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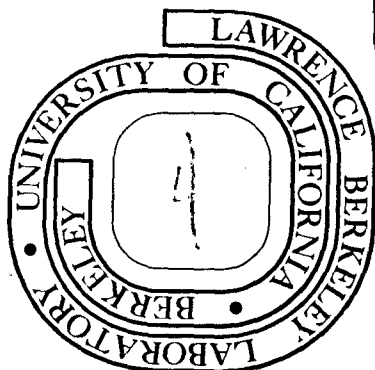
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EFFECT OF CO₂ ON THE
OXIDE DECOMPOSITION PRODUCTS OF CALCITE

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ABSTRACT

Calcium carbonate powder was decomposed isothermally at 700°C in vacuum and in CO₂ pressures from 0.1 torr to 9.0 torr. The surface area, crystallinity, and morphology of the calcium oxide product were evaluated. Calcite decomposed in CO₂ pressures less than 0.9 torr produced linear plots of surface area in m²/mole vs. mole % CaO for each pressure studied, and there was no change in apparent particle shapes. A high degree of line broadening was exhibited by x-ray diffraction patterns of the product from vacuum decomposition. Calcite decomposed in a 9.0 torr CO₂ pressure produced a calcium oxide of very low surface area that exhibited no line broadening. At this high CO₂ pressure, significant changes in the surface morphology were observed which indicated the occurrence of considerable sintering, and possibly the formation of a CaCO₃-CaO eutectic liquid.

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I. INTRODUCTION

In view of the importance of CaO to industry - from traditional uses in cements, soda-lime-silica glasses, and refractories to more advanced applications such as SO₂ getters in stack gases - it is desirable to be able to control the properties of the calcium oxide which is obtained from calcite (CaCO₃).

Calcite decomposition, $\text{CaCO}_3(\text{s}) = \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$, has been studied extensively.¹⁻⁶ There is considerable evidence that CO₂ catalyzes the crystallization and sintering of CaO powders.^{4,6,7} However, previous work has provided no clear correlations between the surface area, crystallinity, and surface morphology of CaO produced when calcite is decomposed under accurately controlled CO₂ pressures.

Various theories have been proposed to describe the evolution of surface area as decomposition progresses. The micelle theory by Gregg⁸ attempts to explain the production of an "active" solid by the presence of a large internal surface and by the existence of a strained lattice in which the atoms would be displaced from their normal positions in a perfect lattice. The micelles are hypothesized to form when the strained lattice recrystallizes into the stable oxide lattice, thus increasing the surface area. The surface area is then expected to decrease by sintering according to the following guidelines: when $T/T_m < 0.2$, where T_m is the absolute melting temperature, adhesion between the micelles predominates; in the range of $0.2 < T/T_m < 0.5$ surface diffusion is more important; for $T/T_m < 0.5$ bulk diffusion is the major method of mass transport. Nicholson⁹ developed a model that predicts a maximum surface area will be reached shortly before the sample is fully decomposed.

Searcy and Beruto¹⁰ have developed a general theory for decomposition reactions that also predicts an increase in surface area during decomposition. In this theory, a solid AB decomposes to a porous solid A plus a gas B. The model can be shown schematically as illustrated in Fig. 1. Pillars of solid A are formed as AB decomposes. This model differs from that of the micelle theory in that the area increase is present from the beginning of decomposition and does not require recrystallization to account for the increase in area. For CaCO_3 the external dimensions remain constant during decomposition,⁵ so the porosity can be calculated from the relative molar volumes of CaO and CaCO_3 . These calculations show that CaO produced from CaCO_3 should have a porosity of about 55%. If the spacing between adjacent pillars of CaO along the reaction front is small, the internal surface area of the porous CaO particles produced by CaCO_3 decomposition can be very high.

Another feature of this theory is that it incorporates the possibility of formation of a metastable CaO phase. Metastable oxide molecules (not a separate phase) had earlier been assumed to be a possible intermediate product of calcite decomposition.⁶ In fact an amorphous, and therefore metastable, form of CaO has recently been identified.¹

Glasson³ has studied the surface area of CaO produced from decomposition in vacuum and air of CaCO_3 which had an initial surface area of $2.5 \text{ m}^2/\text{g}$. Using standard 5 hour runs, he found a maximum surface area of $43 \text{ m}^2/\text{g}$ at 750°C . Glasson attributed the increase in area to the recrystallization of CaO from a pseudo CaCO_3 lattice to very small crystallites with a more stable lattice. He reported that further calcination after complete decomposition always reduces the surface area.

In a parallel study Glasson⁴ examined the effect of CO₂ on the surface properties of the CaO product. The surface area was observed to decrease from 31 m²/g to 16 m²/g when a fully recrystallized CaO sample was calcined for 5 hours at 750°C in a CO₂ pressure of 30 torr (≈1/2 the equilibrium pressure). A limestone sphere decomposed in a CO₂ pressure of 30 torr at 750°C had a reaction rate only 20% less than the vacuum rate, but a reduction in surface area of 70%. Glasson attributed this reduction in area to an enhancement of sintering caused by calcite formed at the surface by reaction of CaO with chemisorbed CO₂. Glasson argued that surface diffusion becomes important at lower temperatures when CO₂ is present due to the lower carbonate melting temperature and thus a larger T/T_m ratio.

The effect of CO₂ on grain size has been studied by Cremer and Nitsch.⁷ Samples of CaCO₃ were decomposed at 850°C in CO₂ pressures ranging from 120 to 220 torr (P_{eq} ≈400 torr). The results indicated an increase in CaO grain size (which implies a decrease in surface area) as the CO₂ pressure increased.

Glasson's data thus appears to support the Gregg model, which predicts that surface areas will not vary linearly with the fraction of completion of the reaction, while the Searcy and Beruto model suggests that it may. The experimental program was designed to a) test the appropriateness of the alternate models to describe CaO formation from calcite, and b) to clarify the apparent catalysis of CaO condensed phase diffusion and crystallization by CO₂. As work progressed it became apparent that the measured rates of decomposition of powders provided interesting information about the reaction mechanism, despite the

difficulties of assessing the fraction of the surface area of the powder that contributes to the measured flux. Obtaining kinetic data thus became another objective for this study.

II. EXPERIMENTAL

Mallinckrodt analytical reagent CaCO_3 powder (see appendix I for spectrographic analysis) was used for all experiments. The average particle size was $3\mu\text{m}$ (Fig. 2), and the specific surface was $0.7 \text{ m}^2/\text{g}$ ($70 \text{ m}^2/\text{mole}$). A sample with a weight of $0.7 \pm 0.001\text{g}$ was placed in a platinum foil basket 2 cm square. The basket was hung from a Cahn RG recording microbalance in a resistance furnace (Fig. 3). For vacuum experiments a silicone oil diffusion pump maintained the pressure below 1×10^{-4} torr. When backpressures of CO_2 were required the desired pressure was maintained by simultaneously opening a leak valve and throttling the exhaust valve to the mechanical roughing pump. The pressure was measured with a capacitance manometer having a range of 0.001 - 10.0 torr with an accuracy to within 1% of the reading. The CO_2 pressure could be maintained to within ± 0.02 torr at 0.9 torr and ± 0.1 torr at 6.0 torr throughout the entire decomposition. At 9.0 torr the initial rate of decomposition was so slow that a very long time would have been required to decompose the sample. Therefore, for the runs at 9.0 torr the samples were heated in 9.0 torr of CO_2 , the pressures were reduced to initiate decomposition, and then were increased to 9.0 ± 0.1 torr for the remainder of the decomposition.

Tungsten elements were used for the first experiments. A bluish substance was deposited in the furnace at higher CO_2 pressures (>3.0 torr). This product is presumed to be a tungsten oxide produced by reaction of CO_2 with the tungsten elements. The reaction would also yield CO. To determine the concentration of CO in the furnace atmosphere, samples of the atmosphere were analyzed with a gas chromatograph. A

maximum of 8% CO was found. CO was not expected to influence the decomposition kinetics, but to be certain that the CO did not influence the reaction, the tungsten elements were replaced with Pt-10% Rh elements. Experiments repeated with the platinum elements were in good agreement with similar experiments using tungsten elements.

The microbalance was used to monitor the weight loss during decomposition as well as to obtain kinetic data. When a desired fraction of decomposition was achieved in a run made in CO₂, the CO₂ was pumped out and the sample was cooled as rapidly as possible to prevent further decomposition. Decomposition usually stopped within 1 to 2 minutes from the time the furnace power was reduced. This corresponded to a maximum of 5% of the total weight lost.

To minimize reaction of the CaO product with atmospheric moisture and CO₂, the furnace chamber was filled with Ar or dry N₂ to atmospheric pressure. The sample was removed and weighed as rapidly as possible, and stored in a 15 x 45 mm sealed bottle. The total weight loss during each decomposition was determined by comparing before and after weighings of the sample and basket. The results obtained by this method were within 8% of the values obtained from the continuous recording microbalance. These weight changes were used to calculate the fraction of sample decomposed at the time the run was discontinued. The sample was stored until needed in a vacuum desiccator to further reduce hydration.

Surface Area Determination

The surface area was determined by the BET¹² method immediately after the final weighing. The BET apparatus was manufactured by Quantachrome Corp. In this apparatus N₂ is adsorbed on the surface of

the sample from a mixture of He and N₂ when the sample is cooled by liquid N₂. A thermal conductivity detector measures the amount of N₂ that desorbs when the sample is warmed to ambient temperature. The amount of N₂ adsorbed at various partial pressures can be used to determine the surface area. Even though no outgassing procedure was used, the reproducibility was within 1% regardless of the sample's surface area. The manufacturer claims¹³ that the areas obtained with this apparatus are within 3% of the areas obtained using other sorption devices.

X-ray Analysis

The sample was packed in an aluminum holder and irradiated in a Picker x-ray diffractometer using Cu K_α radiation. The operating conditions were: 14 ma, 40 Kv, 2 degrees 2θ/minute, τ = 3 sec, and counts/sec = 400. The first scan was from 2θ = 28° to 2θ = 45°. This range includes the major peaks of the three possible phases: CaO - 37.4°, CaCO₃ - 29.4°, and Ca(OH)₂ - 34.1° (see appendix II for complete data). The CaO hydrated rapidly, so the first scan was the best indication of the crystallinity of the CaO product. A second scan was made over a wider range to determine the extent of the hydration. The hydration was accompanied by an expansion which raised the sample out of the holder. The sample was pressed flat when necessary between the two scans.

Morphology Analysis

Samples were dispersed in CCl₄ since a tendency of the powder to form large agglomerates otherwise made examination with a scanning electron microscope difficult. The dispersion was dropped on a carbon coated holder using an eyedropper, and a layer of gold approximately

200 Å thick deposited on the sample. Alternate methods of preparation included using acetone in place of CCl_4 , and dropping the powder directly on a wet carbon coated surface. Samples prepared by these methods gave results similar to those found for samples prepared using the CCl_4 technique.

III. RESULTS

Weight Loss Data

Weight losses were measured isothermally as a function of time for reactions carried from 15% completion to 100% completion for samples heated in vacuum and in CO_2 pressures for 0.1, 0.9 and 9.0 torr. A few runs were made at pressures between 0.9 and 9.0 torr. All runs were made at 973°K where the equilibrium decomposition pressures is 30 torr.¹⁴ Results from the original chart were replotted as shown in Fig. 4. The hump in the beginning part of the curve that appears to be a weight gain is due to the recoil force of the CO_2 molecules acting on the holder. The kinetic data shown are for the linear range of the plot for which the rates were the maximum value. The area used in the calculations is the cross section area of the basket (4cm^2). Good reproducibility was obtained in the rates for vacuum runs and for runs at $P_{\text{CO}_2} = 0.1$ torr. At $P_{\text{CO}_2} = 0.9$ torr, some variations in the rates were encountered. The rates for vacuum and for CO_2 pressures of 0.1 torr and 0.9 torr were all equal within experimental error, with a standard deviation of 0.4 mg/min cm^2 . As the pressure increased above 0.9 torr the rates decreased sharply (Fig. 5). At 9.0 torr the initial rate was very slow (Fig. 6). Samples for which the pressure was lowered to about 1.5 torr for 3 minutes (Fig. 6, point A) had faster rates when the CO_2 pressure was increased back to 9.0 torr.

Surface Area

Figures 7-10 show the changes in surface area as the reaction proceeded. For vacuum and $P_{\text{CO}_2} = 0.1$ torr the plots of area vs. mole % CaO are linear. At $P_{\text{CO}_2} = 0.9$ torr some of the points fall on a linear

plot, but others show lower areas. These low points were always associated with a slower rate of linear decomposition than that which was observed when the points fell on the linear plot. The surface areas produced by heating under the intermediate range of pressures (1.5, 3.0, 4.5, and 6.0 torr) do not show any clear trend except that they are all lower than the corresponding areas at 0.9 torr. Decomposition at pressures of 9.0 torr produced sharp reductions in surface areas in three of four runs. The exception probably reflected the fact that the initial decomposition was carried out for a longer time than the others in a low CO_2 pressure. One sample was fully decomposed in vacuum, then heated in 9.0 torr of CO_2 for 24 hours. This procedure produced a surface area one fifth that for a vacuum decomposition.

X-ray Analysis

The x-ray patterns were examined for the presence of CaO. The CaO produced from vacuum decomposition (Fig. 11) showed a high degree of line broadening. The CaO peaks became progressively higher and sharper as the CO_2 pressure present during decomposition was increased (Figs. 12-14). At 9.0 torr the CaO peaks were very sharp (Fig. 15). CaO produced from vacuum decomposition and then sintered in a 9.0 torr CO_2 pressure has a very sharp CaO pattern and a small peak of CaCO_3 (Fig. 16). As little as 3 mole % CaO was detectable when CaCO_3 was decomposed at 9.0 torr, whereas in vacuum the lower limit of detection was about 50 mole% CaO. Peak heights and widths at half maximum intensities were measured, and the height to width ratios were calculated. The height to width ratios generally shifted towards larger values as the CO_2 pressure increased. Quantitative evaluation of the crystallinity was difficult because of

variations introduced during x-ray specimen preparation and because of hydration. Hydration generally produced very broad Ca(OH)_2 peaks while reducing the intensity and increasing the width of the CaO peaks.

Scanning Electron Microscopy

The CaCO_3 powder consists of block-like particles (Fig. 2) with an average particle cross section of about $3\mu\text{m}$. The external dimensions do not change when the particles are decomposed in vacuum or in CO_2 pressures less than 9.0 torr (Fig. 17). The porosity can be calculated from the molar volumes of CaCO_3 and CaO to be about 55%. Figures 18-20 show scanning electron micrographs of CaO produced from CaCO_3 decomposition at CO_2 pressures less than 9.0 torr. At a 9.0 torr CO_2 pressure, two interesting changes in the morphology are observed. A first change that appears is the formation of "dimples" on the surface of some particles (Fig. 21). Second, the particles show some sintering with such features as neck formation (Figs. 22 and 23). Decomposition in vacuum followed by sintering in 9.0 torr CO_2 produced similar neck formation (Fig. 24).

IV. DISCUSSION

A plot of area in m^2/g vs. mole % CaO (Fig. 25) gives a misleading impression that the surface area increases more rapidly as the reaction approaches completion. The curvature is due to the different molecular weights of CaCO_3 and CaO (100.1 and 56.1 respectively). Plots of area in m^2/mole vs. mole % CaO (Figs. 7-10) are linear at CO_2 pressures less than 0.9 torr. In this range of pressures, the CaO product has a constant molar area throughout the entire decomposition.

In the measurements at low CO_2 pressures, no decrease in total surface area was noted as the fraction of decomposed calcite approached 100%. This observation at first sight appears to disagree with Glasson's^{3,4} experimental observations, and disagrees with predictions of Nicholson's model,⁹ which was designed to explain data like Glasson's. Glasson observed^{3,4} in vacuum decompositions that the CaCO_3 diffraction pattern was apparent after CO_2 evolution was complete. This justifies the hypothesis of the existence of the CaO in the form of a pseudo lattice of CaCO_3 . In Glasson's experiments further heating first increased then decreased the surface area. Glasson attributed the increase in area to the recrystallization of the oxide from the CaCO_3 -like transition structure. The decrease was explained by sintering of the CaO. The exact time for complete decomposition is not clear from the paper since time measurements apparently were used, rather than weight measurements. The changes observed could have occurred before the sample was fully decomposed.

In the present study, decompositions in vacuum gave surface areas that varied linearly with the mole fraction of CO_2 evolved and reached a maximum at $\approx 99\%$ theoretical decomposition. No reduction in area was

observed in this study when a sample decomposed in vacuum was heated for an additional 17 hours at 700°C or when a sample decomposed in a 0.1 torr CO₂ pressure was heated for an additional 15 hours at 700°C. Beruto and Searcy found that a CaO formed by vacuum decomposition at similar temperatures did not develop sharp x-ray peaks when heated to 1050°C.⁵

It seems probable that Glasson's samples which were nominally decomposed in vacuum may in fact have relatively high CO₂ pressures inside the powder beds of unspecified size³ and CaCO₃ lumps.⁴ Circumstantial evidence for this supposition is the fact that his highest observed surface area at 750°C was 43 m²/g compared to 95 m²/g found in the present work. The present study shows a change in the decomposition behavior at high CO₂ pressures to a behavior more similar to that reported by Glasson, in that surface areas probably decreased with time because of sintering after reaction was completed. This question was not quantitatively studied. A second observation that suggests that Glasson's pressures were higher than he supposed is his observation that rates in vacuum were only about twice as fast as in air. A much greater difference would be expected because in air diffusion would be rate limiting, rather than a step of the chemical decomposition.

The surface area data of the present study obtained at CO₂ pressures less than 0.9 torr would support the model developed by Beruto and Searcy. In this model the plot of area vs. mole % CaO would be linear as long as no sintering of CaO occurs subsequent to its formation. Sintering is usually slow for oxides at a temperature which is such a small fraction (here 0.27) of the melting point.

When decomposition was carried out in CO_2 pressures of 0.1 and 0.9 torr the areas were lower than found for decomposition in vacuum, but the plots remained linear (Fig. 8 and 9). Rates of decomposition at these pressures were nearly the same as in vacuum (Fig. 5). These results imply that at pressures of 0.9 torr and less the decomposition mechanism is probably essentially the same as in vacuum, but the spacings between pores and pore diameters probably increase somewhat when the pressure of CO_2 is increased. In consequence, the surface areas would decrease with pressure.

Early attempts to observe the pores in CaO from calcite decomposition in vacuum with a scanning electron microscope were unsuccessful.⁵ Recent work in which air was more rigorously excluded has shown ridges, which probably separate tubular pores, that are about 1 μm apart.¹⁵

The CaO produced in vacuum had a high degree of line broadening. Line broadening in x-ray diffraction patterns can be the result of a small particle size, internal strains in the lattice, impurities, or irregularities in ordering of the ions of the lattice.^{16,17} From the data it is impossible to determine which of these effects is responsible for the observed line broadening. Furthermore, because of possibly large effects of variations in packing and hydration on the diffraction pattern of the CaO produced from CaCO_3 decomposition, calculations from line broadening measurements should be viewed cautiously. But if strain and disorder are assumed to be negligible, the CaO particle size calculated from the line broadening for a vacuum decomposition is about 120 Å. It is probable that the CaO is in fact strained with some local disorder

in the ions.

Pressures of CO_2 in the range between 0.9 and 9.0 torr affected the surface area and crystallinity of the CaO somewhat erratically. In this pressure range, decomposition of some samples was significantly slower than decomposition of samples decomposed at lower pressures. Slower decomposition rates produced lower surface areas and sharper CaO diffraction peaks.

No significant line broadening was exhibited by samples decomposed at a 9.0 torr CO_2 pressure. Surface areas were distinctly smaller and decomposition rates were very much slower than found when pressures were lower. Changes in particle shapes (dimpling, neck formation, and sintering) could be observed by scanning electron microscopy for these samples (Figs. 21-23).

It is apparent that the decomposition mechanism is different at 9.0 torr than at 0.9 torr or lower. At high pressures, CO_2 must by some means catalyze the sintering and crystallization of ordered CaO from smaller and probably strained CaO particles thus reducing the surface area and producing sharp x-ray patterns.

The driving force for sintering and crystallite annealing must be the reduction in surface free energy and strain energy. The mechanism of sintering and annealing could be surface diffusion. Bulk diffusion, which would be enhanced by solution of CO_2 as CO_3^- ions in the CaO lattice, might also occur. It has been reported that CaO dissolves up to 4% CO_2 at 900°C.¹⁸ The present study showed only 98-99% of the theoretical weight loss for complete decomposition could be obtained, and the difference between the theoretical and actual weight losses

increased as the CO_2 pressure increased. But non-stoichiometry in the original CaCO_3 could also account for this discrepancy.

The sample decomposed in vacuum and then heated in a 9.0 torr CO_2 pressure absorbed 8 mole % CO_2 . On cooling, this sample showed a sharp CaO diffraction pattern and a weak CaCO_3 diffraction pattern (Fig. 16). The CaCO_3 pattern was not expected since the pressure was below the equilibrium pressure for the stable oxide. But a metastable form of CaO, such as produced in vacuum, could react with CO_2 at a pressure below the normal equilibrium pressure. A difference in free energy between the stable and metastable oxide of 3000 cal/mole¹⁰ would correspond to an equilibrium pressure of 6.4 torr for the metastable phase, so that reaction of the metastable phase with a 9.0 torr CO_2 pressure would be thermodynamically favorable.

One explanation for the almost liquid-like appearance of some parts of the oxide after annealing at 9.0 torr is that a viscous eutectic liquid was formed. A eutectic point between CaO and CaCO_3 has been reported at 1240°C, much higher than 700°C.¹⁹ However, the presence of a metastable CaO would lower the eutectic temperature.

The effect of CO_2 on the decomposition rate was consistent with findings of previous work.²⁰ At pressures below 0.9 torr the decomposition rate is nearly independent of pressure, but at 9.0 torr the rate is markedly reduced. In fact, at 9.0 torr the initial rate was almost too low to measure. The rate was increased by lowering the pressure for a short time then raising the pressure back to 9.0 torr. Originally it was believed this process increased the number of nuclei. If nucleation limited the rate of decomposition, one would expect an increase in the

rate during the initial period of decomposition. The rate would increase because more nuclei would be formed with time as sites for additional decomposition. A linear rate would imply that nucleation is not rate limiting. Here sufficient nuclei are present for growth (decomposition of CaCO_3 to form CaO) to occur at a linear rate. The one experiment performed at a constant pressure of 9.0 torr throughout the entire length of the decomposition did not produce conclusive results on the effect of time on the rate. The slow rate at 9.0 torr could also be explained by the production of a different form of CaO at higher pressures. The stable form of CaO might be produced directly at 9.0 torr, rather than from formation of amorphous CaO followed by subsequent transformation as is apparently required at lower pressures. The rate of direct formation of crystalline CaO should be slower than the rate of decomposition to a metastable CaO since more atomic rearrangement is required.

One final point to consider concerning the rate data is the large discrepancy between the flux from a single crystal decomposed in vacuum and the flux from a powder decomposed in vacuum. The flux from the powder sample, when the entire area of the powder as determined from BET measurement is used as the area factor, is about two orders of magnitude lower than the flux from a single crystal.¹ The flux obtained using the cross section area of the holder gave good agreement with the single crystal flux. Surface areas on samples taken from the top and bottom of a powder bed decomposed 50% gave equal values. This result indicates that each particle in the bed decomposed at a rate per unit area about 0.01 times that characteristic of single crystals. This result would be

easily understood if the decomposition rate at low pressures were sensitive to background CO₂ pressures. Then one would simply conclude that a pressure buildup in the pores of each particle reduces the flux per unit area of a particle. But below a 0.9 torr CO₂ pressure the rate is pressure independent. Surface cooling of the particles could not explain this difference because a drop of about 170°C would be required to explain the low flux from powders. A maximum drop of 20°C was observed. At present no explanation for this unusual behavior of the powders is apparent.

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APPENDIX I

Semi-quantitative spectrographic analysis for Mallinckrodt AR CaCO₃

<u>Element</u>	<u>Percent (reported as oxide)</u>
Ca	Principal constituent
Sr	0.025
Mg	0.02
Fe	0.003
Mn	0.002
Ba	0.001
Al	0.001
Cu	< 0.001
K	< 0.5
Na	< 0.05
Si	< 0.005

APPENDIX II

Calcite (CaCO_3) JCPDS* number 5-0586

d	I/I ₁	2θ
3.86	12	23.0
3.035	100	29.4
2.845	3	31.4
2.495	14	36.0
2.285	18	39.4
2.095	18	43.2
1.927	5	47.1
1.913	17	47.5
1.875	17	48.5
1.626	4	56.5
1.604	8	57.4

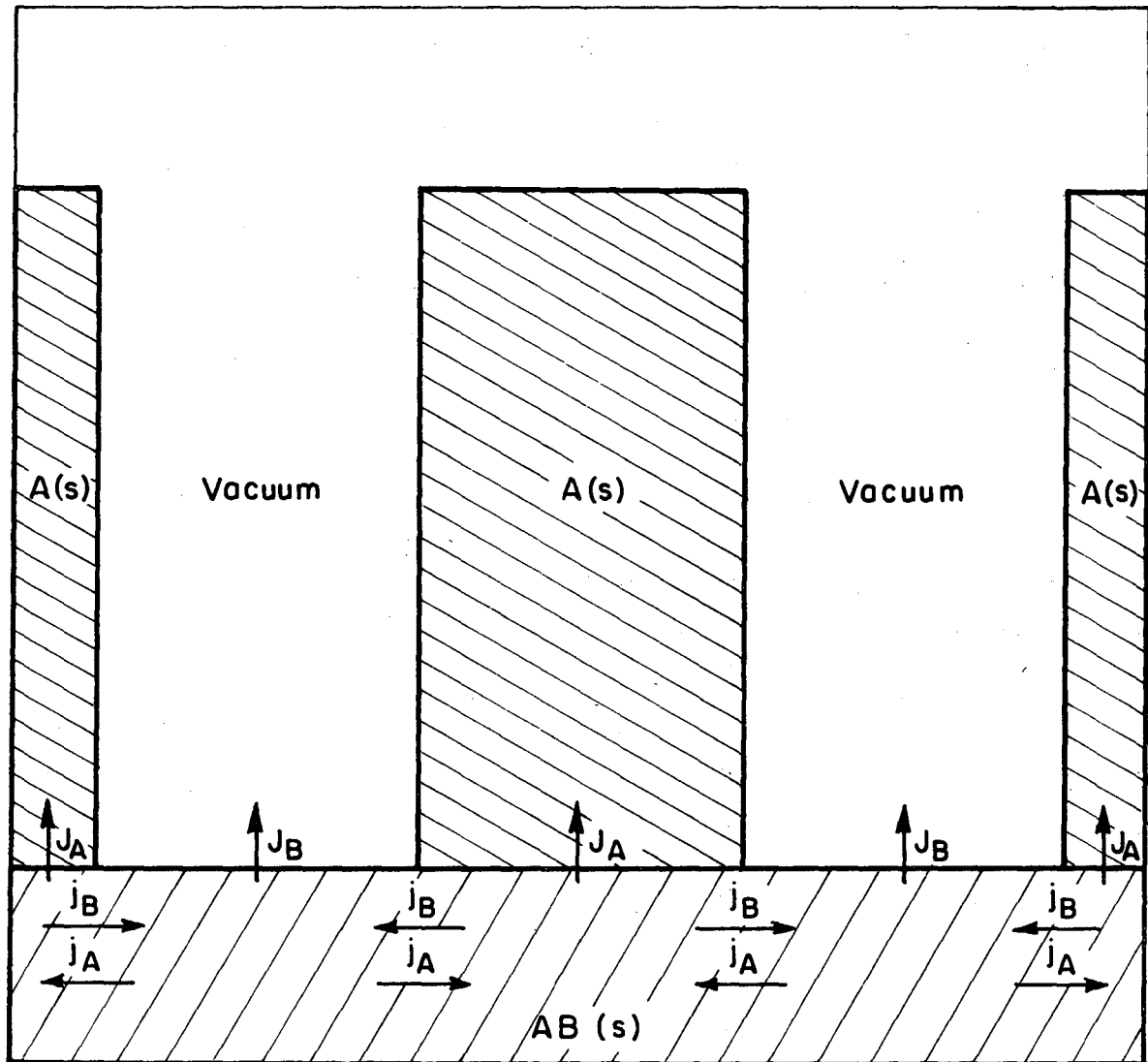
Calcium oxide (CaO) JCPDS number 4-0777

d	I/I ₁	2θ
2.778	34	32.2
2.405	100	37.4
1.701	45	53.9
1.451	10	64.1
1.390	5	67.3
1.203	4	79.6
1.1036	4	88.5
1.0755	9	91.5

Calcium hydroxide (Ca(OH)_2) JCPDS number 4-0733

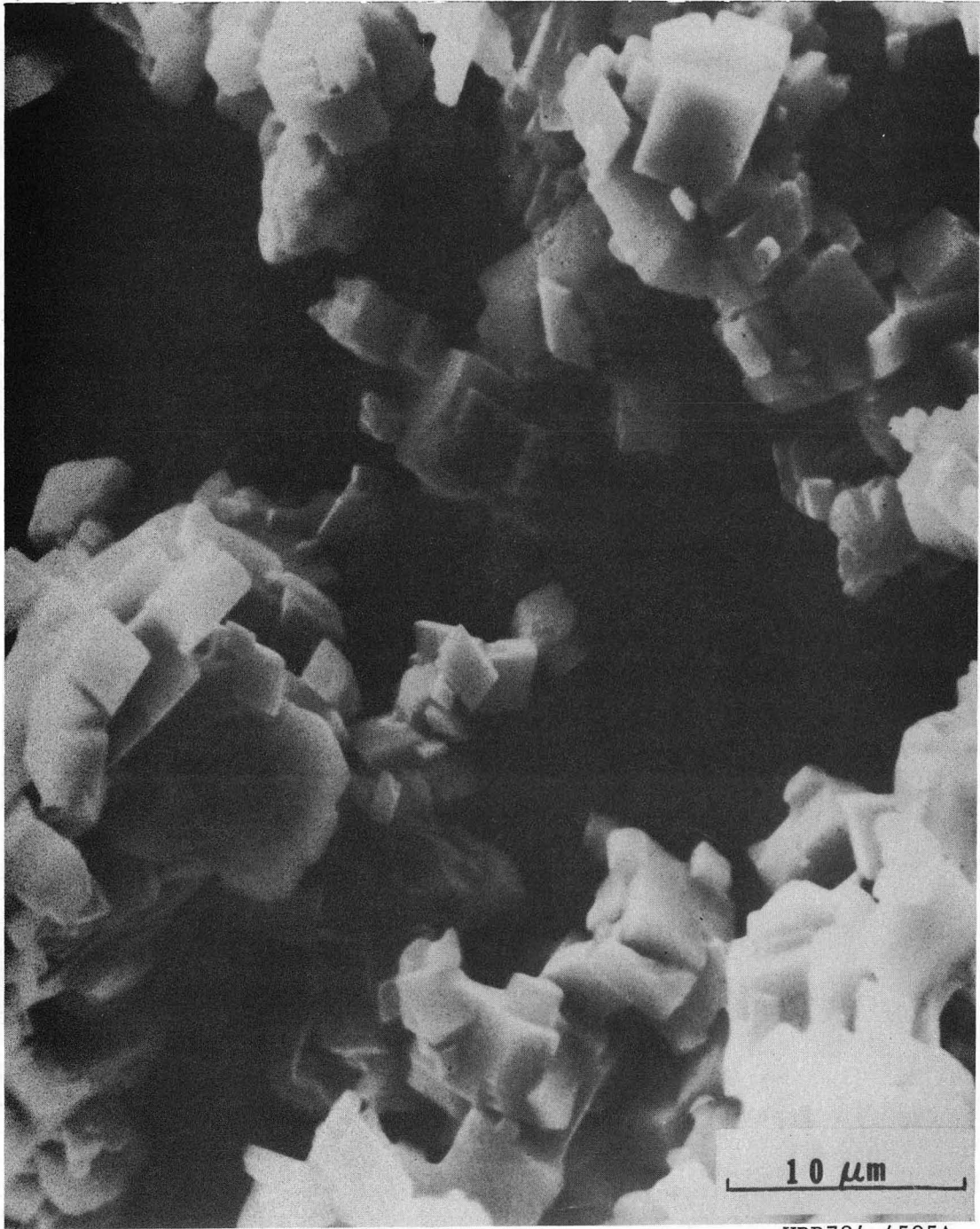
d	I/I ₁	2θ
4.90	74	18.1
3.112	27	28.6
2.628	100	34.1
1.927	42	47.1
1.796	36	50.8
1.687	21	54.3
1.484	13	62.5
1.449	13	64.2

* Joint Committee on Powder Diffraction Standards



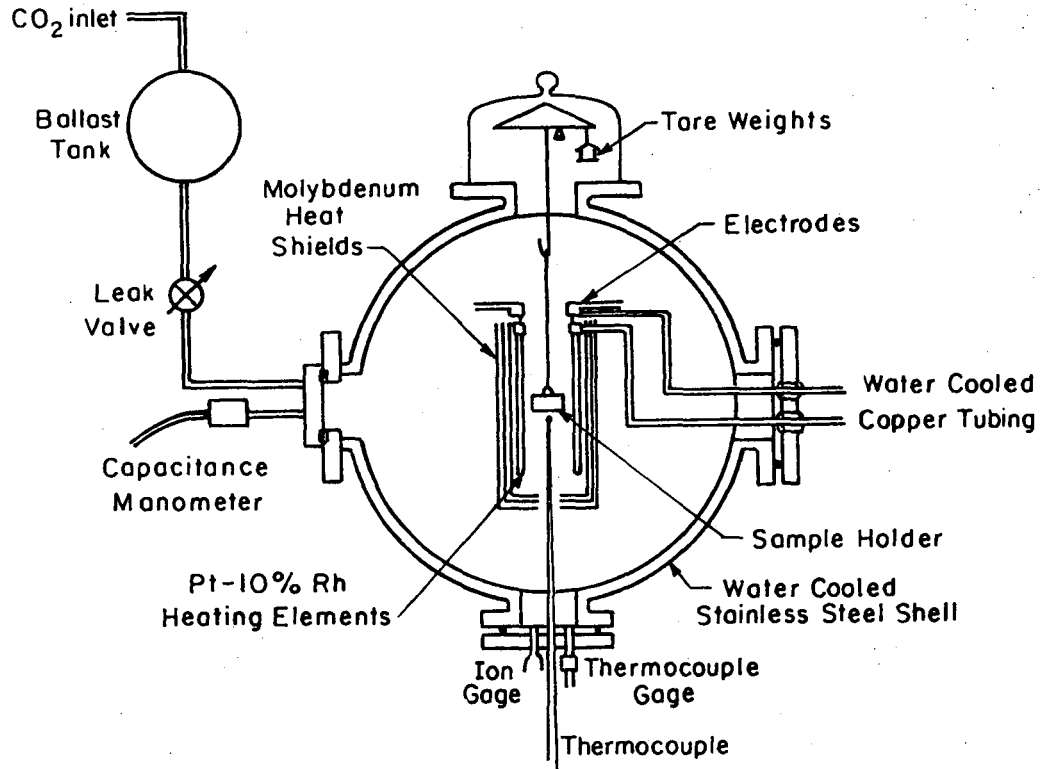
XBL 748-6867

Fig. 1. Schematic drawing showing the spatial relations for steady state decomposition: $AB_{(s)} \rightleftharpoons A_{(s)} + B_{(g)}$.



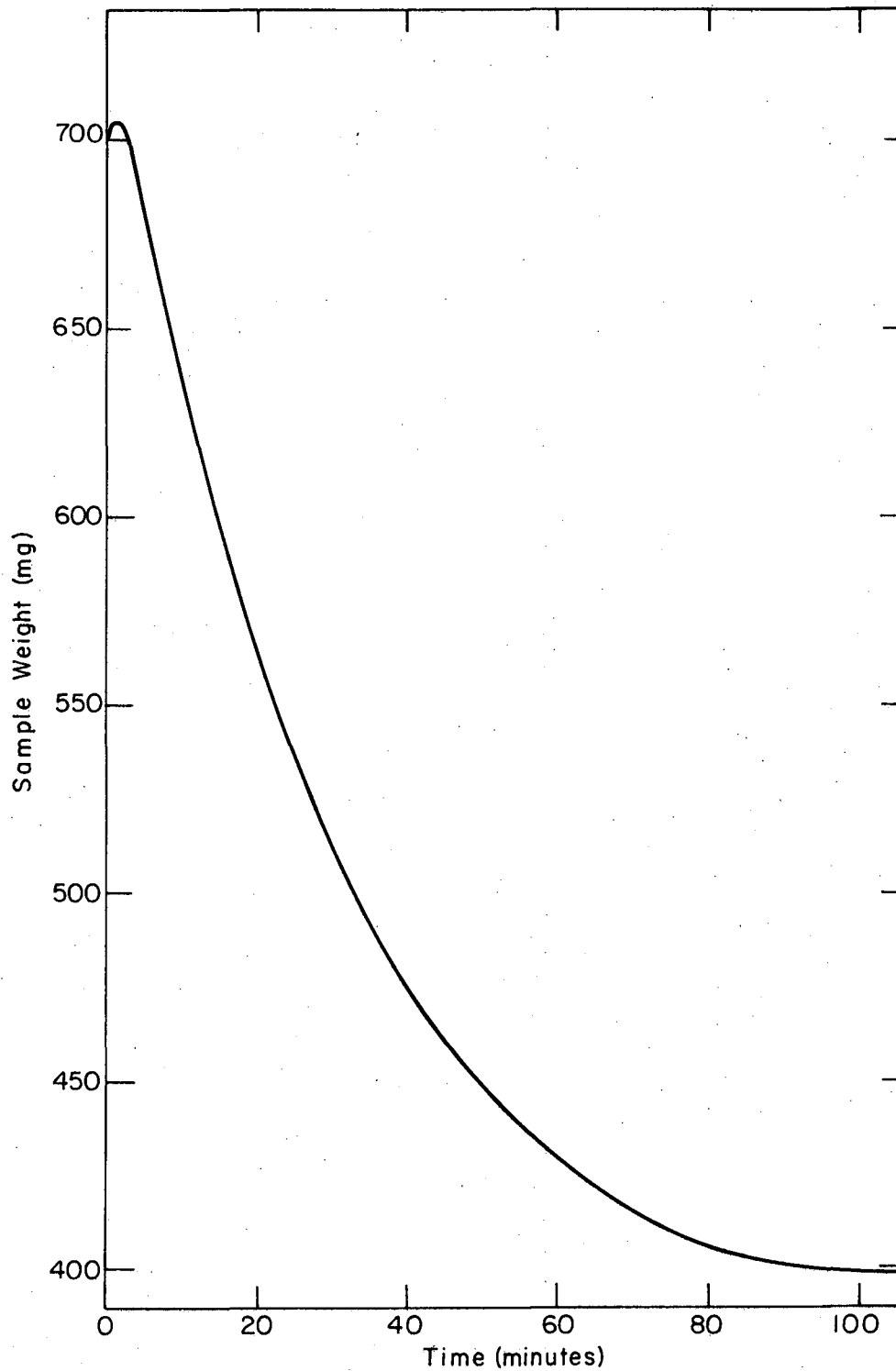
XBB784-4505A

Fig. 2. Scanning electron micrograph of CaCO₃ powder.



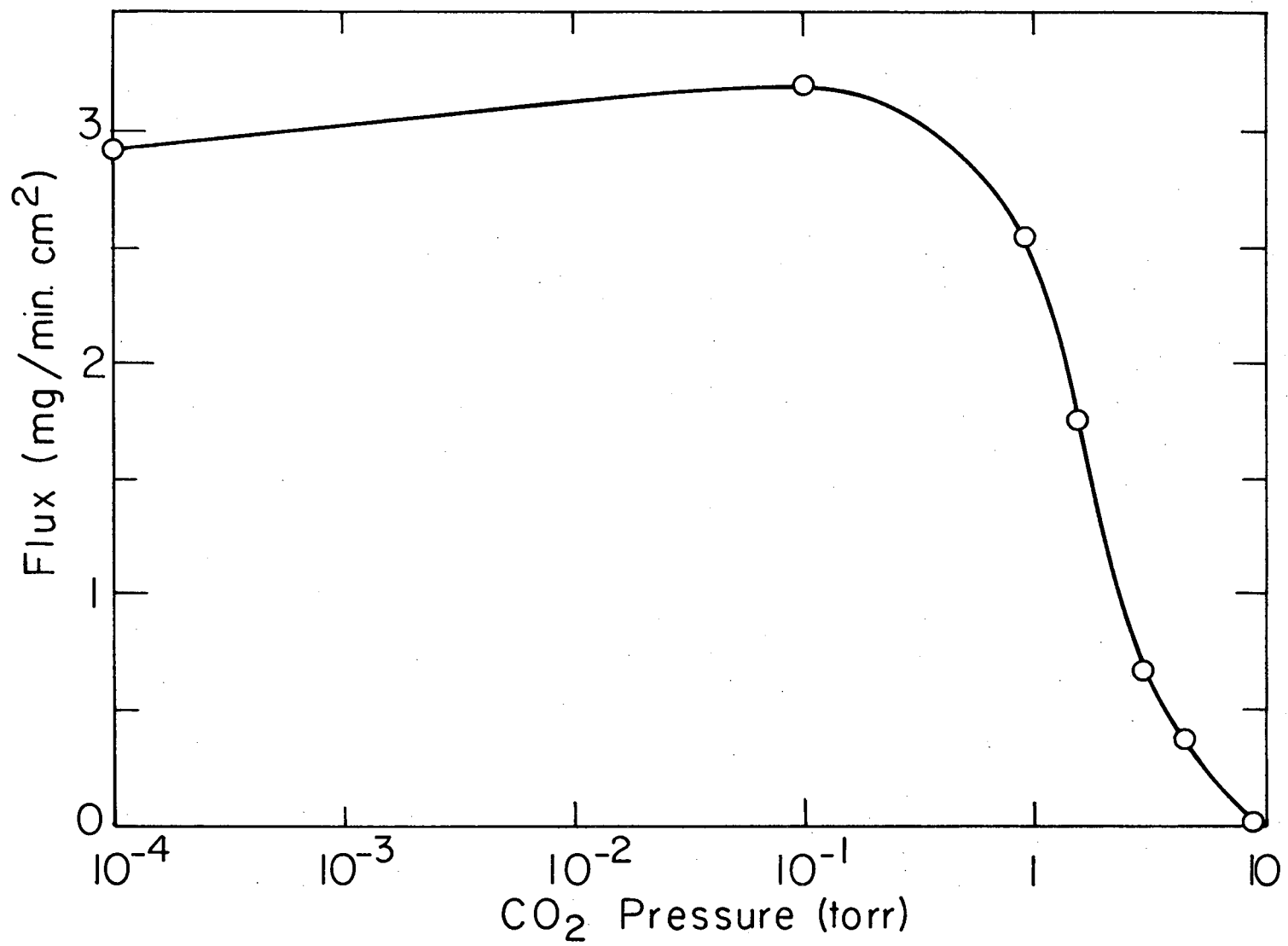
XBL784-4857

Fig. 3. Experimental apparatus for decomposing CaCO_3 in a controlled atmosphere.



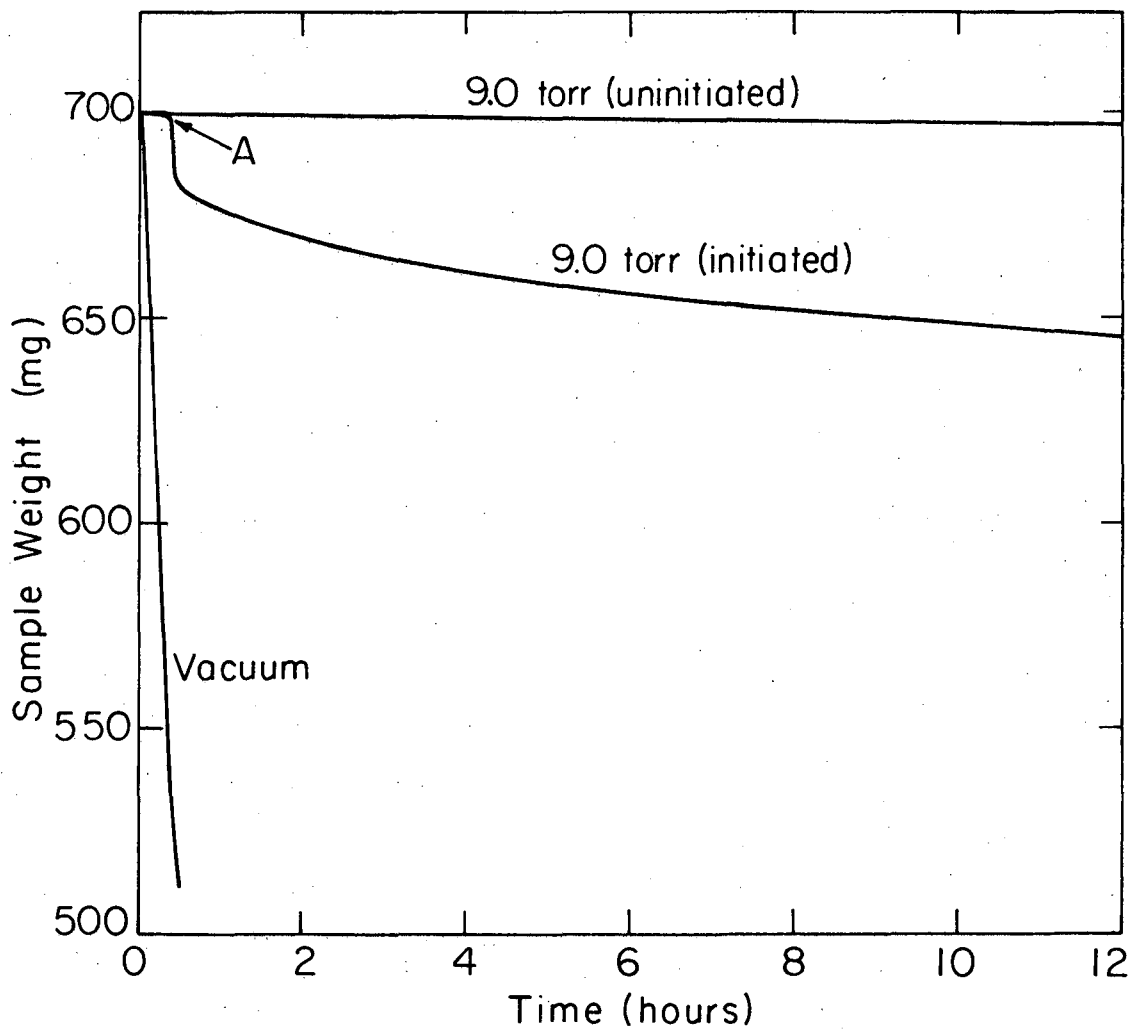
XBL 784-4841

Fig. 4. Typical curve of sample weight vs. time in vacuum.



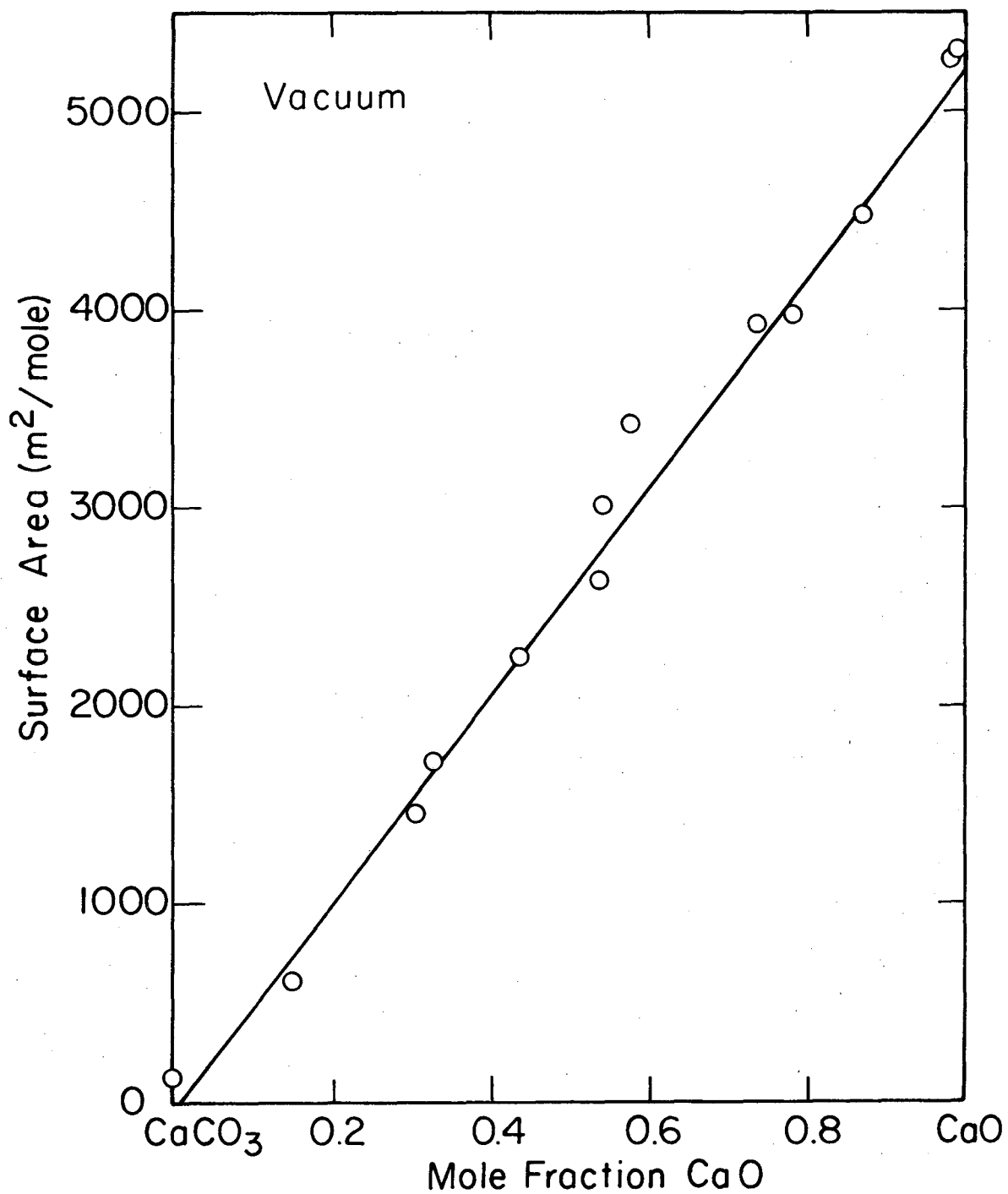
XBL 785-5050

Fig. 5. Rate vs. CO₂ pressure.



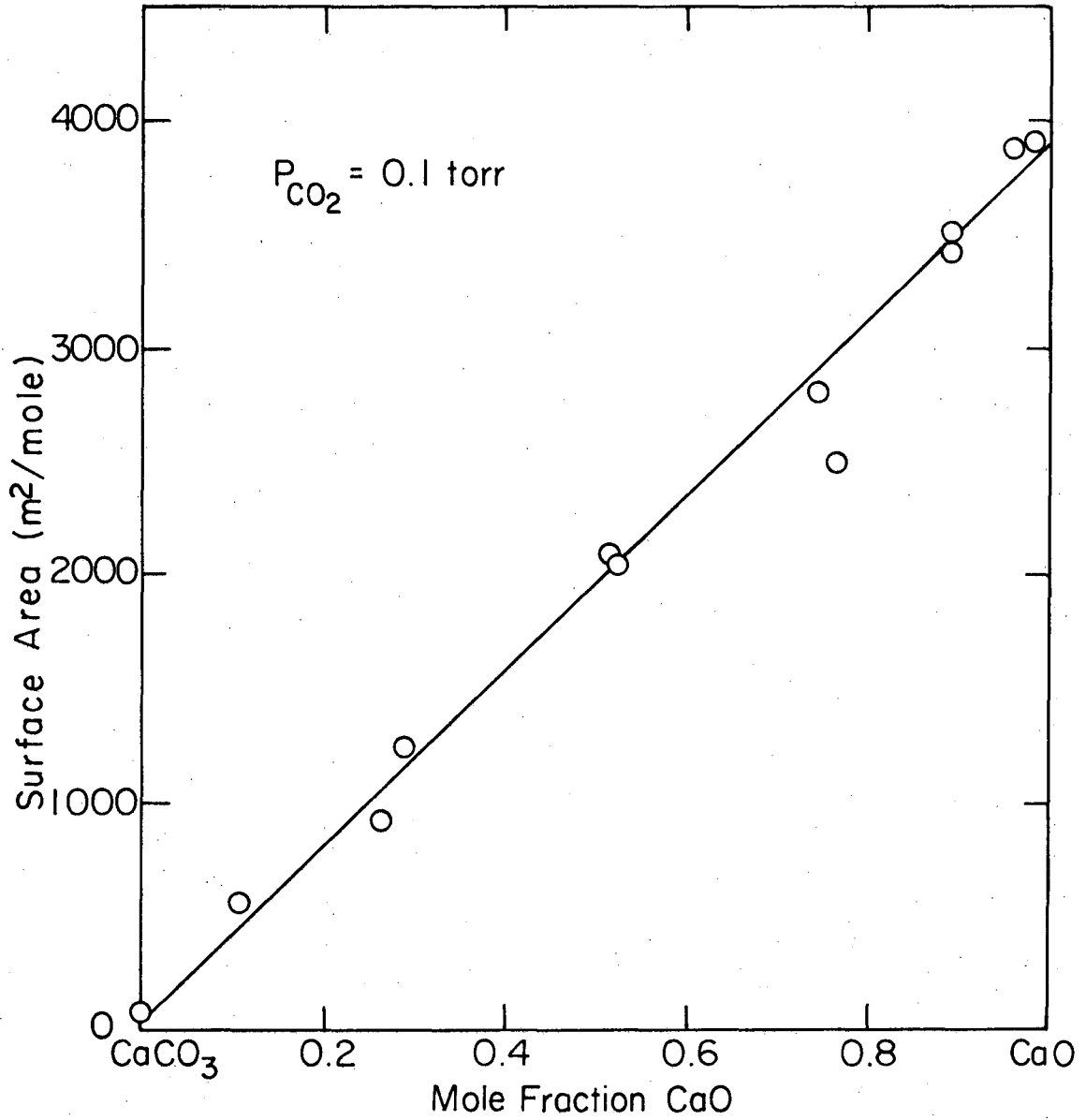
XBL 785-5051

Fig. 6. Sample weight vs. time in vacuum and in $P_{CO_2} = 9.0$ torr.



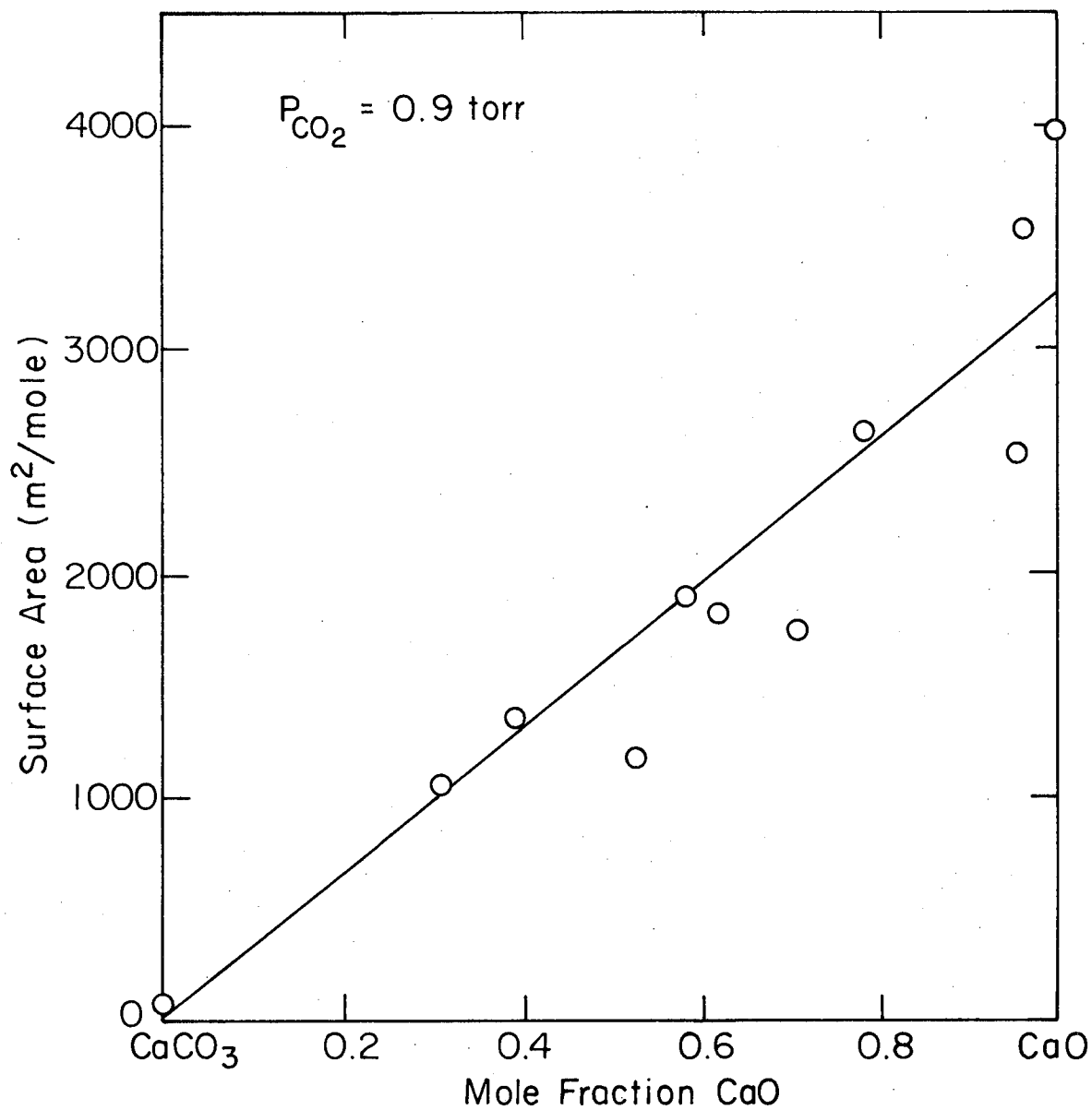
XBL 784- 4839

Fig. 7. Surface area vs. mole % CaO for CaCO₃ decomposed in vacuum.



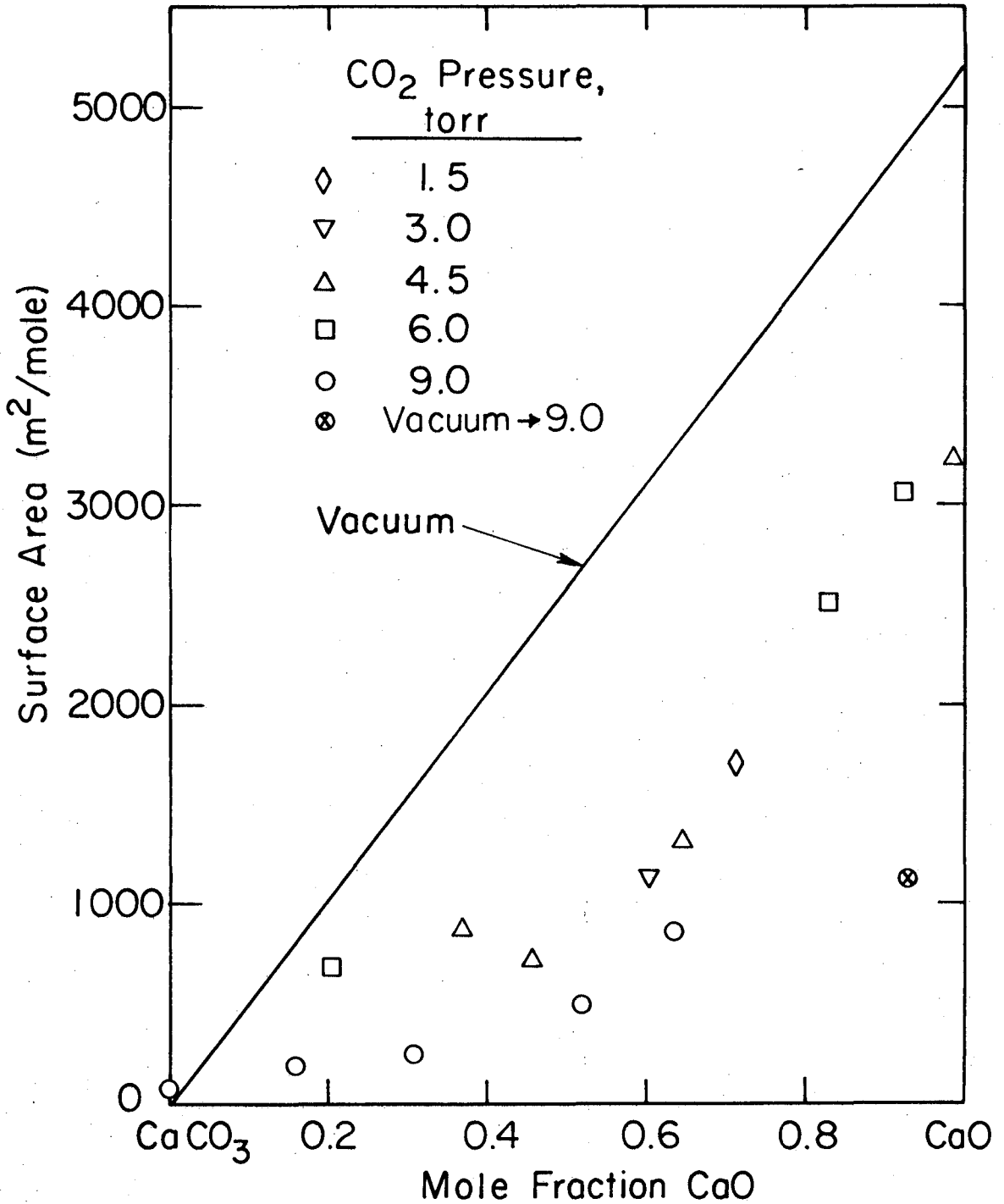
XBL 784-4836

Fig. 8. Surface area vs. mole % CaO for CaCO_3 decomposed in $P_{\text{CO}_2} = 0.1$ torr.



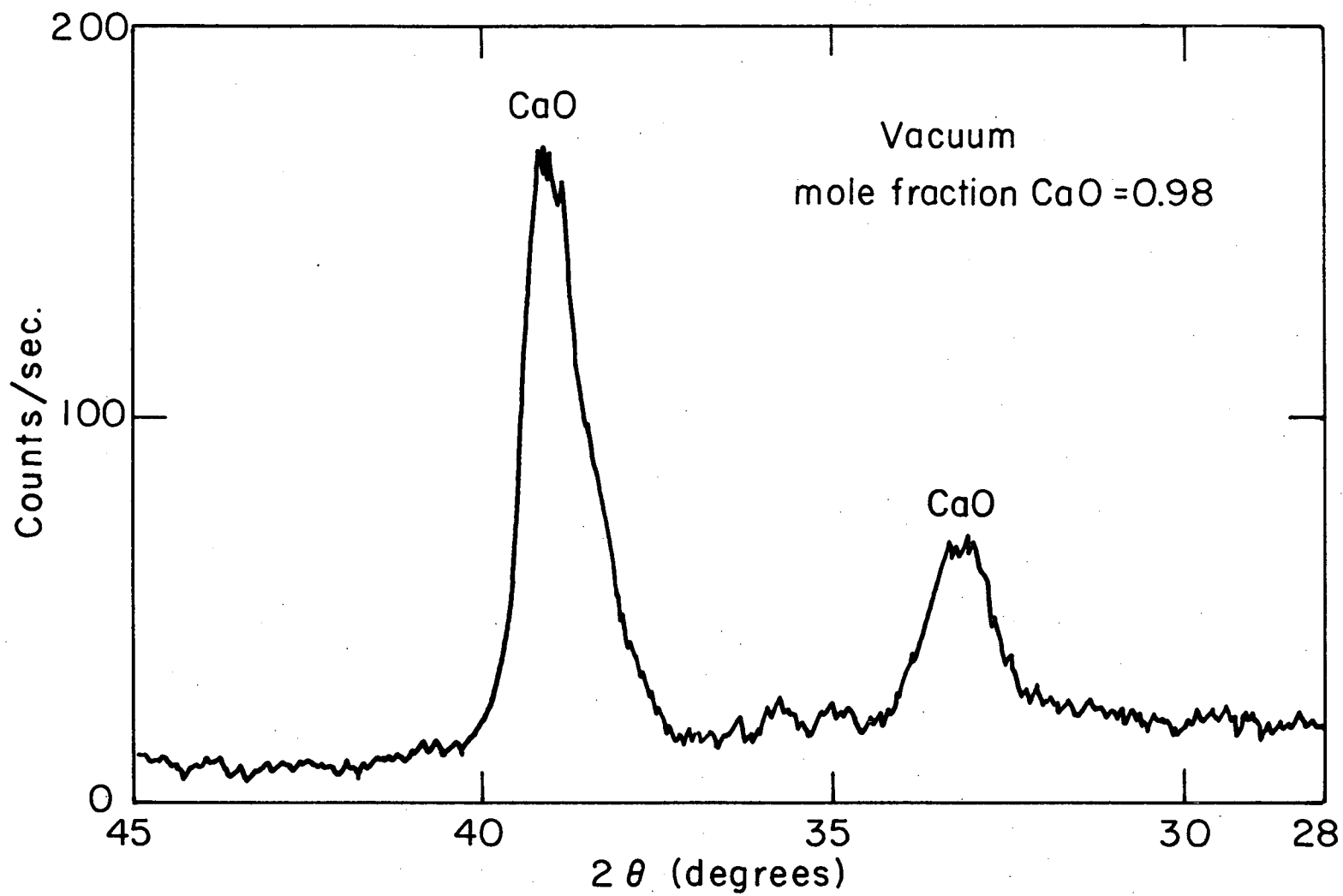
XBL784-4837

Fig. 9. Surface area vs. mole % CaO for CaO_3 decomposed in $P_{CO_2} = 0.9$ torr.



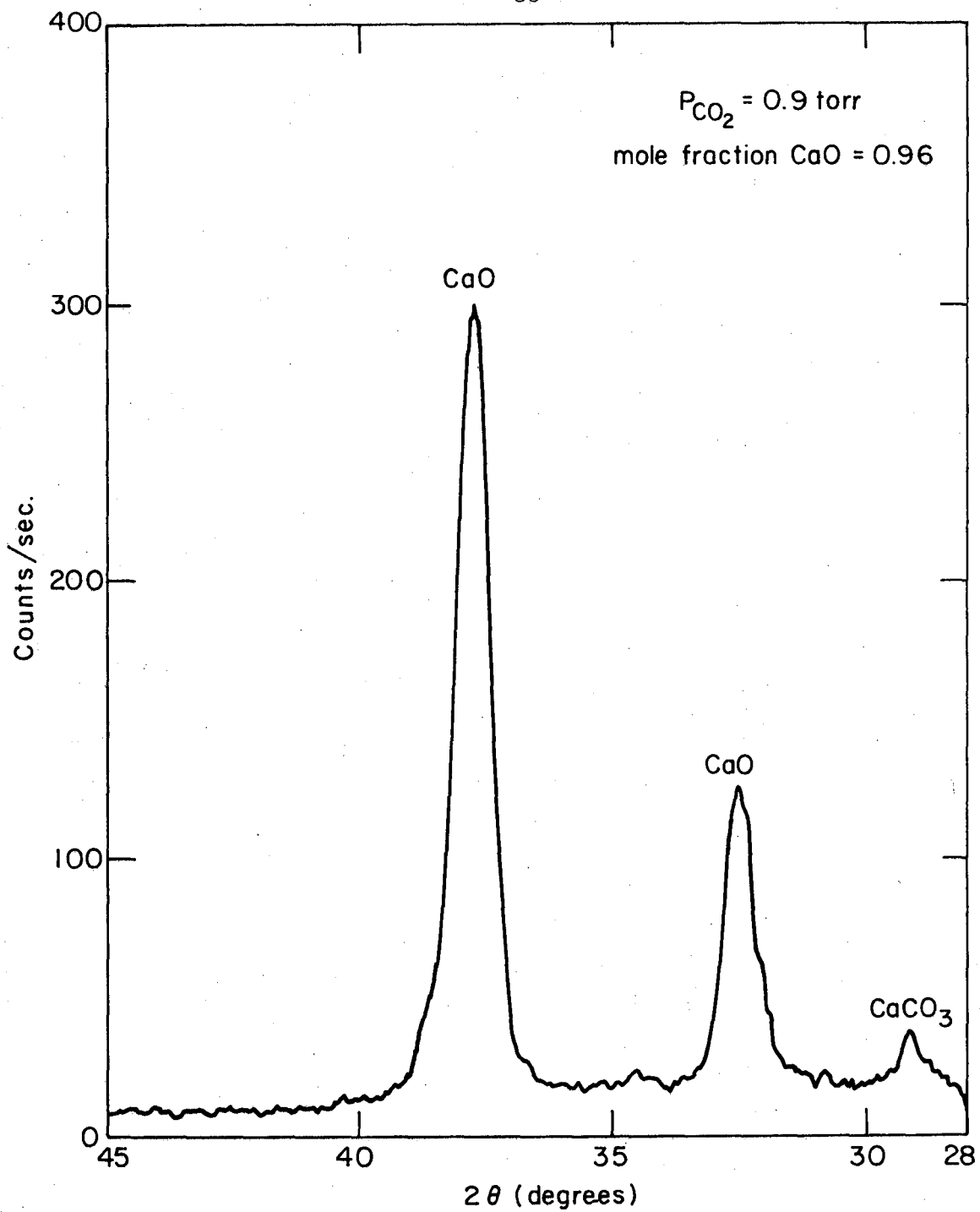
XBL 784-4840

Fig. 10. Surface area vs. mole % CaO for CaCO₃ decomposed in various CO₂ pressures.



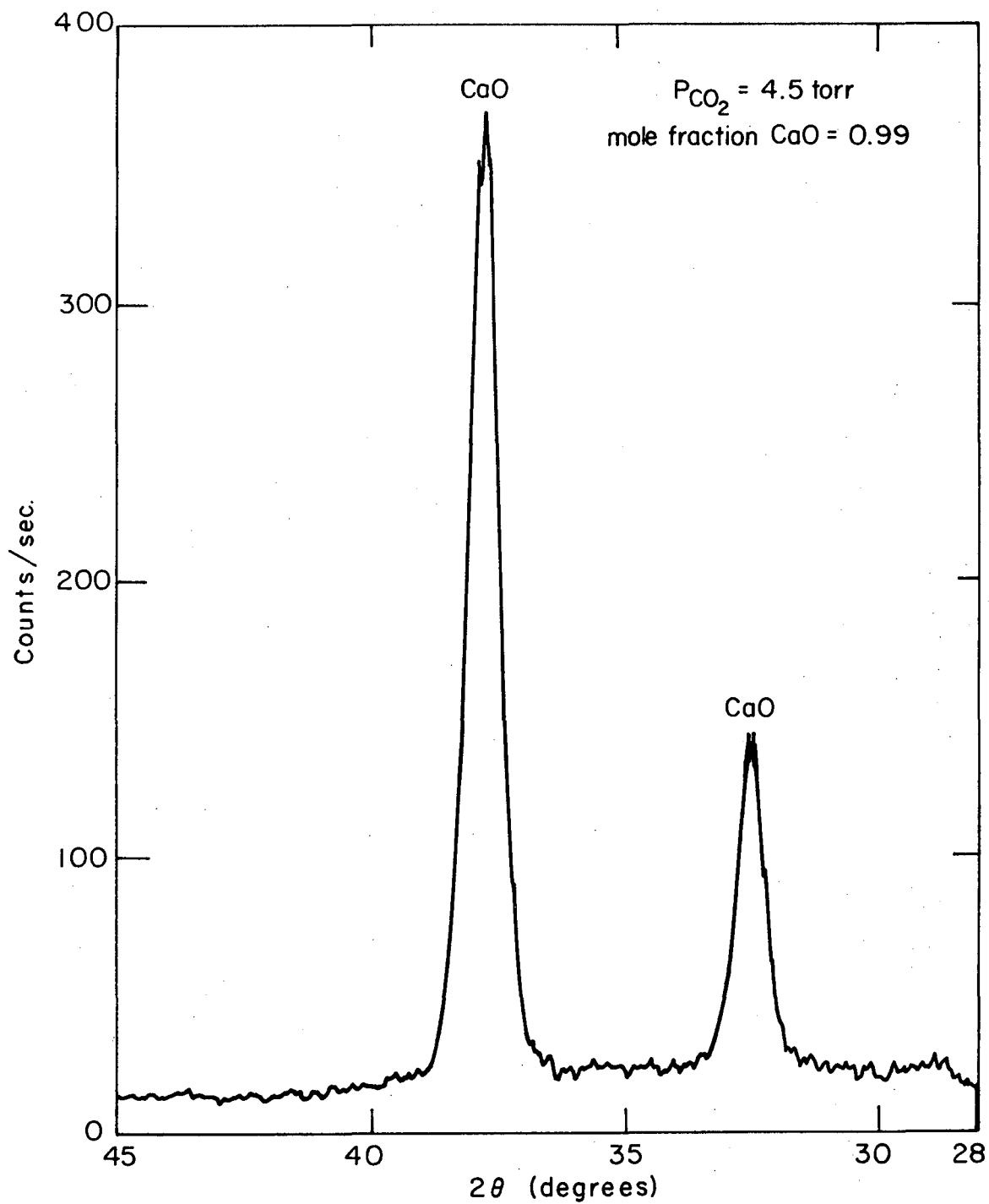
XBL784-4842

Fig. 11. X-ray pattern for CaO produced from CaCO₃ decomposed in vacuum.



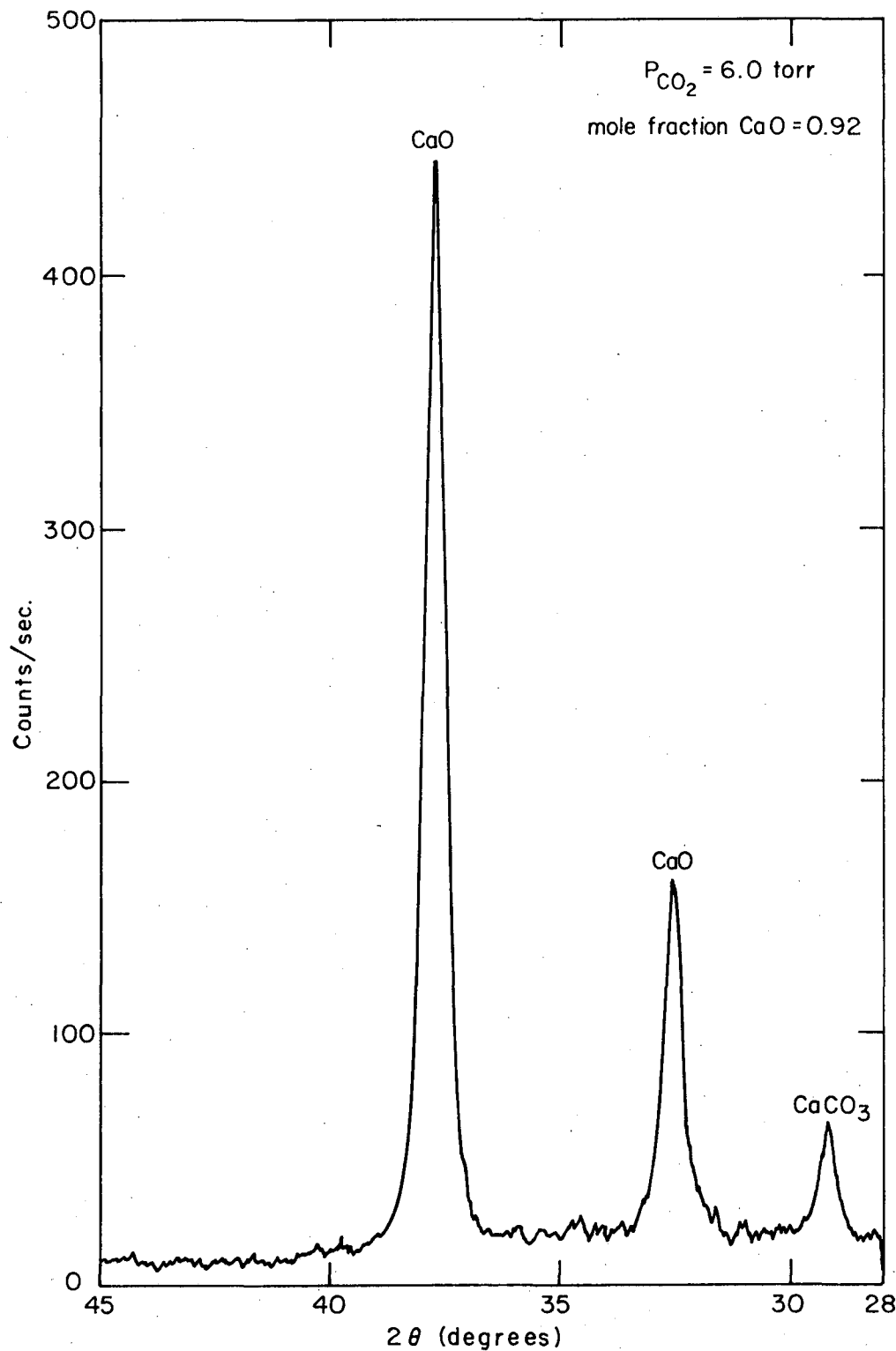
XBL 784-4843

Fig. 12. X-ray pattern for CaO produced from CaCO₃ decomposed in P_{CO₂} = 0.9 torr.



XBL 784-4844

Fig. 13. X-ray pattern for CaO produced from $CaCO_3$ decomposed in $P_{CO_2} = 4.5$ torr.



XBL 784-4845

Fig. 14. X-ray pattern for CaO produced from CaCO₃ decomposed in P_{CO₂} = 6.0 torr.

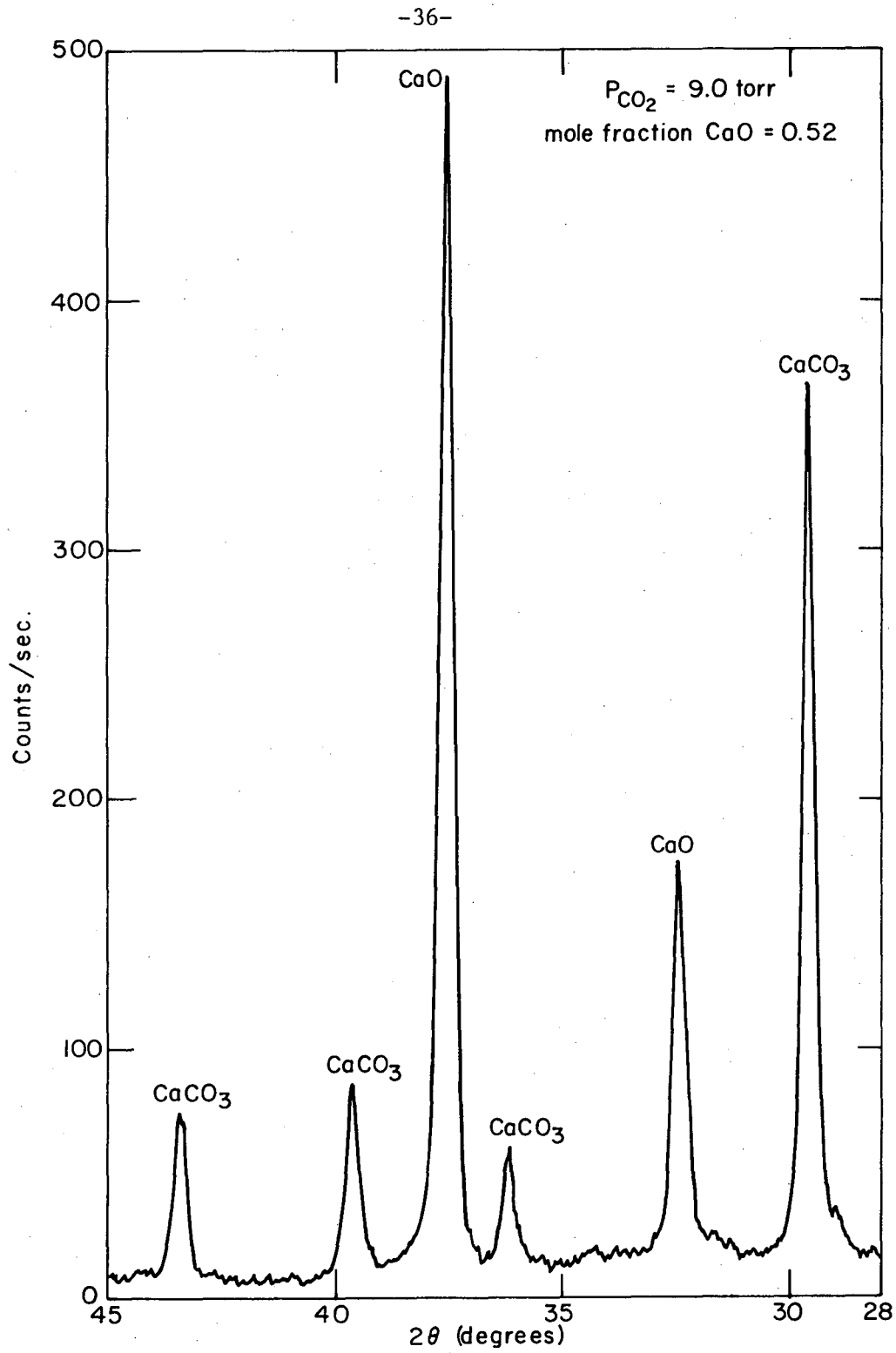
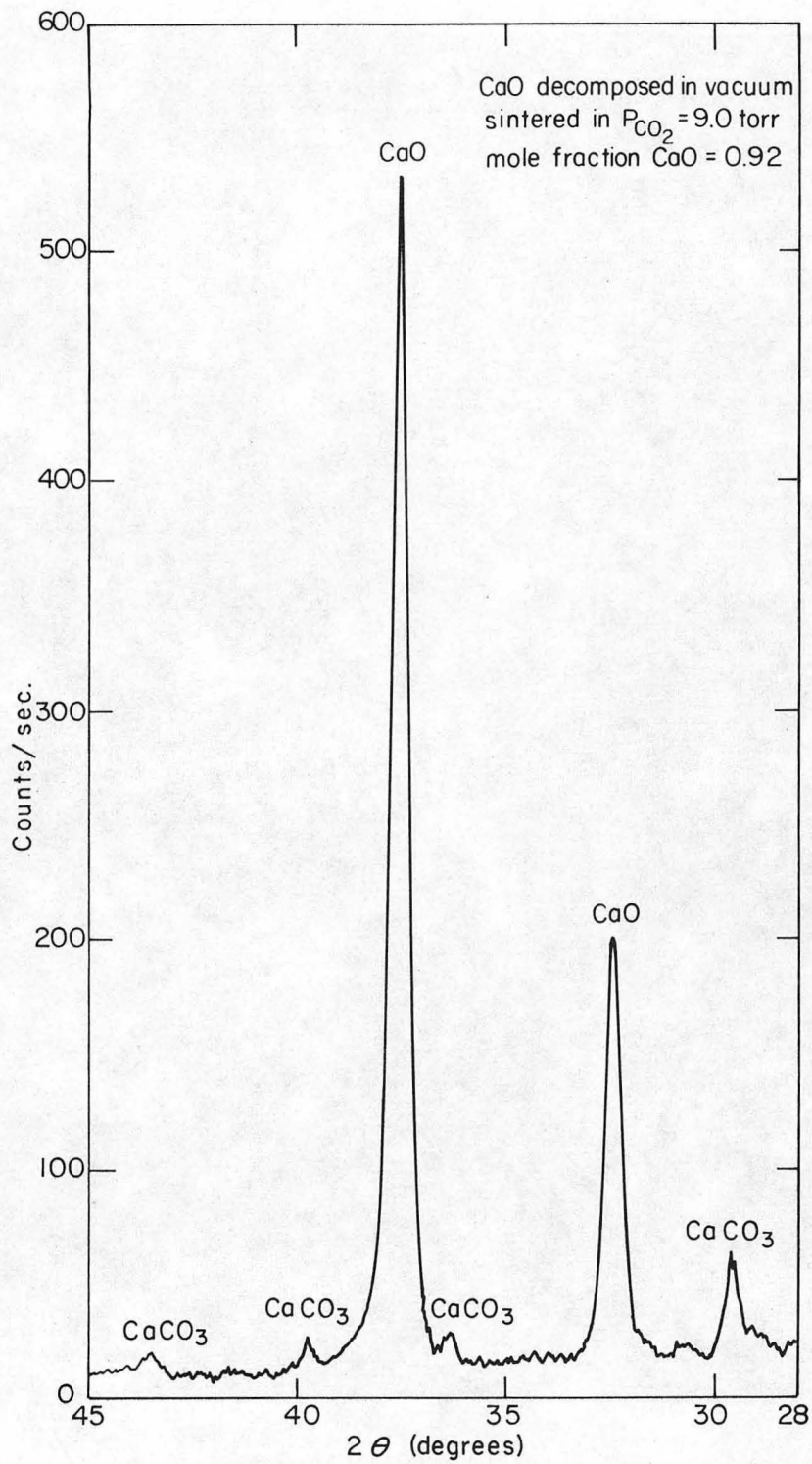


Fig. 15. X-ray pattern for CaO produced from CaCO_3 decomposed in $P_{\text{CO}_2} = 9.0 \text{ torr}$.



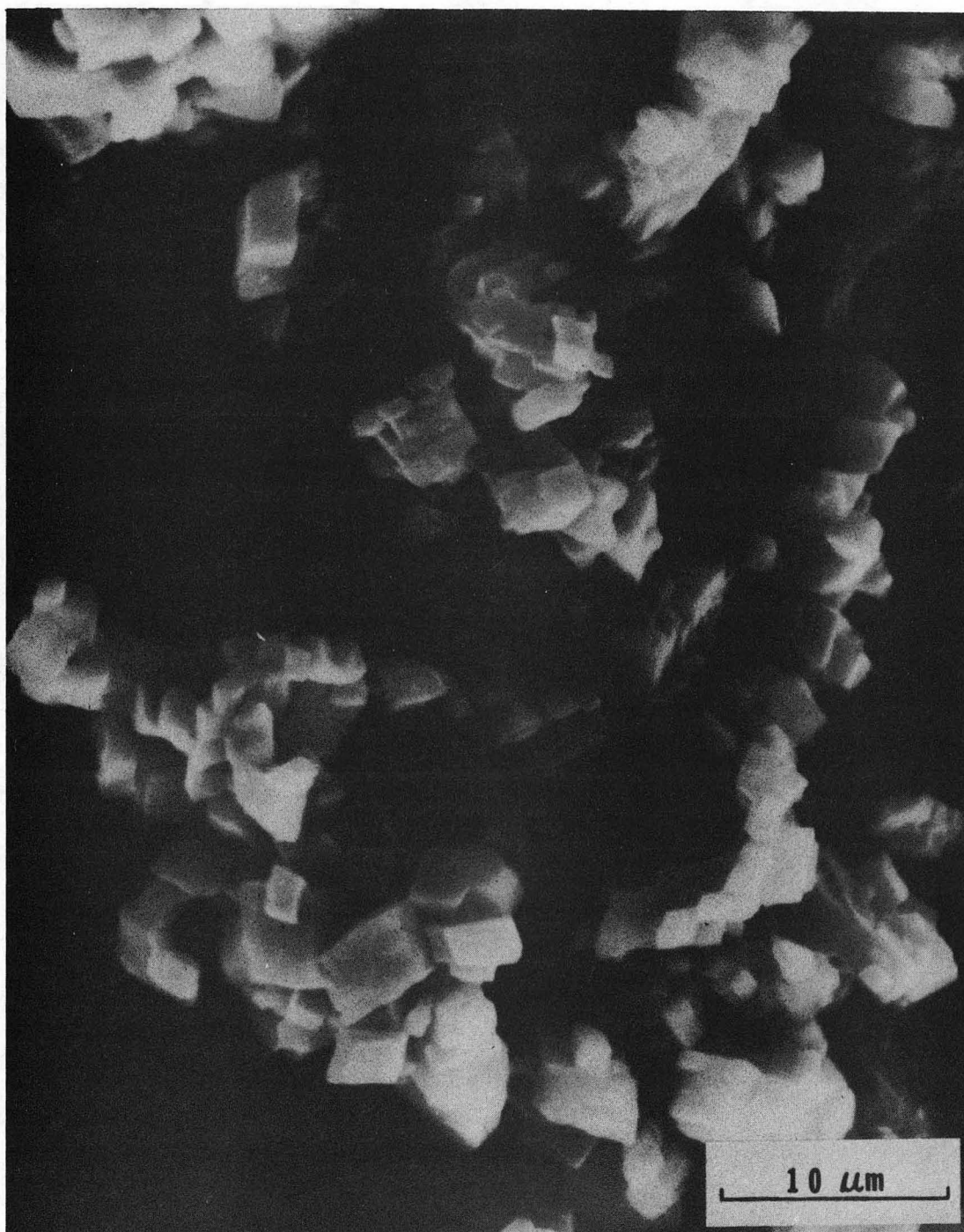
XBL 785-5052

Fig. 16. X-ray pattern for CaO produced from CaCO₃ decomposed in vacuum then heated in P_{CO₂} = 9.0 torr.



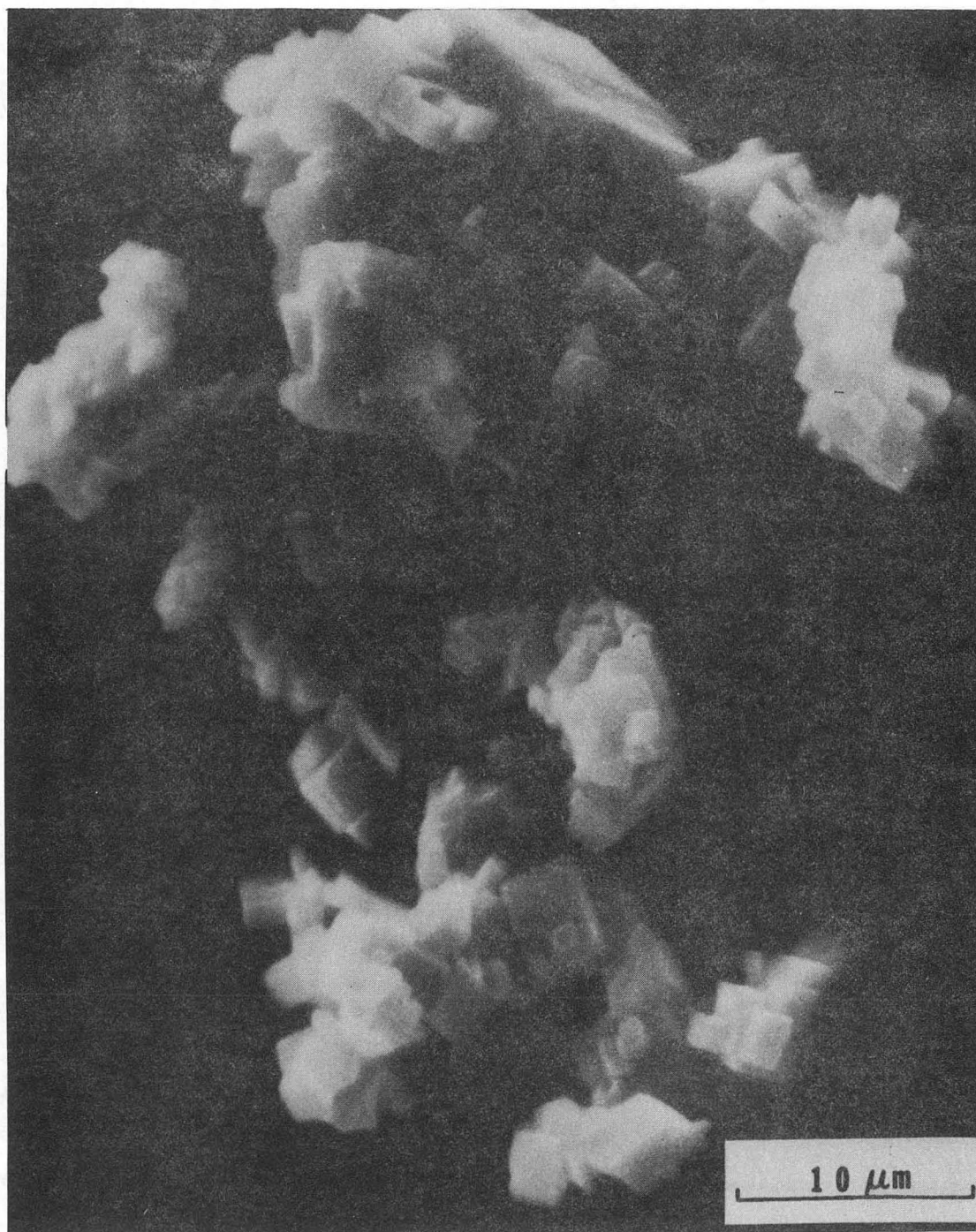
XBB784-4504A

Fig. 17. Scanning electron micrograph of CaO produced from CaCO_3 decomposed in vacuum.



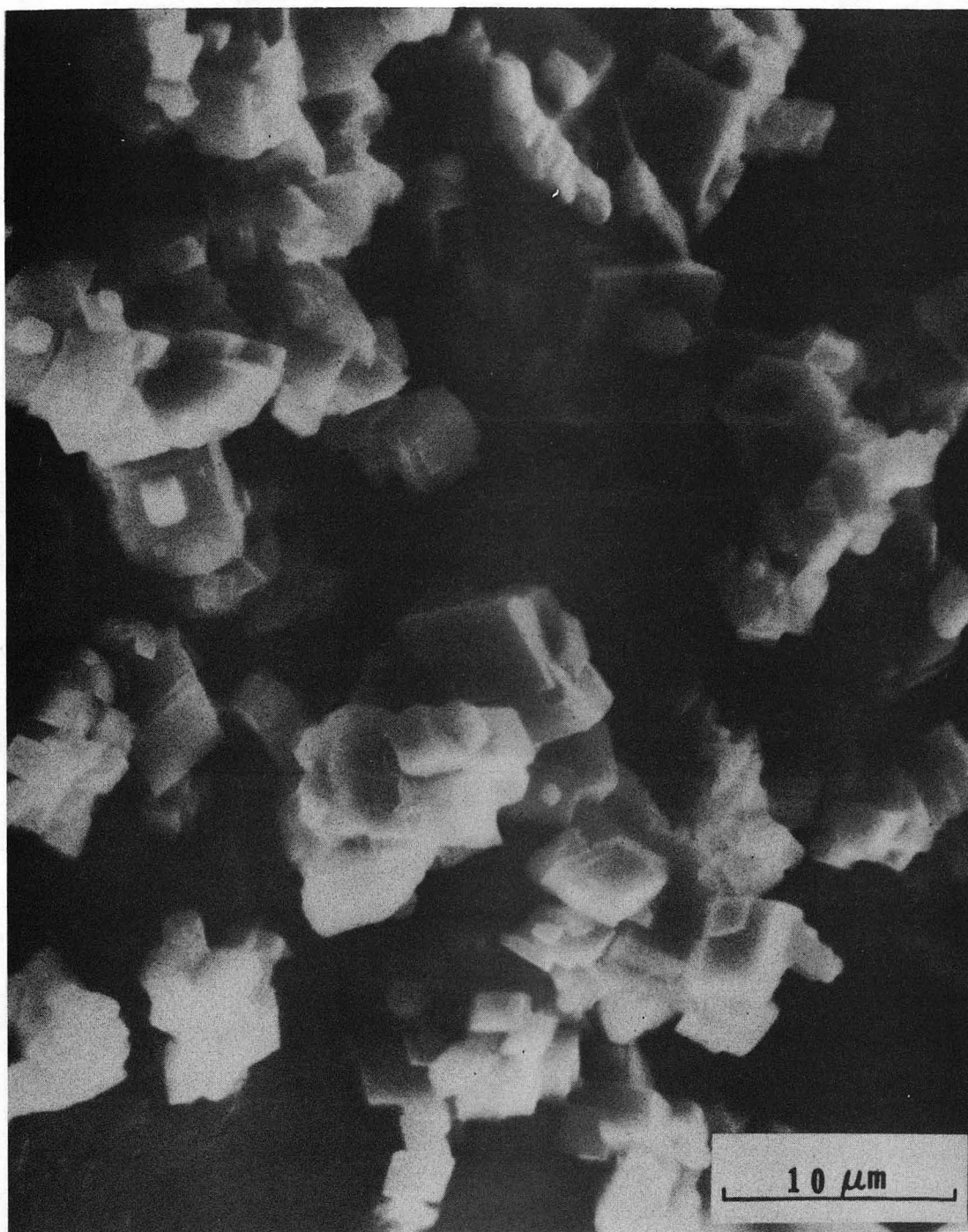
XBB784-4503

Fig. 18. Scanning electron micrograph of CaO produced from CaCO_3 decomposed in $P_{\text{CO}_2} = 0.9$ torr.



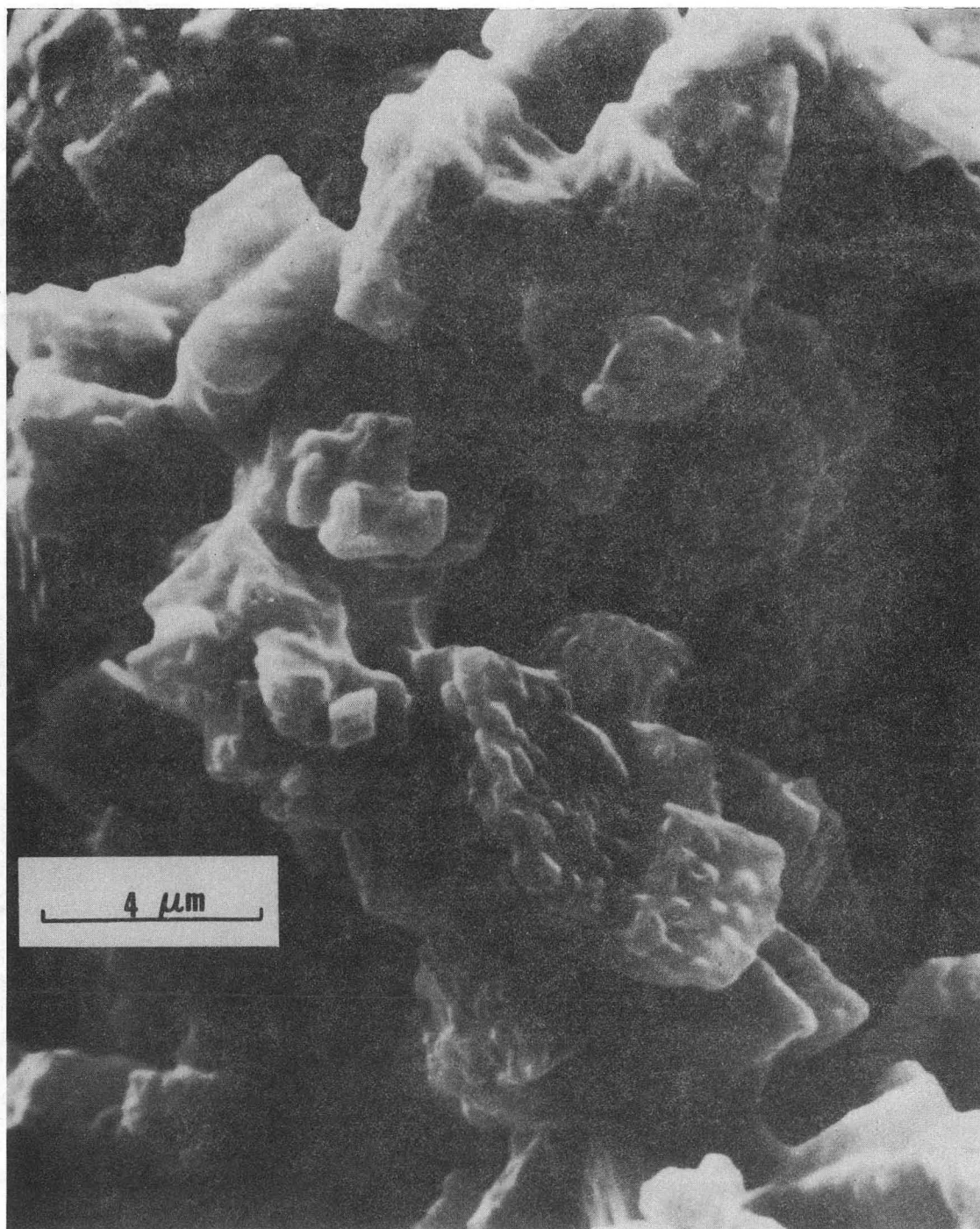
XBB784-4502

Fig. 19. Scanning electron micrograph of CaO produced from CaCO_3 decomposed in $P_{\text{CO}_2} = 4.5$ torr.



XBB784-4501A

Fig. 20. Scanning electron micrograph of CaO produced from CaCO_3 decomposed in $P_{\text{CO}_2} = 6.0$ torr.



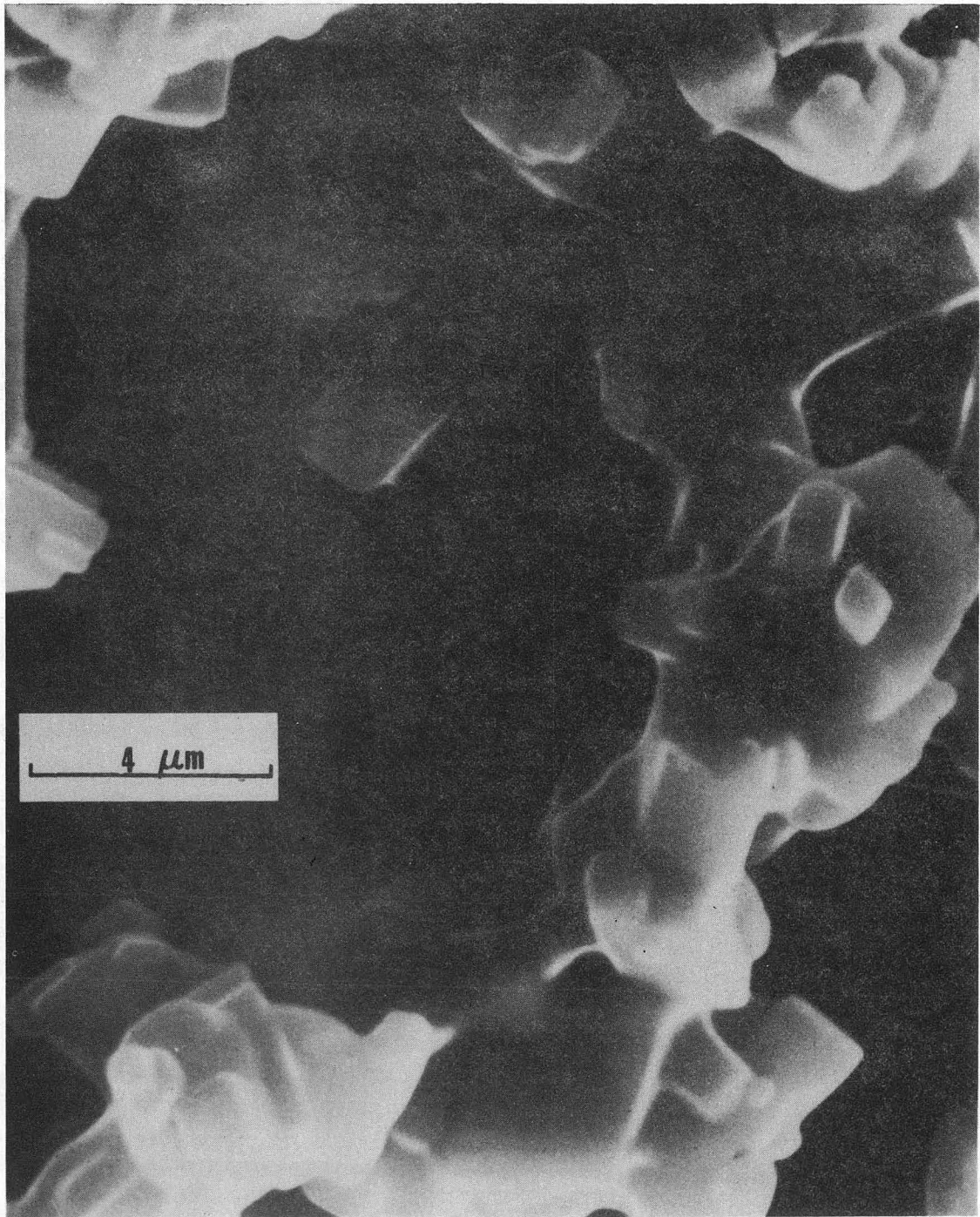
XBB785-3793A

Fig. 21. Scanning electron micrograph of CaO produced from CaCO₃ decomposed in $P_{\text{CO}_2} = 9.0$ torr.



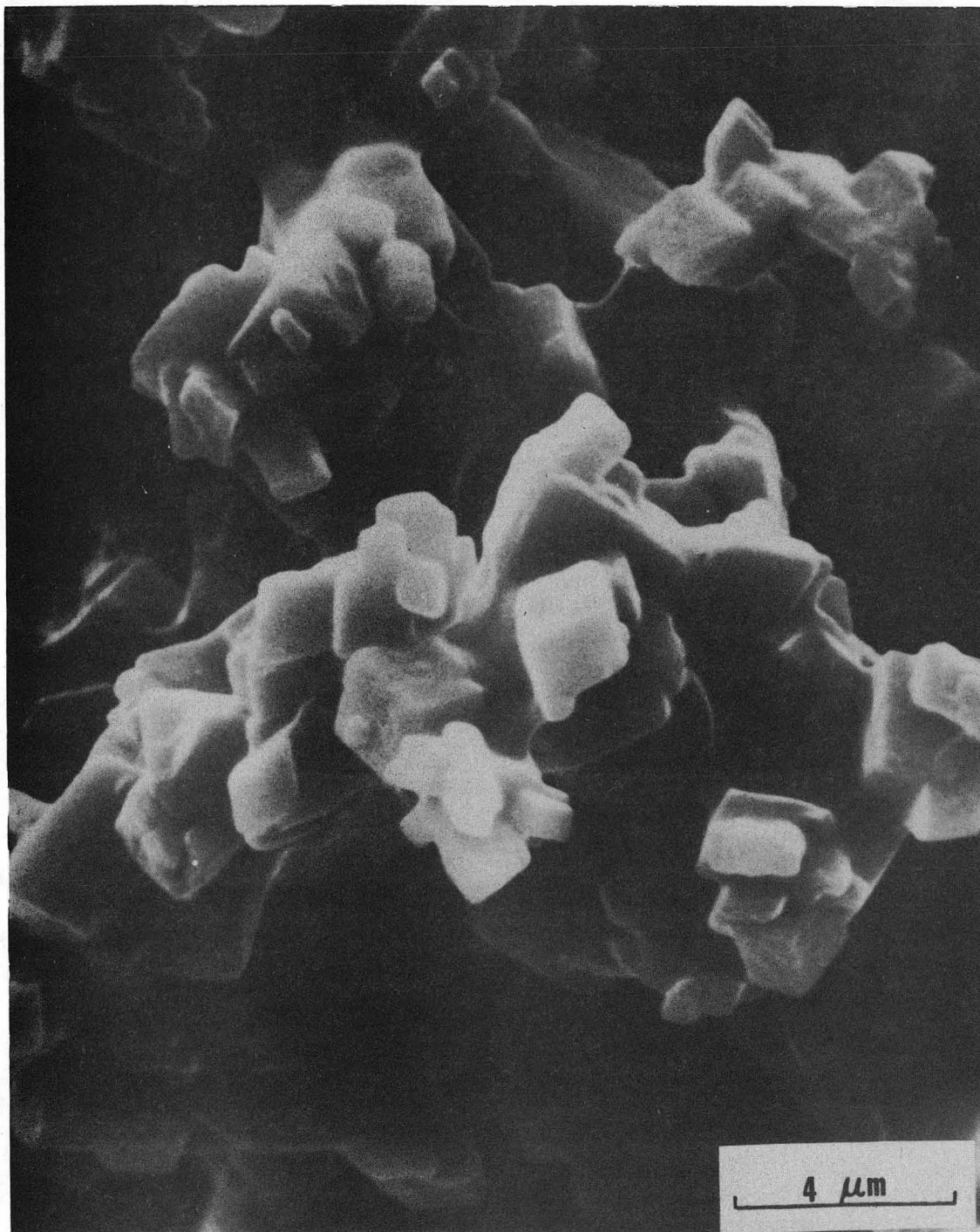
XBB785-6446

Fig. 22. Scanning electron micrograph of CaO produced from CaCO₃ decomposed in P_{CO₂} = 9.0 torr.



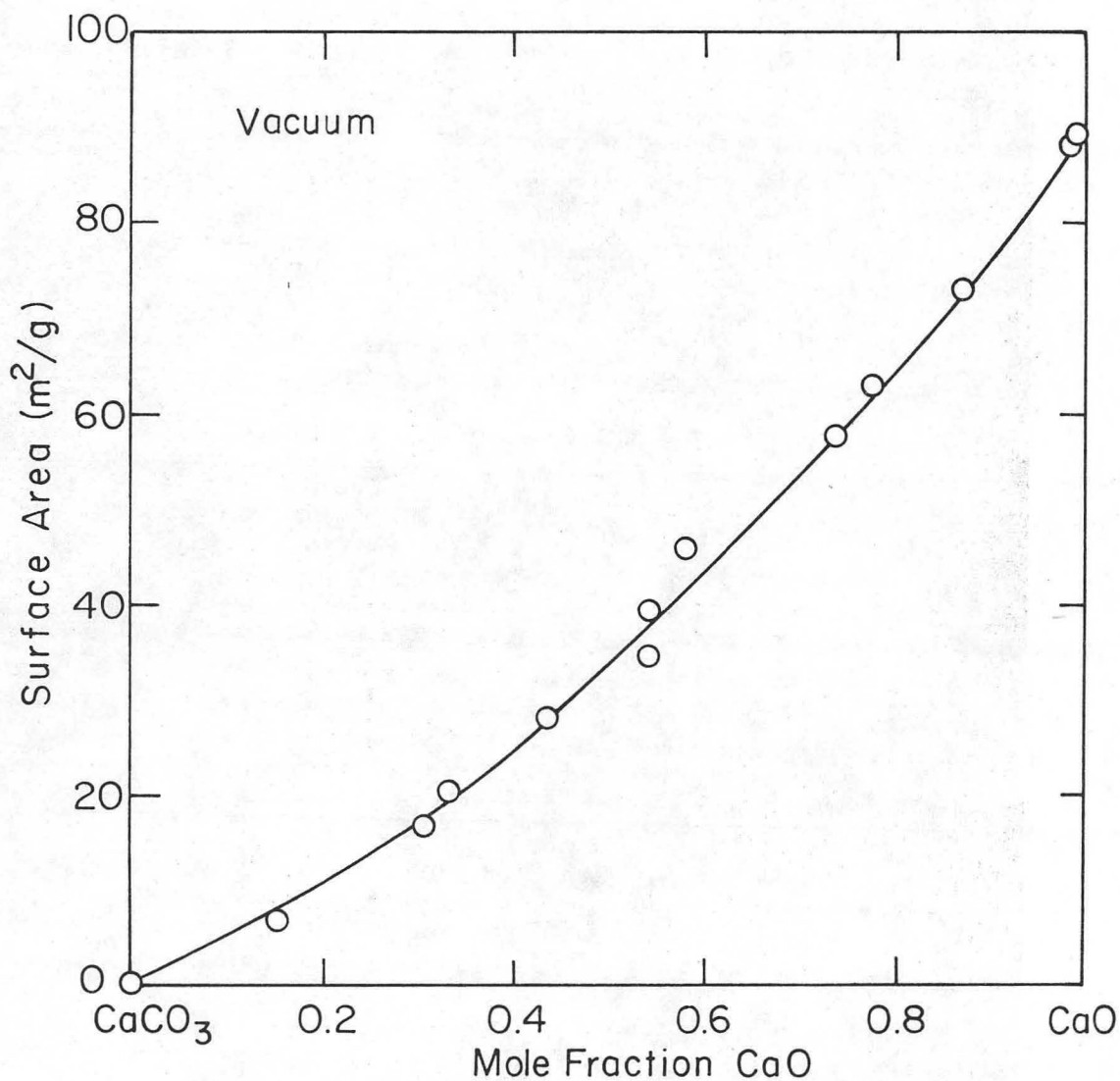
XBB785-6447

Fig. 23. Scanning electron micrograph of CaO produced from CaCO_3 decomposed in $P_{\text{CO}_2} = 9.0$ torr.



XBB785-3791A

Fig. 24. Scanning electron micrograph of CaO produced from CaCO_3 decomposed in vacuum then heated at 700°C in $P_{\text{CO}_2} = 9.0$ torr.



XBL784-3838

Fig. 25. Surface area (m²/g) vs. mole % CaO for CaCO₃ decomposed in vacuum.

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