Mg, Mn)\underline{O}$ to $(Mg, Mn)\overline{O}$ at the second decomposition, will explain the redistribution of Mn in periclase-and-lime solid solutions. In this atmosphere, the oxidation of Fe from bivalent to trivalent states is also recognized. The DTA curve in CO_2 + CO (50% CO) (Fig. 5D) shows two endotherms which are very similar to the two step decomposition of dolomite. They consider that in the first step $CaCO_3$ and $(Mg, Mn, Fe)\underline{O}$ are formed, and then the equilibrium distribution of Fe and Mn occurs between $(Mg, Mn, Fe)\overline{O}$ and (Ca, Mn, Fe)O at the second step.

Kutnahorite

Of the dolomite group, kutnahorite occurs rarely. DTA curves of kutnahorite were presented by several workers [22,30–32] (Fig. 6). However,

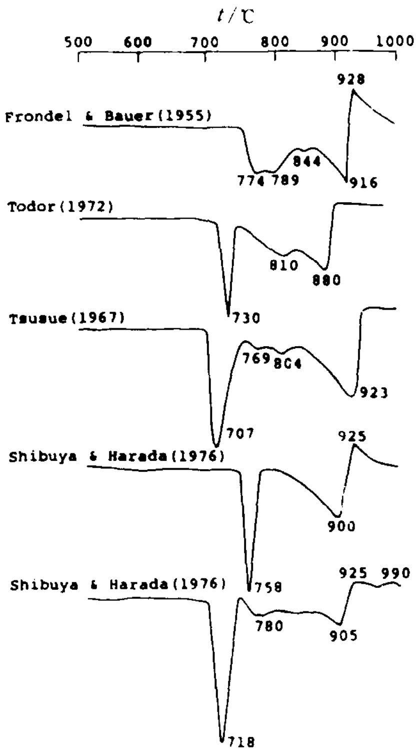


Fig. 6. Some DTA curves of kutnahorite (Iwafuchi et al. [33]).

interpretation of the curves was carried out only by Shibuya and Harada [32]. Further, these curves were obtained for rather large amounts of sample and in static air. Under these conditions, a detailed interpretation of the results would be difficult.

Very recently, Iwafuchi et al. [33], using similar techniques as in the case of the FeMn-dolomite [25], recorded DTA curves of magnesian kutnahorite (abbreviated as Mg-kutnahorite) from the Ryujima mine, Nagano Prefecture, Japan ($Ca_{1.064}(Mn_{0.475}Mg_{0.437}Fe_{0.024})(CO_3)_2$) in three atmospheres: (1) static air, (2) CO_2 flow at 100 ml min^{-1}, (3) mixed gas flow of CO_2 at 95 ml min^{-1} and CO at 5 ml min^{-1} (Fig. 7). The DTA curve in air (Fig. 7A) has a broad and asymmetric endotherm followed by a step-like shoulder, showing a remarkable difference from any of the curves in Fig. 6. This may be attributed to the negligible effect of self-generated CO_2 because of the small amount of sample (5 mg) in this measurement as in the case of FeMn-dolomite. The DTA curve in CO_2 (Fig. 7B) shows four discrete endotherms as well as a very weak exothermic hump immediately after the first one. According to the interpretation by Iwafuchi et al. [33], at the first reaction $CaCO_3$, Mg_2MnO_4, Mn_3O_4 and MgO are formed, $CaCO_3$ reacts with Mg_2MnO_4 and Mn_3O_4 to form $CaMnO_3$ and MgO at the second reaction,

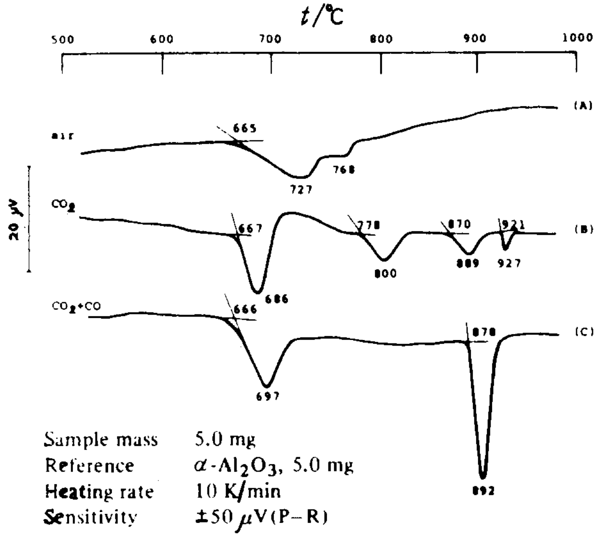


Fig. 7. DTA curves of magnesian-kutnahorite from Ryujima mine, Nagano Pref., Japan under three kinds of atmosphere (Iwafuchi et al. [33]).

and at the third decomposition $CaMnO_3$ reacts with the remaining $CaCO_3$ to form Ca_2MnO_4. At the fourth step, as confirmed by the reverse exotherm on cooling, the residual $CaCO_3$ decomposes. In CO_2, oxidation of Fe from bivalent to trivalent and tetravalent states is observed. The DTA curve in $CO_2 + CO$ (Fig. 7C) shows two endotherms, very similar to the curve of dolomite in CO_2. They interprete that at the first decomposition $CaCO_3$ and (Mg, Mn)$\overline{O}$ are formed, and $CaCO_3$ reacts with (Mg, Mn)$\underline{O}$ to form (Ca, Mn)O and (Mg, Mn)$\overline{O}$ at the second step. From the relation between chemical compositions and lattice parameters in the CaO–MnO and MgO–MnO systems [29], the chemical composition of each of the above solid solutions can be estimated.

(Mg, Mn)$\underline{O}$: $(Mg_{0.454}Mn_{0.546})O$
(Mg, Mn)$\overline{O}$: $(Mg_{0.784}Mn_{0.216})O$
(Ca, Mn)O: $(Ca_{0.700}Mn_{0.300})O$

In addition, based on the thermodynamic calculation, Iwafuchi et al. [33] recognize that the total amount of Mn in the original sample is contained in (Mg, Mn)$\underline{O}$ at the first step, and the equilibrium redistribution of Mn is achieved between (Ca, Mn)O and (Mg, Mn)$\overline{O}$ at the second step.

From the studies mentioned above, we can conclude that ferroandolomite-ankerite and kutnahorite decompose in two steps in a similar manner to dolomite in a $CO_2 + CO$ atmosphere, of which O_2 partial pressure is low enough to keep both Fe and Mn as bivalent cations. The only difference between dolomite and the two minerals is that, in the latter, the reaction products constitute the oxide solid solution.

EFFECTS OF SALTS ON THE MECHANISM OF DECOMPOSITION OF DOLOMITE

It is well established that the mechanism of decomposition of dolomite is remarkably influenced by the presence of foreign materials. In particular, many papers have been published regarding the effects of salts [34–38]. Above all, Murray et al. [36] found that certain salts raise the "characteristic" temperature of the first endotherm by as much as 40°C, or reduce it by as much as 235°C. Garn [10] indicates that dolomite is unstable at temperatures near the first endotherm, and the presence of salts distorts the lattice and lowers the activation energy so that the first endotherm is shifted to a lower temperature.

In the recent publication by Wieczorek-Ciurowa et al. [39], 19 papers about the effects of sodium chloride are listed in the Reference section, including refs. 11, 34, 36 and 37 of this paper. According to them, the literature data do not give a consistent picture, however, all authors agree on one fact: that sodium chloride promotes the decomposition of dolomite, calcite and magnesite.

Recently, this effect has been studied by Bandi and Krapf [11], Wieczorek-Ciurowa et al. [39] and Li and Messing [40]. In particular, Bandi and Krapf [11] performed a detailed study on the salt effect in both O_2 and CO_2 atmospheres by DTA, EGA and TG. In O_2, with increasing salt concentration, the main endotherm is shifted from 700 to 675°C, and a broad endotherm, due to the formation of MgO and $CaCO_3$ from dolomite, appears at about 550°C. In CO_2, sodium chloride in the dolomite causes a 200°C shift of the first endotherm to a lower temperature, or the disappearance of the first endotherm. The disappearance of this peak may be ascribed to the reduction of the activation energy for decomposition. Bandi and Krapf [11] consider that there may be two mechanisms for the decomposition of dolomite in the presence of salt. The first mechanism is that salt in the dolomite causes early formation of MgO by catalyzing the arrangement of calcium and magnesium ions regardless of the atmosphere. The second mechanism involves the intermediate formation of small amounts of magnesite and calcite before formation of MgO, but this has not been detected by the X-ray technique.

However, regarding the effects of salts on the mechanism of decomposition of dolomite, further studies will be necessary.

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