

## Thermal analysis of ground dolomites \*

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### Abstract

The characteristics of ground dolomites which have undergone a change in crystal structure and of those almost free from structural change, were studied mainly by thermal analysis.

Firstly, pulverized samples passed through a 325-mesh Tyler sieve were ground further for 1, 2, 3, 5 and 24 h in order to observe their change with progressive grinding. The X-ray diffraction (XRD) and IR patterns and TG–DTA curves obtained in flowing 100% CO<sub>2</sub> gas indicated a gradual loss of the cation ordering characteristic of dolomite structure up to a grinding period of 24 h when a new phase of lower ordering appeared; this confirmed the results of earlier investigators.

To characterize further the gradually developing new phase which was not apparently distinguished by XRD or IR analysis, TG–DTA curves were obtained under varying CO<sub>2</sub> partial pressures. It was found that the new phase decomposed in a straightforward manner, similarly to that of magnesite and quite differently from that dolomite, its decomposition temperature and rate were dependent upon the CO<sub>2</sub> partial pressure.

In addition, the influence of grain size and particle size distribution on the temperature and shape of the endothermic peak of the DTA curve was studied. It was found that the peak shape is affected by the grain size, and moreover that the temperature range of the endothermic peak is affected by the size and, more importantly, the size distribution of the particles.

### INTRODUCTION

Grinding affects solids as a result of the energy it supplies in the form of normal and shear tension, heat, momentum etc. (see for example ref. 1).

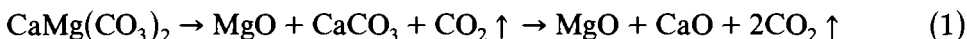
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Thus, in general, with progressive grinding, the following phenomena occur in solids.

(1) With little change in crystal structure, there is a change in shape and reduction in the size of the grains, increase in surface area, surface activation etc.

(2) With a change in crystal structure there is lattice strain, slips, bond breakage etc. which cause phase transition, partial decomposition etc., and finally new phases or amorphous phases are formed.

For example, the well-known dolomite decomposition in CO<sub>2</sub> gas



is considerably affected by grinding. Bradley et al. [2] studied dolomite samples ground for 3–400 h using DTA and X-ray diffraction (XRD). Arai and Yasue [3–5] performed XRD, TA and IR analyses, as well as the measurement of heats of solution of samples ground for 24–550 h.

The above investigators all observed that the first endothermic peak of the DTA pattern was split in two, resulting in an additional peak at a lower temperature (500–600 °C). This new peak increases in area with prolonged grinding at the expense of the original peak, a single peak being the final result; this point is considered as the “attainment of new equilibrium” [2]. The peak temperature of the new broad peak at the lower temperature is constant for all the ground samples, and is in good agreement with the decomposition temperature of magnesite. The second endothermic peak was confirmed as the decomposition of the CaCO<sub>3</sub> portion of dolomite [2].

Bradley et al. [2] proposed that the development of a MgCO<sub>3</sub>-rich portion in the dolomite structure was caused by a combination of glides, based mainly on their observation of the XRD peak intensity: the XRD peaks corresponding to the superstructure reflections decreased in intensity, and this was explained in terms of cation displacements which led to the formation of calcium and magnesium-rich portions. The complete disappearance of the superstructure reflection corresponded to the “attainment of new equilibrium”. However, DTA indicated the presence of two intermediate phases of different activation states: these cannot be fully distinguished by XRD or IR analysis.

The thermal decomposition of dolomite in a systematically controlled atmosphere of varying CO<sub>2</sub> partial pressure, on the other hand, has been studied extensively as it has the advantage of providing more information. It is also known that in the DTA pattern of dolomite, the shape and temperature of the first endothermic peak provide information on the grain size of the powder sample. For example, we have previously reported [6] that Philippine dolomites consisting of minute nearly uniform grains of about 2 μm in size yield a sharp symmetrical peak at a rather high temperature. However, despite the large specific surface area, its decomposition temperature was unexpectedly high; this has been the subject of further investiga-

tion. To attempt to explain this, two naturally occurring dolomites of similar composition but consisting of different grain sizes were compared. Because they are natural occurring samples, it is hoped that lattice distortion, i.e. change in crystal structure induced by grinding, could be eliminated.

Thus the present study describes in greater detail the characteristics of ground dolomites that have undergone structural change, particularly those of the intermediate phases which appear in the course of attaining equilibrium, by applying TG-DTA in controlled  $\text{CO}_2$  gas partial pressure. Another objective of the study is to interpret the DTA curves as a source of information concerning the grain size and particle size distribution of the starting material, that is, of ground samples that have not undergone considerable changes in structure.

## EXPERIMENTAL

### *Samples*

The following samples were used: (a) dolomite from Mitsumine Mining Area, Oogano Mine, Kuzuu District, Tochigi Prefecture, Japan; (b) Taehyangsan dolomite from Jang Won 0 mL, Tong Yang, Korea; (c) dolomite from Cebu Island, the Philippines. The above samples are hereinafter denoted A, K and P respectively. Microscopic examination revealed that A consists of mainly 100–200  $\mu\text{m}$  subhedral dolomite grains in a mosaic structure. Sample K consists of coarser grains, 400  $\mu\text{m}$  on average with smaller grains about 20  $\mu\text{m}$  in size occupying the interstices, whereas sample P comprises fine crystallites less than 2  $\mu\text{m}$  in average grain size (see Figs. 1 and 2). There are minor calcite grains in the intergranular interstices of sample A; these were removed with 2 wt.% acetic acid solution from the

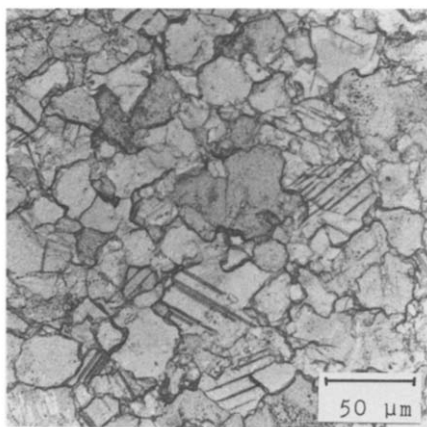


Fig. 1. Micrograph of the sample from Korea (K). Polarizers only.

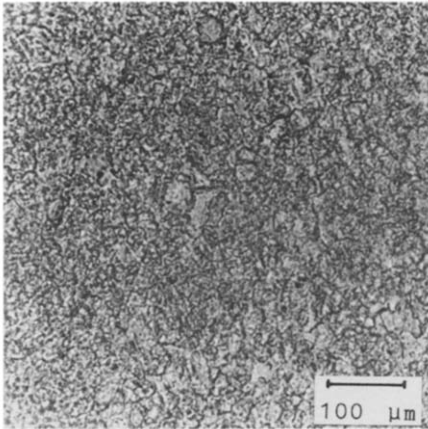


Fig. 2. Micrograph of the sample from the Philippines (P). Polarizers only.

powdered sample which has been passed through a 325-mesh Tyler sieve (this sample is denoted A-0 hereafter). The chemical compositions (mol.%), determined by electron probe microanalysis (EPMA), are given in Table 1.

Grinding was performed using an autorotative pestle (40 mm in diameter, at  $60 \text{ rev min}^{-1}$ ) and an agate mortar (120 mm in diameter and 30 mm thick) for 1, 2, 3, 5 and 24 h on 2.0 g samples. Each sample is labelled with its grinding time in hours; thus A-1 indicates Kuzuu dolomite ground for 1 h, the starting powder being denoted A-0.

### *Procedure*

The EPMA analyses were performed on sample fractions mounted on an epoxy resin block, using a JEOL JXA-733 X-ray electron probe microanalyser operating under routine conditions. In order not to decompose the sample, the beam diameter was enlarged to  $30 \mu\text{m}$  and short counting periods of 10 s were used. Corrections were made using Bence and Albee's method.

Identification of the sample was carried out by XRD and IR spectroscopy. The XRD runs were made on a Rigaku Geigerflex RAD I

TABLE 1

Chemical composition (mol.%) of dolomite samples from Kuzuu (A-0), Korea (K-0) and the Philippines (P-0), determined by EPMA

Sample name	MgCO <sub>3</sub>	CaCO <sub>3</sub>	FeCO <sub>3</sub>	MnCO <sub>3</sub>	Ca/(Mg + Fe + Mn)
A-0	45.75	54.23	–	0.02	1.18
K-0	48.07	51.14	1.01	–	1.04
P-0	49.24	50.67	0.08	0.01	1.03

operating with graphite-monochromatized Cu K $\alpha$  radiation using routine qualitative scanning conditions. IR analysis was carried out by the KBr method using 1.5–3.0 mg samples and 210 mg KBr (–400 mesh). A Hitachi 260-50 IR spectrophotometer was operated under normal parameters for qualitative analyses, over a scanning range of 4000–250 cm<sup>-1</sup>.

The TG–DTA was performed using 5 mg of sample and reference,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, charged in a platinum sample pan mounted on a top-load-type sample holder of a Rigaku Thermoflex simultaneous TG–DTA apparatus. The temperature was detected with a Pt–Pt 13% Rh thermocouple fixed in a position near the sample pan. The programmed heating rate was 10°C min<sup>-1</sup>. The TG–DTA curves were recorded at a TG sensitivity of 5 mg, a DTA sensitivity of  $\pm 50$   $\mu$ V and a chart speed of 5 mm min<sup>-1</sup>. The gas flow was upward from the bottom inlet. The thermal decomposition process was investigated under 100 ml min<sup>-1</sup> CO<sub>2</sub> flow, and then the CO<sub>2</sub> pressure dependence of the decomposition was investigated under various CO<sub>2</sub> gas partial pressures by changing the CO<sub>2</sub>–N<sub>2</sub> gas mixing ratio.

The calculation of the crystallite size and strain was based on Hall's method, using 00·6 and 00·12 XRD reflection profiles recorded with a scanning speed of 0.5° min<sup>-1</sup> and a chart speed of 2 cm min<sup>-1</sup>. The profiles were corrected with Stoke's method.

The specific surface area was determined by the Brunauer–Emmett–Teller (BET) method using a Digisorb 2600 surface-area, pore-volume analyser (Micromeritics Instrument Corporation), with argon as the adsorption gas.

The particle size distribution measurement was carried out on samples K-0 and P-0, using a laser diffraction particle size analyser, Model SALD-1100, manufactured by Shimadzu. The powder samples were dispersed in a 0.2 wt.% sodium hexaphosphate aqueous solution by applying ultrasonic vibration.

## RESULTS AND DISCUSSION

### *Grinding leading to change in crystal structure*

Figures 3–5 show the changes in the XRD, IR spectra and TG–DTA curve patterns of sample A with increasing grinding time. The 10·4 (principal) reflection shifts to the lower angle side; moreover, the 00·6 (basal) and 01·5 (order or superstructure) reflections become diffuse as grinding proceeds. This order reflection, characteristic of dolomite, becomes barely discernible after grinding for 24 h. In the IR absorption spectra, dolomite normally yields three characteristic absorption bands, at around 1440, 880 and 730 cm<sup>-1</sup>. However, grinding causes a change in symmetry and a new band develops at 1080 cm<sup>-1</sup>. In the dolomite structure, the  $\nu_1$  vibration of the CO<sub>3</sub><sup>2-</sup> group at 1080 cm<sup>-1</sup> is essentially IR inactive. The appearance of

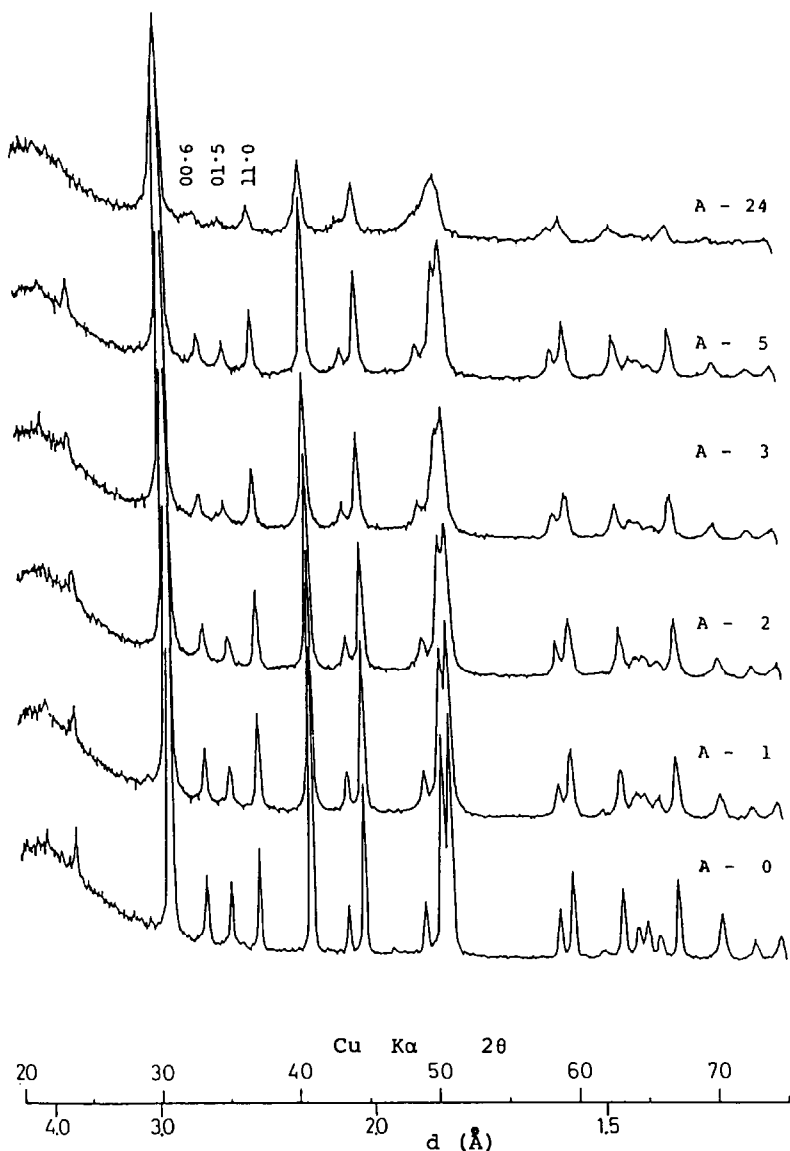


Fig. 3. XRD patterns of the ground samples (numerals attached to the sample name denote grinding hours).

this absorption band may suggest a positional disorder of the  $\text{CO}_3^{2-}$  group itself (see Sterzel [7], Goldsmith and Ross [8] and Sterzel and Schenk [9]). Moreover, the absorption intensity for the band at  $730\text{ cm}^{-1}$ , relative to that at  $880\text{ cm}^{-1}$ , can be seen to reduce gradually with prolonged grinding.

In the TG-DTA curves measured in 100%  $\text{CO}_2$  gas flow, for all the ground samples, the first endothermic peak corresponding to the partial decomposition of the  $\text{MgCO}_3$  portion in dolomite (abbreviated 1st En)

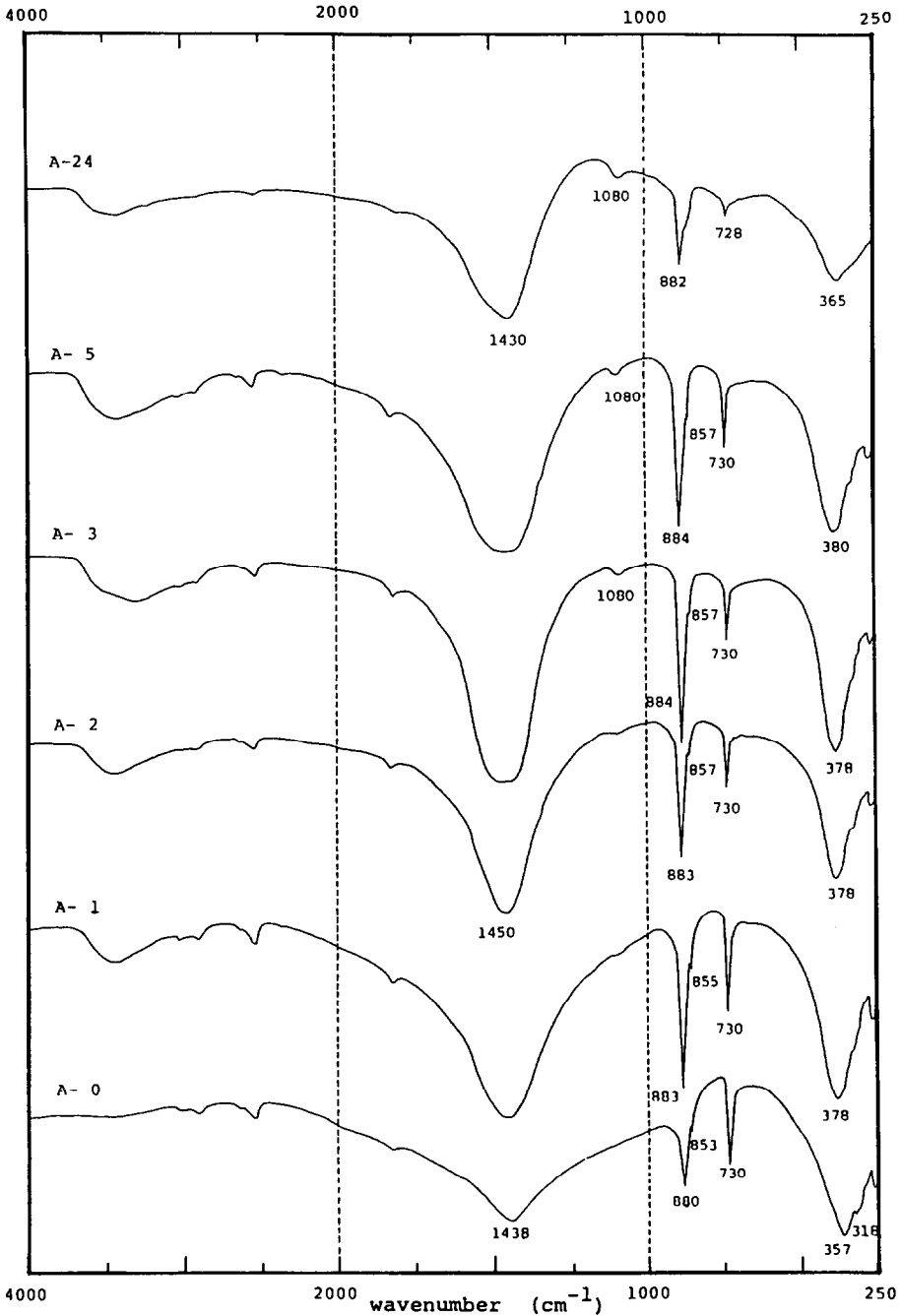


Fig. 4. IR spectra of the ground samples (numerals attached to the sample name denote grinding hours).

shifted to lower temperatures ( $748\text{--}703^\circ\text{C}$ ,  $T_e$ ) and was separated to form a doublet with peak maxima at around  $600^\circ\text{C}$  and  $700^\circ\text{C}$  ( $T_p$ ) (abbreviated 1st En-1 and 1st En-2 respectively). The decomposition temperature ranges

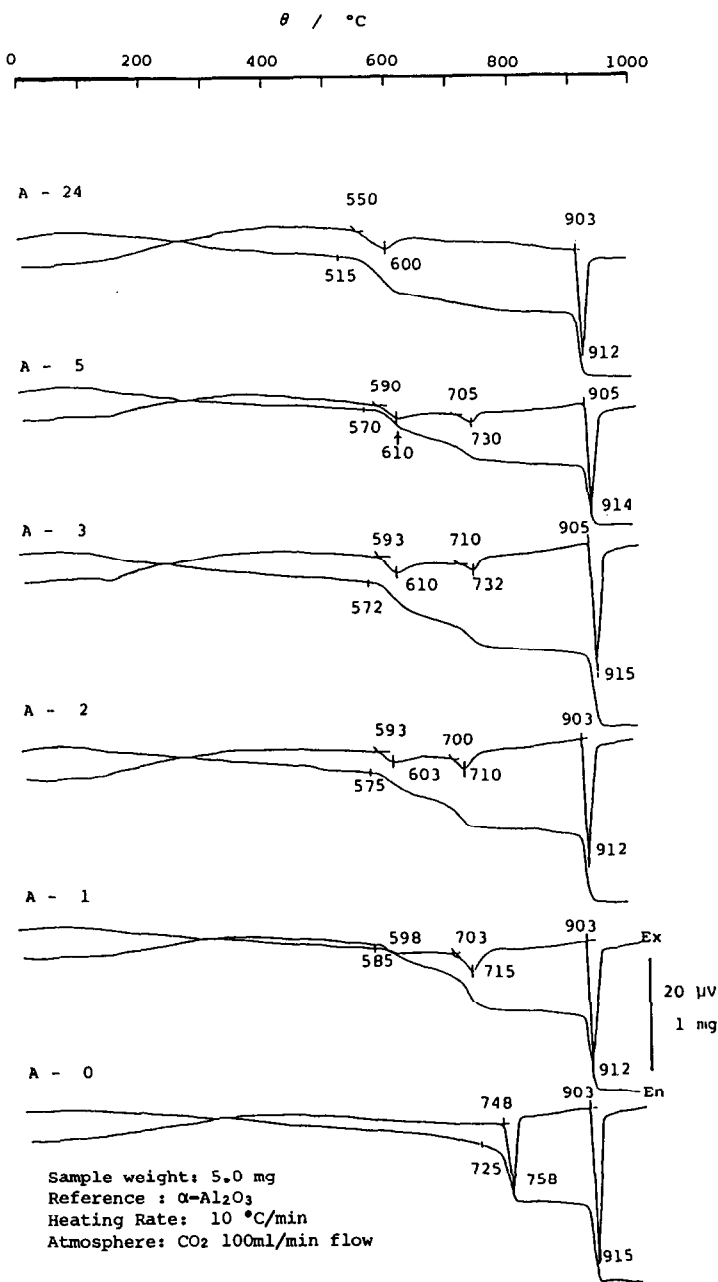


Fig. 5. TG-DTA curves of the ground samples recorded under 100%  $\text{CO}_2$  gas flow (numerals attached to the sample name denote grinding hours).

were maintained for all the samples from A-1 to A-9. The peak area of 1st En-1 increased at the expense of 1st En-2 as grinding proceeded. The TG results indicate that the initial decomposition of the  $\text{MgCO}_3$  portion is



composed of two steps and that it finally stabilizes as a single peak in the temperature range of 1st En-1, i.e. at 550°C (*Te*).

#### *The thermal decomposition in flowing CO<sub>2</sub>*

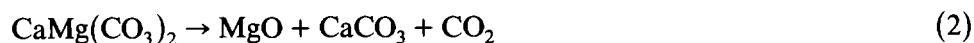
Figure 6 shows the XRD and IR patterns of the products obtained by quenching sample A-5 at the specified temperatures indicated during heating at 10°C min<sup>-1</sup>. The temperatures are indicated on the DTA curve shown at the top of Fig. 6. Here, the products are denoted d (dolomite), d\* (disordered dolomite), c (calcite), p (periclase) and 1 (lime); d\* is defined as a phase showing a superstructure reflection characteristic of dolomite in the XRD pattern, but with the principal 10·4 reflection thereof at a lower angle, indicating that this phase is a lattice-expanded one. The main product at each specified temperature is indicated with a capital letter.

At 550°C, before 1st En-1, the principal 10·4 reflection of dolomite is observed at 30.7° 2θ (Cu Kα). The monophase of disordered dolomite can be identified on the XRD pattern. At 630°C, there is normal dolomite with minor calcite, and a small amount of additional periclase can be identified at 660°C (just before 1st En-2). Dolomite decomposes completely into calcite and periclase at 750°C, after 1st En-2. The intensity for periclase increases with heating up to 900°C.

The IR patterns support the above results. An IR pattern for dolomite alone, with a weak band at 1080 cm<sup>-1</sup>, is obtained at 550°C. With heating to 630°C, the 1080 cm<sup>-1</sup> band disappears due to strain relaxation and generates a band at 713 cm<sup>-1</sup>, assigned to the ν<sub>4</sub> vibration of calcite. The bands at 413 cm<sup>-1</sup> at 660°C and at 530 cm<sup>-1</sup> at 900°C are assigned to MgO and Mg(OH)<sub>2</sub> respectively formed during the quenching process.

The results indicate that the decomposition of the MgCO<sub>3</sub> portion of the disordered dolomite occurs in the temperature range 540–600°C (corresponding to 1st En-1), and that of the original dolomite takes place at around 700°C, yielding the 1st En-2 peak in the DTA curve.

Both endothermic peaks are therefore interpreted as decomposition reactions described by the equation



Because the reactions are not distinguishable in the chemical equations, the decomposition behaviour was investigated in detail under various CO<sub>2</sub> partial pressures by changing the ratio of mixing CO<sub>2</sub> and N<sub>2</sub>.

#### *CO<sub>2</sub> pressure dependence of the decomposition*

The DTA curves for sample A-5 recorded under various CO<sub>2</sub> gas partial pressures (*P*<sub>CO<sub>2</sub></sub>) are shown in Fig. 7. It is observed that the 1st En-1 peak shifts to the lower temperature side with decreasing CO<sub>2</sub> partial pressure, in the same way as for the decomposition of CaCO<sub>3</sub>, whereas the 1st En-2 peak remains within about the same temperature range up to a *P*<sub>CO<sub>2</sub></sub> of 25.33 kPa.

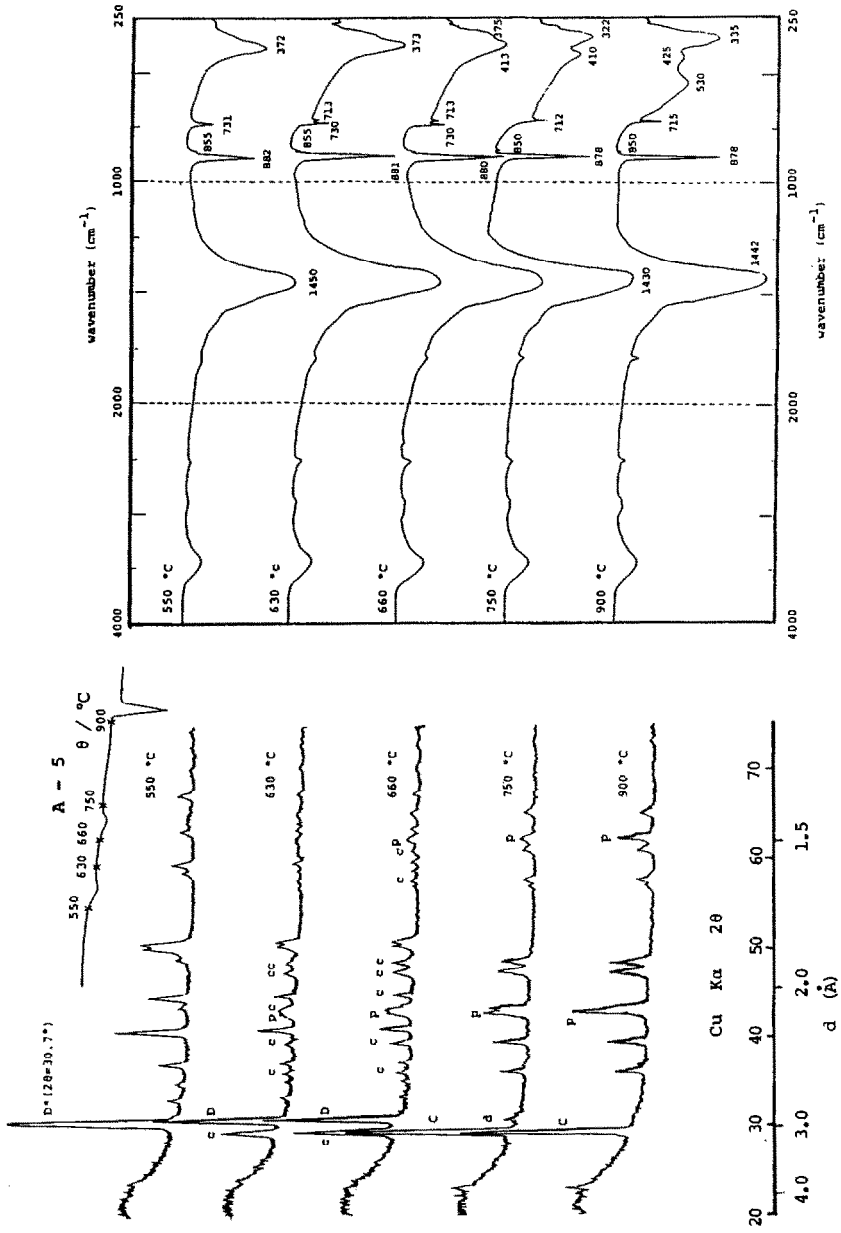


Fig. 6. Identification of products obtained during the decomposition process of a ground sample, A-5.

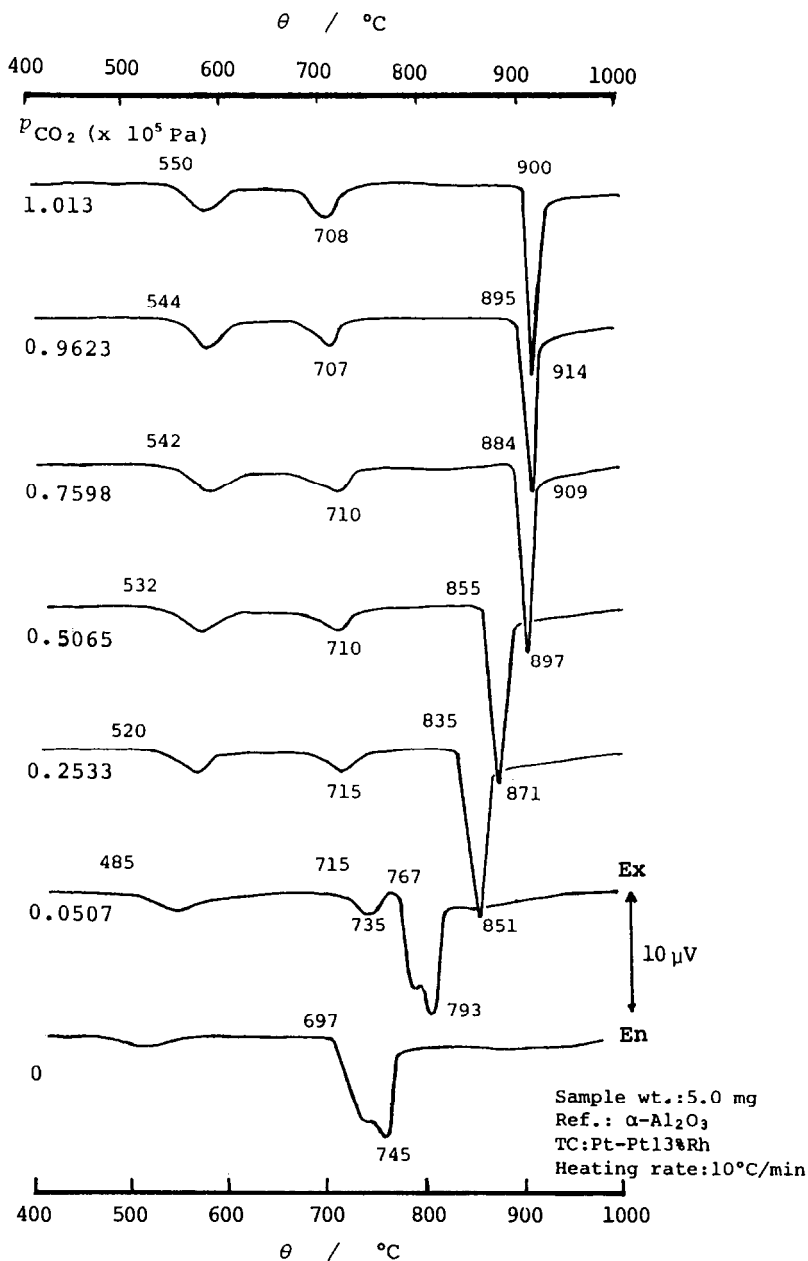


Fig. 7. DTA curves for sample A-5 recorded under systematically changed  $\text{CO}_2$  partial pressure.

Then the values of  $\ln(P_{\text{CO}_2})$  were plotted against  $T_e$  (K) for each sample, using the  $T_e$  values of 1st  $\text{En-1}$  and 1st  $\text{En-2}$  of the DTA curves recorded in varying  $\text{CO}_2$  partial pressures ( $\times 10^5 \text{ Pa}$ ): 0.0507, 0.2533, 0.5065, 0.7598 and 1.013.

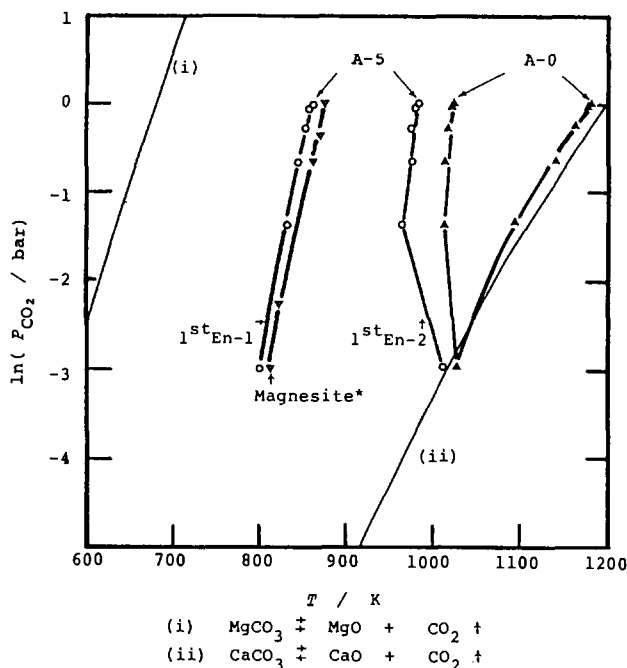


Fig. 8. Plots of  $T_e$  obtained in a mixed gas flow of  $CO_2$  and  $N_2$ . Equilibrium  $CO_2$  partial pressure vs. temperature curves are also shown. \* Experimental data for magnesite taken from the literature [19].

Figure 8 is one such curve for sample A-5: the open circles ( $\circ$ ) are for A-5; the data for magnesite ( $\nabla$ ) and for 1st En and 2nd En of the starting material A-0 ( $\blacktriangle$ ) are also given for reference. The plots of equilibrium  $CO_2$  partial pressure against temperature were calculated using the data of Robie et al. [10], and are shown as solid lines (i) and (ii) for the reactions (i)  $MgCO_3 \rightleftharpoons MgO + CO_2$  and (ii)  $CaCO_3 \rightleftharpoons CaO + CO_2$ . The data for 1st En-1 peak of A-5 agree fairly well with those of magnesite. Both observed curves are shifted considerably towards temperatures higher than the calculated values: this is explained by the extremely low rate of the decomposition reaction of magnesite (see, for example, ref. 11). Hashimoto [12] reported that this reaction becomes more sluggish with decreasing  $CO_2$  partial pressure, and that the deviation of the observed value from the calculated one increases under lower  $CO_2$  partial pressures.

The plots for 1st En-2, however, resemble fairly closely those for 1st En of the original dolomite (A-0). These features are more apparent in Fig. 9.

Figure 9 shows the superimposed TG patterns of A-5 under various  $CO_2$  partial pressures. The TG curves clearly show a decreasing rate and a decrease in the temperature range of the decomposition with a lowering of the  $CO_2$  partial pressure, whereas 1st En-2 is completely independent of the  $CO_2$  partial pressure in this range; this is known to be characteristic of

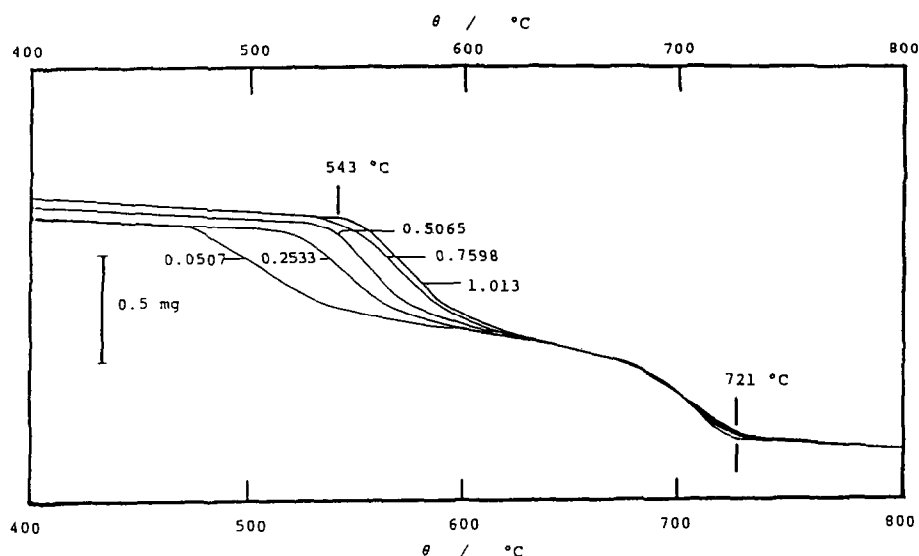


Fig. 9. TG curves obtained for sample A-5 in a mixed gas flow of  $\text{CO}_2$  and  $\text{N}_2$ . Numerical values in the figure denote the  $\text{CO}_2$  gas partial pressure,  $P_{\text{CO}_2} \times 10^5$  Pa.

dolomite (see Haul and co-workers [13–15], Hashimoto [12], Hashimoto et al. [16] and Otsuka et al. [17]). It is therefore concluded from the above results that the decomposition reactions corresponding to the 1st En-1 and 1st En-2 peaks are essentially different; the former is attributed to the decomposition of the  $\text{MgCO}_3$  portion in disordered dolomite, whereas the latter represents the partial decomposition of the original dolomite. Thus the decomposition represented by 1st En-1 is similar to that of the straightforward decomposition of magnesite, whereas that of the original dolomite represented by 1st En-2 requires another process to effect cation diffusion, or one which lowers the activation energy in order to initiate decomposition.

#### *DTA patterns of ground dolomites with little change in structure*

Under the microscope, sample K consists of coarser grains ( $400 \mu\text{m}$  on average) accompanied by smaller grains ( $20 \mu\text{m}$ ) in the interstices; sample P consists of minute uniform grains less than  $2 \mu\text{m}$  in size (see Figs. 1 and 2 above).

In Table 2 are given the physical parameters of the sample grains. Sample K-0 consisted of crystallites three times as large as those of sample P-0, while the specific surface area of the former was about one-third of the latter. The lattice strain values show, as expected, little difference between the two samples.

The DTA patterns obtained in 100%  $\text{CO}_2$  gas flow are given in Fig. 10. Concerning the 1st En peak, sample K-0 yields a broad peak at about

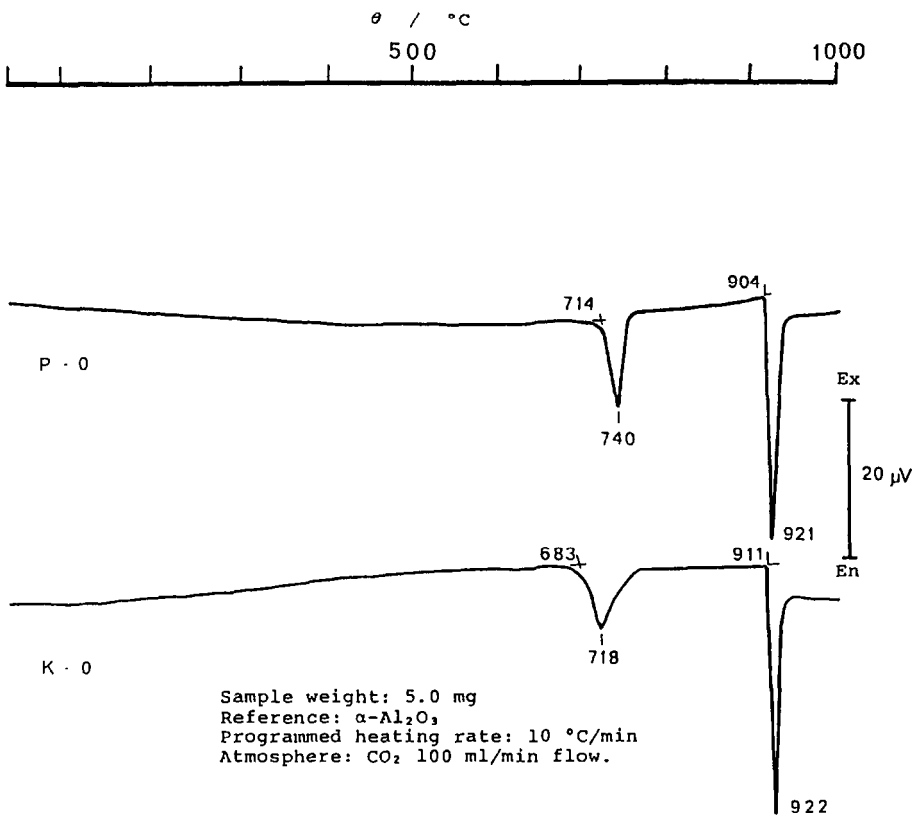
TABLE 2

Grain size, crystallite size, specific surface area and lattice strain for samples K-0 and P-0

Sample	Grain size under microscope ( $\mu\text{m}$ )	Crystallite size by XRD $D(00\cdot l)$ ( $\text{\AA}$ )	Specific surface area ( $\text{m}^2 \text{g}^{-1}$ )	Lattice strain $\eta$ ( $\times 10^{-3}$ )
P-0	$\approx 2$	389.4	1.55	2.60
K-0	20 and 400	993.2	0.51	2.75

680°C, whereas sample P-0 yields a sharp symmetrical peak at a temperature as high as 710°C, about 30°C higher than that of K-0.

Since the compositional differences between the samples are negligible in this case, this difference in temperature cannot be explained fully in terms of the substituent cations. Furthermore, as explained above, there is no substantial difference in lattice strain, and therefore the disorder in the crystal structure is considered to be about the same for both samples.

Fig. 10. DTA curves for the initial samples K-0 and P-0 recorded in  $\text{CO}_2$  gas flow.

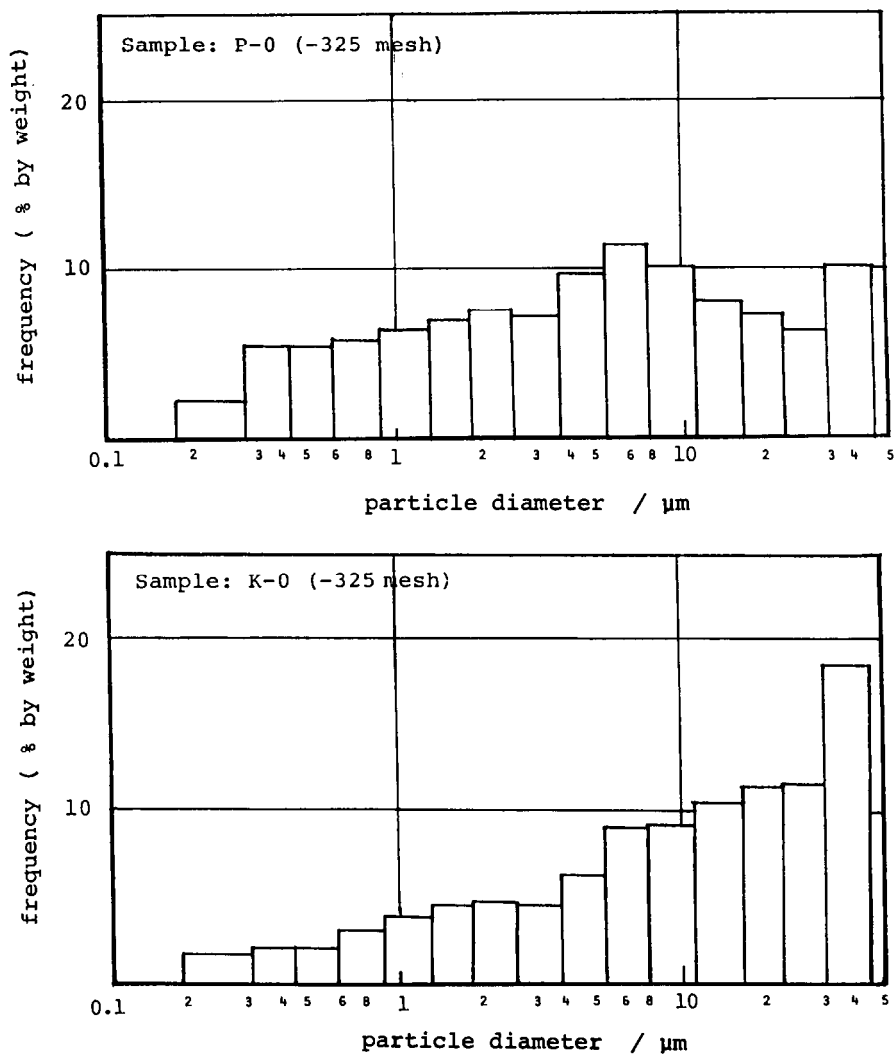


Fig. 11. Particle size distribution for samples K-0 and P-0.

Figure 11 shows the particle size distribution for sample K-0 passed through a 325-mesh sieve; particles about  $40 \mu\text{m}$  in size occur most frequently, and the remainder are distributed over a wide range of grain size, tailing smoothly to a particle size as small as  $0.2 \mu\text{m}$ . This suggests that a catalytic effect is predominant in the decomposition of sample K-0, which is quite similar to that occurring in dust explosion as reported and explained by Ochiai et al. [18]. The decomposition of sample K-0 is maintained for a longer period at a higher temperature, which is ascribed to the high population of coarser grains about  $40 \mu\text{m}$  in size. In contrast, the particle size distribution for sample P-0 is symmetrical, with a slight maximum at about  $10 \mu\text{m}$  and with a low population of grains as small as  $0.2 \mu\text{m}$  in size. Thus,

in this case, the catalytic effect ascribed to a smooth distribution of smaller grains cannot be expected, and therefore a higher temperature is necessary to effect decomposition of the whole sample.

## CONCLUSIONS

Thermal analysis was used to investigate the effect of grinding on dolomites. It was found that the temperature and shape of the first endothermic peak of the DTA curve in CO<sub>2</sub> may provide information on the particle size distribution as well as on the particle size. In addition, thermal analysis in a systematically controlled atmosphere is sensitive to the presence of two different phases which are not distinguished positively by XRD and IR analysis.

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## REFERENCES

- 1 J. Šesták, Thermophysical Properties of Solids, in G. Svehla (Ed.), Comprehensive Analytical Chemistry, Vol. XII part D, Elsevier, Amsterdam, 1984.
- 2 Y. Arai, Material Chemistry, Baifu-kan, Tokyo, 1987.
- 3 W.F. Bradley, J.F. Burst and D.L. Graf, *Am. Mineral.*, 38 (1953) 207.
- 4 Y. Arai and T. Yasue, *Kogyo Kagaku Zasshi*, 72 (1969) 1980.
- 5 Y. Arai and T. Yasue, *Gypsum Lime*, 103 (1969) 319.
- 6 Y. Arai and T. Yasue, *Gypsum Lime*, 104 (1970) 17.
- 7 R. Ozao, R. Otsuka and J. Arai, *Gypsum Lime*, 201 (1986).
- 8 W. Sterzel, *Naturwissenschaften*, 51 (1964) 505.
- 9 J.A. Goldsmith and S.D. Ross, *Spectrochim. Acta*, 22 (1966) 1069.
- 10 W. Sterzel and C. Schenk, *Naturwissenschaften*, 55 (1968) 180.
- 11 R.A. Robie, B.S. Hemingway and J.R. Fischer, *U.S. Geol. Surv. Bull.*, 1452 (1979).
- 12 R.L. Stone, *J. Am. Ceram. Soc.*, 37 (1954) 46.
- 13 H. Hashimoto, *Gypsum Lime*, 146 (1977) 33.
- 14 R.A.W. Haul and H. Heystek, *Am. Mineral.*, 37 (1952) 166.
- 15 R.A.W. Haul and J. Markus, *J. Appl. Chem.*, 2 (1952) 298.
- 16 H.G.F. Wilsdorf and R.A.W. Haul, *Nature*, 167 (1951) 945.
- 17 H. Hashimoto, T. Tomisawa and S. Hara, *Gypsum Lime*, 188 (1984) 27.
- 18 R. Otsuka, S. Tanabe and K. Iwafuchi, *J. Min. Metall. Inst. Jpn.*, 96 (1980) 581.
- 19 M. Ochiai, R. Ozao, Y. Yamazaki, R. Otsuka and A. Holz, *Proc. Inst. Stat. Math.*, 38 (1990) 257.
- 20 K. Iwafuchi, M. Sc. Thesis, Waseda University, Tokyo, Japan, 1979.