Title

THE NATURE OF CaO PRODUCED BY CALCITE POWER DECOMPOSITION IN VACUUM AND IN CO2

Author

Ewing, J.

Publication Date

1978-10-01

Submitted to the American Ceramic Society

LBL-8312
Preprint

THE NATURE OF CaO PRODUCED BY CALCITE POWDER DECOMPOSITION IN VACUUM AND IN CO_2

Jay Ewing, Dario Beruto and Alan W. Searcy

October 1978

Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48

THE NATURE OF CaO PRODUCED BY CALCITE POWDER DECOMPOSITION IN VACUUM AND IN CO_2

Jay Ewing, Dario Beruto and Alan W. Searcy

Materials and Molecular Research Division, Lawrence Berkeley Laboratory
and Department of Materials Science and Mineral
Engineering, University of California
Berkeley, California

ABSTRACT

Specially reactive (sr-) CaO can be produced by decomposing 1 to 10 μm particles of $CaCO_3$ in vacuum at 700°C. Particles of sr-CaO appear unchanged in dimensions from the original $CaCO_3$, but have internal pores with surface areas of 92 m^2/g, more than twice the surface areas reported in a previous study for CaO made from calcite in vacuum at the same temperature. Weak and broad x-ray diffraction peaks in normal CaO first become discernable only after about half the CO_2 content of a calcite sample has been lost, but the molar surface areas of samples decomposed in vacuum or in 0.1 torr CO_2 are linear functions of the extent of reaction. The sr-CaO, therefore, must be a phase with ion positions and spacings like those of normal CaO, but without its usual long range order. Background pressures of CO_2 in the range up to about 1 torr influence the surface area of the CaO by increasing the pore dimensions at the $CaCO_3$-CaO reaction interface. Sintering of the CaO is negligible at 700°C in CO_2 pressures of 0.1 torr or less, but sintering is pronounced in CO_2 at 9 torr pressure.

INTRODUCTION

Models for use in analysis of the kinetics of decomposition reactions, that is reactions of the general form $AB(s) \rightarrow A(s) + B(g)$, recognize that the rate is influenced by the pressure of the gaseous reaction product.[1,2] But if the solid product is porous, possible influences of its properties on the reaction rate are usually ignored.

It has been shown that the chemical activity of the solid product appears in the rate equations for some decomposition reaction steps and that escape of the gaseous reaction product through a porous layer of the solid products may also influence decomposition rates.[3,4]

In recognition of these possibilities, two of the present writers examined the structure and morphology of partially decomposed calcite ($CaCO_3$) single crystals as part of a kinetic study.[5] A 30 μm layer of a poorly crystalline material was found between the undecomposed part of the $CaCO_3$ and a layer of normal, oriented, polycrystalline CaO. It was hypothesized that the material of this 30 μm layer is a metastable form of CaO that transforms irreversibly to the stable polycrystalline oxide when the accumulated strain exceeds a critical value.

As could be predicted from the hypothesis, decomposition in vacuum of calcite ground to a powder with cross sections less than 10 μm yielded metastable CaO.[6] This CaO was formed of particles that had very different shapes from the particles formed in air or dry N_2, showed only a very weak diffraction pattern of normal CaO, and reacted much more readily with water than does normal CaO.

In earlier studies, Glasson[7,8] found that when $CaCO_3$ is decomposed in vacuum the CaO produced has a higher surface area than does CaO produced in air. But in either vacuum or air the surface area varied with the fraction of solid converted to CaO in a non-linear way. He reported that the x-ray pattern of $CaCO_3$ was still observable after decomposition was complete, but that longer heating yielded crystalline CaO, either in vacuum or air.

Glasson's observations have been explained[7-9] in terms of a model first proposed by Gregg.[10] That model supposes that diffusion of CO_2 from calcite particles leaves the CaO in a pseudo-calcite crystal form, with no significant change in molar volume. The pseudo-calcite form of CaO is supposed to transform to normal crystalline CaO at a rate that lags behind the escape of CO_2 so that at the time that CO_2 evolution is complete some CaO remains in the pseudo-calcite form. Transformation of the oxide to its normal form increases the surface area, but sintering of the normal oxide acts to decrease the area. In consequence a maximum surface area is found at a time different from the time of complete decomposition.

It seemed evident that the CaO produced in vacuum decompositions in our laboratories differs more from CaO produced in air than did that of Glasson. To clarify the nature of CaO produced by $CaCO_3$ decomposition in vacuum, a new study has been made of the variations of surface areas and x-ray patterns of $CaCO_3$-CaO mixtures as functions of the fraction of reaction completed in vacuum or in CO_2 atmospheres. The new study does not support the existence of a $CaCO_3$- type CaO phase. Some reasons for differences in experimental results of the two investigations are suggested, and a new description of the structural form of the CaO produced by $CaCO_3$ decomposition in vacuum is proposed.

EXPERIMENTAL

Mallinckrodt analytical reagent $CaCO_3$ powder (see Table I for spectrographic analysis) was used for all experiments. The average particle cross section was 3 μm and the specific surface area was 0.7 m^2/g

(70 m^2/mole). A sample with a weight of 0.7 g weighed to ± 0.001 g was placed in a platinum foil basket of 4 cm^2 cross sectional area. The basket was hung from a Cahn RG recording microbalance in a resistance furnace. For vacuum experiments a silicon oil diffusion pump maintained the pressure below 1×10^{-4} torr. When back pressures 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 to 10.0 torr with an accuracy within 1% of the reading. The CO_2 pressure could be maintained within ± 0.02 torr at 0.9 torr and ± 0.1 torr at 6.0 torr throughout a decomposition. At 9.0 torr the initial rate of decomposition was so low that many days would have been required to decompose a sample. Therefore, for the runs at 9.0 torr the samples were brought to temperature 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.

A platinum tube surrounded the basket to provide a zone of uniform temperature and to prevent transport to the cell of products of CO_2 reaction with the heating elements. Tungsten elements were used for the first experiments. A bluish substance deposited in the furnace at higher CO_2 pressures (> 3.0 torr). This deposit is presumed to be a tungsten oxide. Reaction of CO_2 with the heating elements would also yield CO. A gas chromatograph was used to determine that the maximum CO concentration in the furnace atmosphere was 8%. To be certain that the decomposition reaction was not influenced by CO, the tungsten elements were replaced with Pt-10% Rh elements. Experiments repeated with these elements were in good agreement with experiments using tungsten elements.

The microbalance was used to monitor the weight loss during decomposition. When a desired fraction of decomposition was achieved in a run made in CO_2, the CO_2 was pumped out and the sample was cooled as rapidly as possible to prevent further decomposition. Decomposition usually became immesurably slow within 1 to 2 minutes from the time the furnace powder was reduced, which corresponded, at most, to 5% of the total weight lost.

To minimize reaction of the CaO product with atmospheric moisture and CO_2, the furnace chamber was filled with Ar or dry N_2 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 with this method were within 8% of the values obtained from the continuous recording microbalance. Total weight changes were used to calculate the fraction of sample decomposed at the time the run was discontinued. To further reduce hydration, the sample was stored until needed in a vacuum desicator.

All runs were made at 700°C where the equilibrium decomposition pressure is 30 torr. Surface areas were measured for samples after from 15% to 100% of the CO_2 content had been driven off by heating in vacuum or in CO_2 pressures of 0.1, 0.9, and 9 torr. A few runs were made at various CO_2 pressures between 0.9 and 9 torr.

The $CaCO_3$ powder filled the bucket to a depth of about 1 cm. Samples taken from the bottom layer of several partially decomposed powder beds had surface areas as high as samples taken from the top of the same powder bed. This result indicates that under the experimental conditions used, decomposition occurred at about the same rate for particles throughout the sample, so that, for example, surface areas measured after 50% decomposition were characteristic of particles that had all been about half converted to CaO rather than characteristic of a mixture of 50% fully decomposed particles and 50% undecomposed particles.

Surface areas were measured in a Quanachrome Corp. BET apparatus immediately after the samples were weighed. Repeated measurements were reproducible within 1%, regardless of the surface area of a sample. The manufacturer claims that surface areas obtained with this apparatus agree with surface areas measured with other sorption devises to within 3%.

For x-ray measurements, samples were packed in an aluminum holder and irradiated with Cu k_α radiation in a Picker x-ray diffractometer. The first scan from 2 - 28° to 2 - 45° required 12 minutes. This range includes the major peaks of the three possible phases: CaO - 37.4°, $CaCO_3$ - 29.4°, and $Ca(OH)_2$ - 34.1°. The CaO hydrated rapidly, so the first scan was the best indication of the crystallinity of the CaO product.

All samples were examined with a scanning electron microscope. Samples were first dispersed in CCl_4, and the dispersion was dropped on a carbon coated holder from an eyedropper. Finally, a layer of gold approximately 200 Å thick was 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.

RESULTS AND DISCUSSION

Glasson[7,8] showed that the surface area of CaO is higher if $CaCO_3$ is decomposed in vacuum than if $CaCO_3$ is decomposed in air, and he demonstrated that CO_2, which escapes more slowly when air is present, is responsible for the low surface areas found after air decompositions. The present study confirms these findings, but yields much higher surface areas from vacuum decompositions than reported by Glasson. CO_2 is shown to influence surface areas by one mechanism at low CO_2 pressures and by a second mechanism at pressures close to the equilibrium decomposition pressure, 33 torr at 700°C.

SEM pictures taken after complete decomposition at CO_2 pressures of 0.1 torr or less show that the particles have the same apparent size distribution and shapes as before decomposition (Fig. 1). From the difference in molar volume between $CaCO_3$ and CaO, the particles after conversion to CaO are calculated to have 55% porosity. The fact that the pores are not visible in SEM photographs implies that they are less than 5×10^{-2} μm in cross section. If the pores are assumed to be tubular, their diameters in particles decomposed in vacuum are calculated to be 8×10^{-3} μm and in particles decomposed in 4 to 6 torr CO_2, to be 1 to 2×10^{-2} μm. The porosity of the CaO was not reduced when a sample that was prepared in 0.1 torr CO_2 was heated at that CO_2 pressure for 15 hrs more than the 2 hrs required for complete decomposition. This proves that CO_2 influences the surface in the low pressure range by changing the geometry of the pores that are initially formed and not by promoting sintering.

Particles partially decomposed at 9 torr, however, showed coalescence, dimpling, and rounding that indicate condensed phase movement occurred over distances of the order of micrometers (Fig. 2).

When a sample underwent the first 10% decomposition in vacuum and then was fully decomposed in dry N_2, blocks of the original $CaCO_3$ were separated into more than 100 rounded particles (Fig. 3), of dimensions comparable to the dimensions of the dimples that can be seen in Fig. 2. The change in morphology produced by the N_2 atmosphere must be, as Glasson decided to be true for air atmospheres, a consequence of an increase in the effective partial pressure of CO_2 at the sample. Confirmation of the conclusion that N_2 has no direct catalytic effect on condensed phase diffusion is provided by the observation that a sample decomposed in 9 torr N_2 had a surface area comparable with that of samples decomposed in only 0.1 torr CO_2.

One sample was first completely decomposed in vacuum at 700°C and then was exposed to CO_2 at 9 torr pressure without cooling. That sample gained about 8% in weight and showed a surface area of about 1200 m^2/mole, which is less than one-fourth the area of a sample decomposed in vacuum. SEM pictures showed rounding and coalescence of particles much like that observed when samples of $CaCO_3$ were partially decomposed in the same pressure of CO_2. The x-ray diffraction pattern included peaks of $CaCO_3$ of heights comparable to those found for a sample that had been 92% decomposed in 6 torr CO_2.

This result proves that condensed phase diffusion of CaO at 700°C is associated with the presence of a high concentration of CO_2 in the sample. Because the CaO with which the CO_2 reacted is in a metastable form, the reaction product could be $CaCO_3$ even though the CO_2 is present at pressures below the equilibrium decomposition pressure. It seems more probable, however, that the CO_2 reacts to form either a metastable eutectic liquid or a metastable solution of CO_2 dissolved (as CO_3^{-2}) in CaO. These possibilities are being investigated in a separate study.[11]

Findings of the present study are not consistent with Glasson's conclusions about the sequence of condensed phase processes that leads to the final solid product. He concluded that in either air or vacuum the variation of surface area with time is a consequence of three processes which occur at different rates: Evolution of CO_2 leaves the CaO in a pseudo-calcite structure with essentially no change in surface area. Transformation of CaO to its normal crystalline (NaCl- type) modification increases the sample surface area, but that area does not reach a maximum at the time that all the CO_2 has evolved because some CaO then has not yet transformed from its pseudo-calcite structure. Sintering acts at a slower rate to reduce the surface area of normal CaO from the time it first forms until heating is discontinued, so that surface areas are reduced by sintering after the last CaO has transformed to its stable modification.

At the higher CO_2 pressures, the x-ray diffraction data of the present study show that a pseudo-calcite form of CaO is not produced in significant quantities. When $CaCO_3$ which was heated in 9 torr CO_2 had lost only 3% of its CO_2 content, the diffraction pattern of normal CaO was detectable. This observation shows that formation of normal CaO does not lag behind the evolution of CO_2. Furthermore, the diffraction peaks of $CaCO_3$ became undetectable when 98 to 99% of the CO_2 content of a sample had been evolved, which shows that no pseudo-calcite phase remained in a fully decomposed sample.

Glasson found that a significant quantity of CO_2 can be pumped out of CaO that has been formed by what was apparently complete decomposition of $CaCO_3$ in CO_2 at about one-half its equilibrium decomposition pressure. The present study shows that when the CaO formed by decomposition in vacuum is exposed to similar high CO_2 pressures the CaO absorbs 8 mole % CO_2 and subsequently shows $CaCO_3$ peaks in its diffraction pattern. Perhaps the $CaCO_3$ diffraction pattern reported by Glasson to persist after decomposition was complete was not a pattern of a pseudo-calcite CaO phase, but instead a pattern of $CaCO_3$ itself.

When decompositions are carried out in low pressures of CO_2 or in vacuum, the disappearance of the x-ray diffraction pattern of calcite is also well-correlated with the escape of CO_2 from the sample. But in vacuum, peaks characteristic of CaO are not observed in the x-ray pattern until a sample has lost about 50% of its CO_2 content. This observation alone could be interpreted as evidence that CaO is produced only in a pseudo-calcite form until the reaction is half complete. But that interpretation is disproved by the observation that the surface area per mole of solid is a linear function of the fraction of CO_2 evolved in vacuum or in 0.1 torr CO_2 (Figs. 4 and 5).

The initial solid product of decomposition in vacuum has a porosity almost identical to that of the poorly crystalline CaO that is the product of complete decomposition in vacuum. For the porosities to be nearly the same requires that the molar volumes be similar. The nearest ion neighbor coordination numbers are 6 in calcite and in normal CaO. Probably the initial product of $CaCO_3$ decomposition in vacuum is a form of CaO (perhaps with some residual CO_3^{-2}) which also has ions coordinated with 6 nearest neighbors and which has ion spacings close to those of normal CaO, but which has too little long range order and too much strain to permit coherent x-ray diffraction. When dolomite is decomposed in vacuum similar diffraction results are obtained, and the decomposition pressures measured for the dolomite decomposition are consistent with pressures predicted for decomposition to a glass-like solution of MgO and CaO.[12]

At CO_2 pressures of 0.9 to 6 torr the surface areas vary erratically from run to run (Figs. 6 and 7). Decomposition rates also vary erratically in this range, and the higher surface areas are systematically correlated with higher rates of decomposition. Probably, this pressure range is one of transition between two rate limiting reaction processes. There is no reason to invoke a pseudo-calcite form of CaO in this pressure range because such a phase does not appear to be observable when decomposition is carried out at either higher or lower CO_2 pressures.

It is important to identify as completely as possible the reasons why the results of this study differ from the results of Glasson's study. Possible reasons for differences in interpretation of x-ray data have already been discussed. Reasons why surface areas were found in this study to be linear functions of the fraction of reaction completed in vacuum or in low pressures of CO_2, but were found to be non-linear by Glasson should also be sought.

The different behavior probably does not arise from differences in impurity levels in the calcite used in the two studies. Samples with different low impurity levels do not appear usually to differ much in decomposition behavior. Differences in size of the individual $CaCO_3$ particles, however, is a clear source of different results, and differences in masses of powdered samples may well have been another source of different results.[13]

Some of Glasson's conclusions were drawn from observations of the decomposition of 1 inch diameter limestone spheres. These particular samples did not go through a maximum in surface area, but rather decreased in specific surface area continuously over the range from 20% to 100% reaction. Such a variation is consistent with the observations that surface areas are reduced by heating in high CO_2 partial pressures. The CO_2 partial pressures inside the pores of CaO formed from such large spheres might well be high enough to promote extensive sintering and cause the kind of reduction in specific surface area observed.

Glasson reports isothermal surface area versus fraction of reaction data for decomposition of only a single powder sample in vacuum, and he does not mention the size of the sample used. The fact that the maximum surface area reached by the sample was only 43 m^2/g suggests that it may have been large enough to develop high internal CO_2 pressures. In the present study, decomposition in vacuum yielded CaO with surface areas over twice as high, 93 m^2/g at about the same temperature, and decomposition in 4 to 6 torr CO_2 yielded CaO with surface areas of over 50 m^2/g.

CONCLUSIONS

Specially reactive (sr-) CaO can be produced by decomposition of particles of $CaCO_3$ of dimensions of the order of 1 to 10 μm in vacuum at 700°C. The sr-CaO so produced shows the normal CaO diffraction pattern, but with peaks that are broad and of heights less than half those of CaO formed by decomposition of $CaCO_3$ at high CO_2 partial pressures or in air. The sr-CaO which is first formed on a partially decomposed particle of $CaCO_3$ may have less long range order than does the product of complete decomposition, but the molar volume of the initial sr-CaO is similar to that of the final product. There is no evidence that in either vacuum or in high CO_2 pressures significant quantities of a pseudo-calcite modification of CaO is formed.

Sr-CaO is formed of particles of internal surface areas of the order of 90 to 100 m^2/g. The pores are too small to be observed by SEM, but can be estimated from the surface areas to be less than 10^{-2} μm in cross section. Our previous study[6] showed sr-CaO to react much more rapidly with water vapor than does ordinary CaO.

The crystallinity of CaO produced by $CaCO_3$ decomposition is increased and the surface area is decreased by background pressures of CO_2, which may become high enough inside samples of a gram or more in mass to have a significant effect on the properties of the CaO.

At 700°C low pressures of CO_2 appear to influence the CaO morphology mainly by increasing the initial dimensions of the pores, but CO_2 pressures of the order of one-third the equilibrium decomposition pressure cause changes in particle shape that must require extensive condensed phase diffusion.

Studies of the influence of decomposition temperature and $CaCO_3$ particle size on the properties of sr-CaO are in progress in our laboratories.

ACKNOWLEDGMENTS

Technical advice was provided by D. J. Meschi and James A. Roberts, Jr. This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract No. W-7405-Eng-48.

Table I. Spectrographic Analysis of Metallic Elements in Mallinckrodt AR $CaCO_3$.

Element	Percent (reported as oxide)
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

REFERENCES

1. D. A. Young, Decomposition of Solids, Pergamon, Oxford, England, 1966.
2. H. Schmalzreid, Solid State Reactions, Academic Press, New York, 1974, Chapter 8.
3. A. W. Searcy and D. Beruto, "Kinetics of Endothermic Decomposition Reactions 1. Steady State Chemical Steps," J. Phys. Chem. 80, 425-29 (1976).
4. A. W. Searcy and D. Beruto, "Kinetics of Endothermic Decomposition Reactions 2. Effects of the Solid and Gaseous Products," ibid. 82, 163-67 (1978).
5. D. Beruto and A. W. Searcy, "Use of the Langmuir Method for Kinetic Studies of Decomposition Reactions: Calcite ($CaCO_3$)," J. Chem. Soc., Faraday Trans. I, 70, 2145-53 (1974).
6. D. Beruto and A. W. Searcy, "Calcium Oxides of High Reactivity," Nature 263, 221-22 (1976).
7. D. R. Glasson, "Reactivity of Lime and Related Oxides. I. The Production of Calcium Oxide," J. Appl. Chem., 8, 793-97, (1958).
8. D. R. Glasson, "Reactivity of Lime and Related Oxides. VII. Crystal Size Variations in Calcium Oxide Produced from Limestone," J. Appl. Chem., 11, 201-6, (1961).
9. D. Nicholson, "Variation of Surface Area During the Thermal Decomposition of Solids," Trans. Faraday Soc., 61, 990-98, (1965).
10. S. J. Gregg, "The Production of Active Solids by Thermal Decomposition. Part 1. Introduction," J. Chem. Soc., 3940-44, (1953).

11. G. Knutsen, D. Beruto and A. W. Searcy, work in progress, University of California, Berkeley.

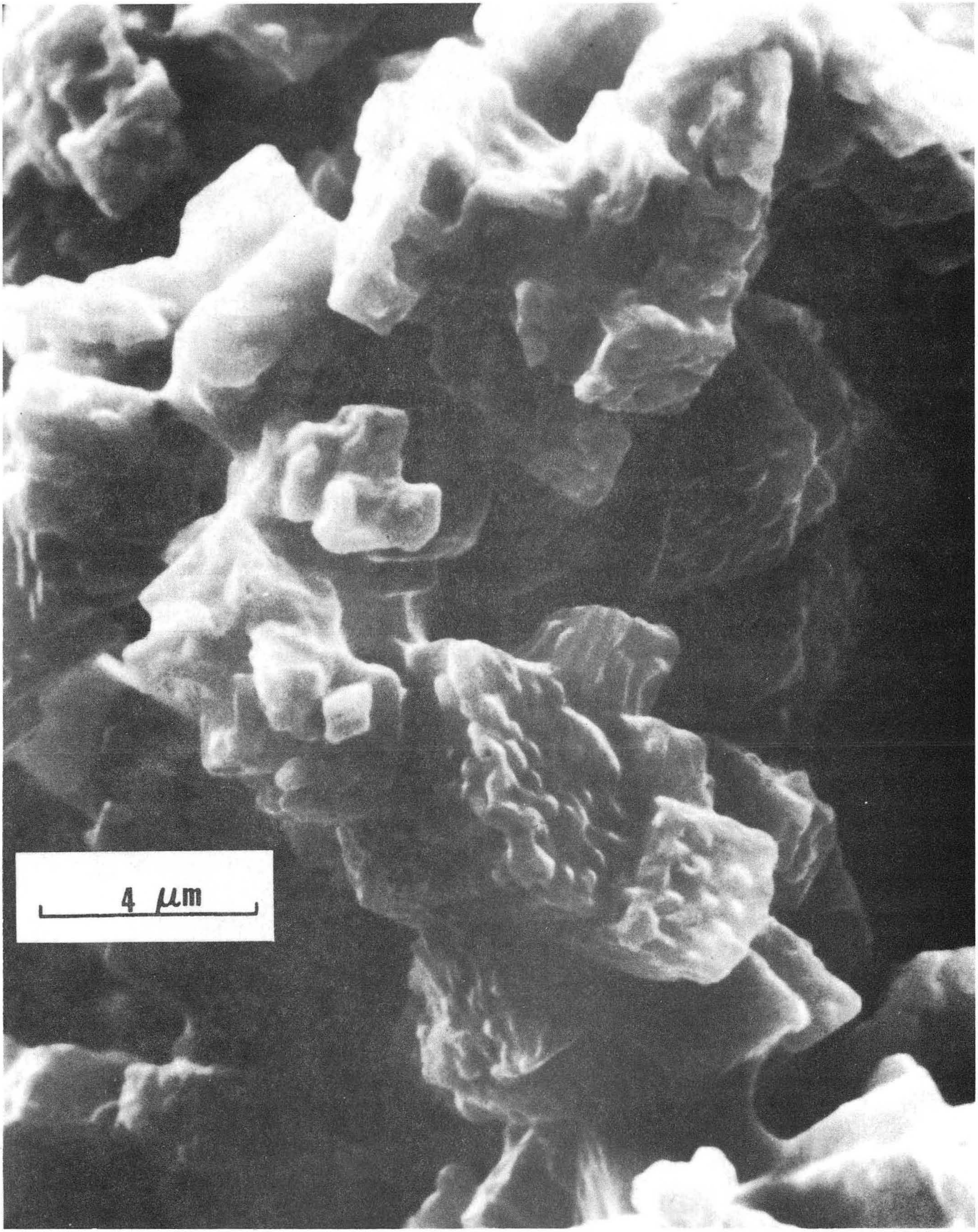
12. E. K. Powell and A. W. Searcy, "The Kinetics and Thermodynamics of Decomposition of Dolomite to a Metastable Solid Product," J. Amer. Ceram. Soc., 61, 216-20, (1978).

13. P. J. Anderson and R. F. Horlock, "Thermal Decomposition of Magnesium Hydroxide," Trans. Faraday Soc., 58, 1993-2004 (1962).

FIGURES

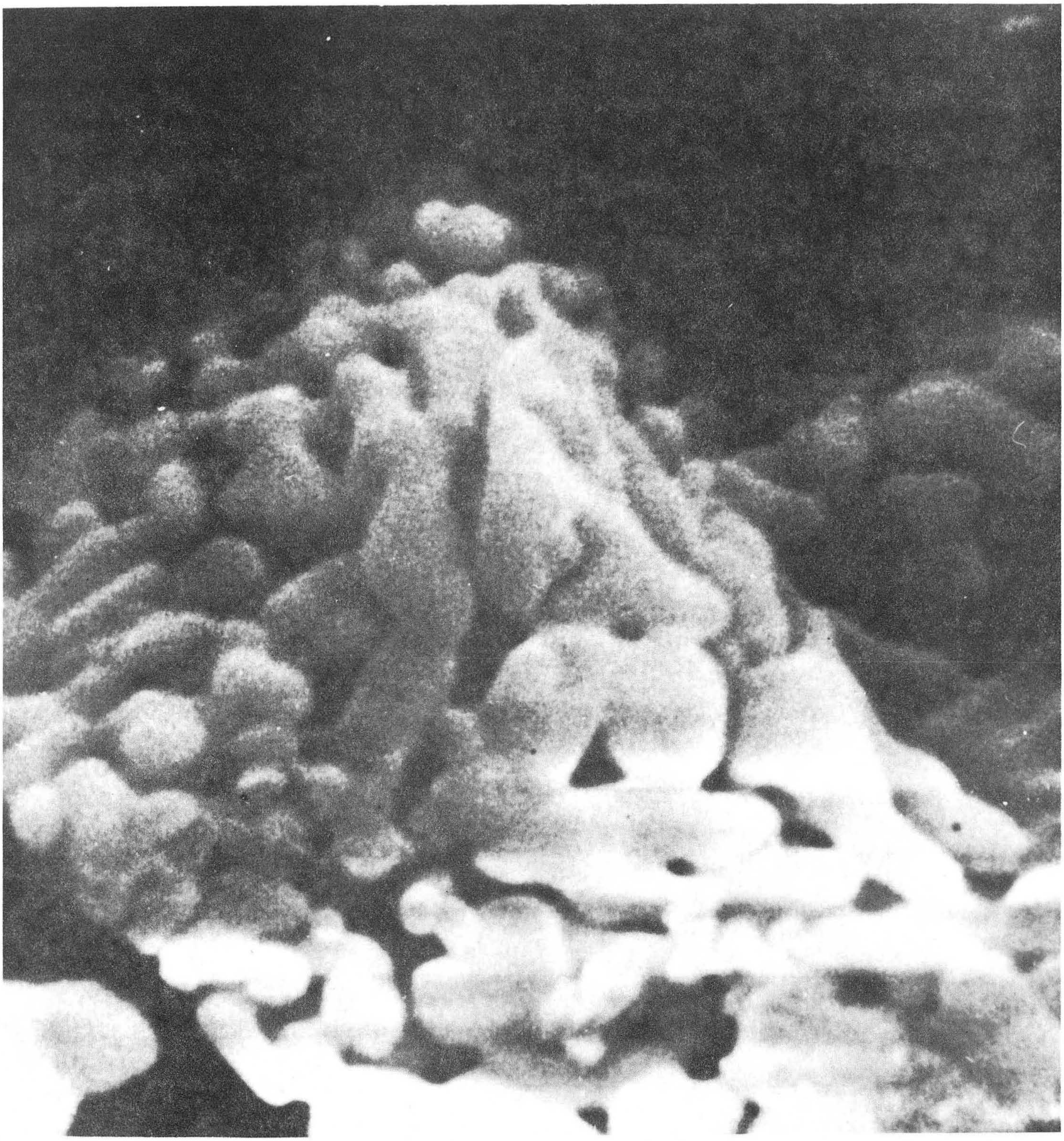
XBB784-4504-A

Fig. 1



XBB785-3793-A

Fig. 2



XBB7610-9883

Fig. 3

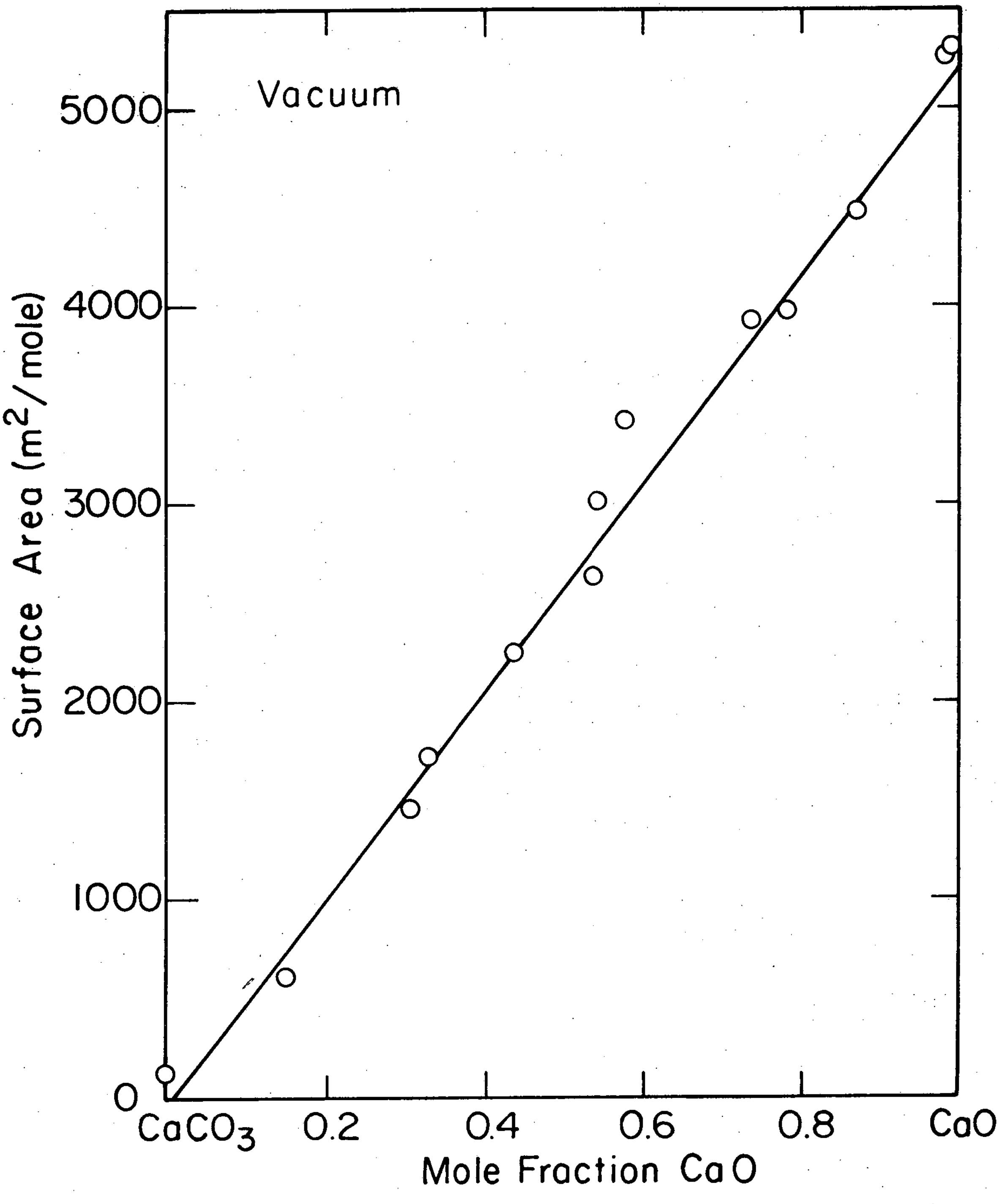
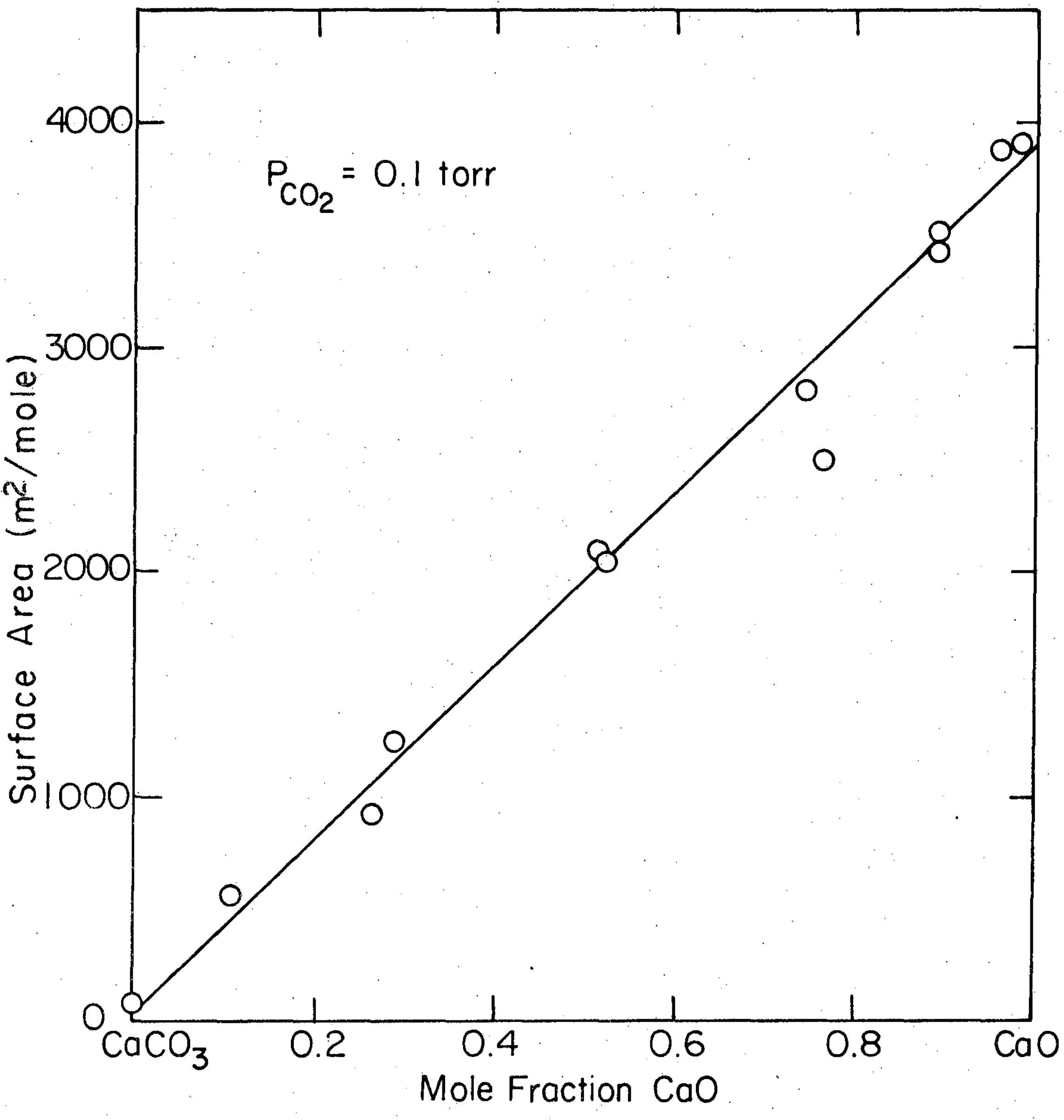
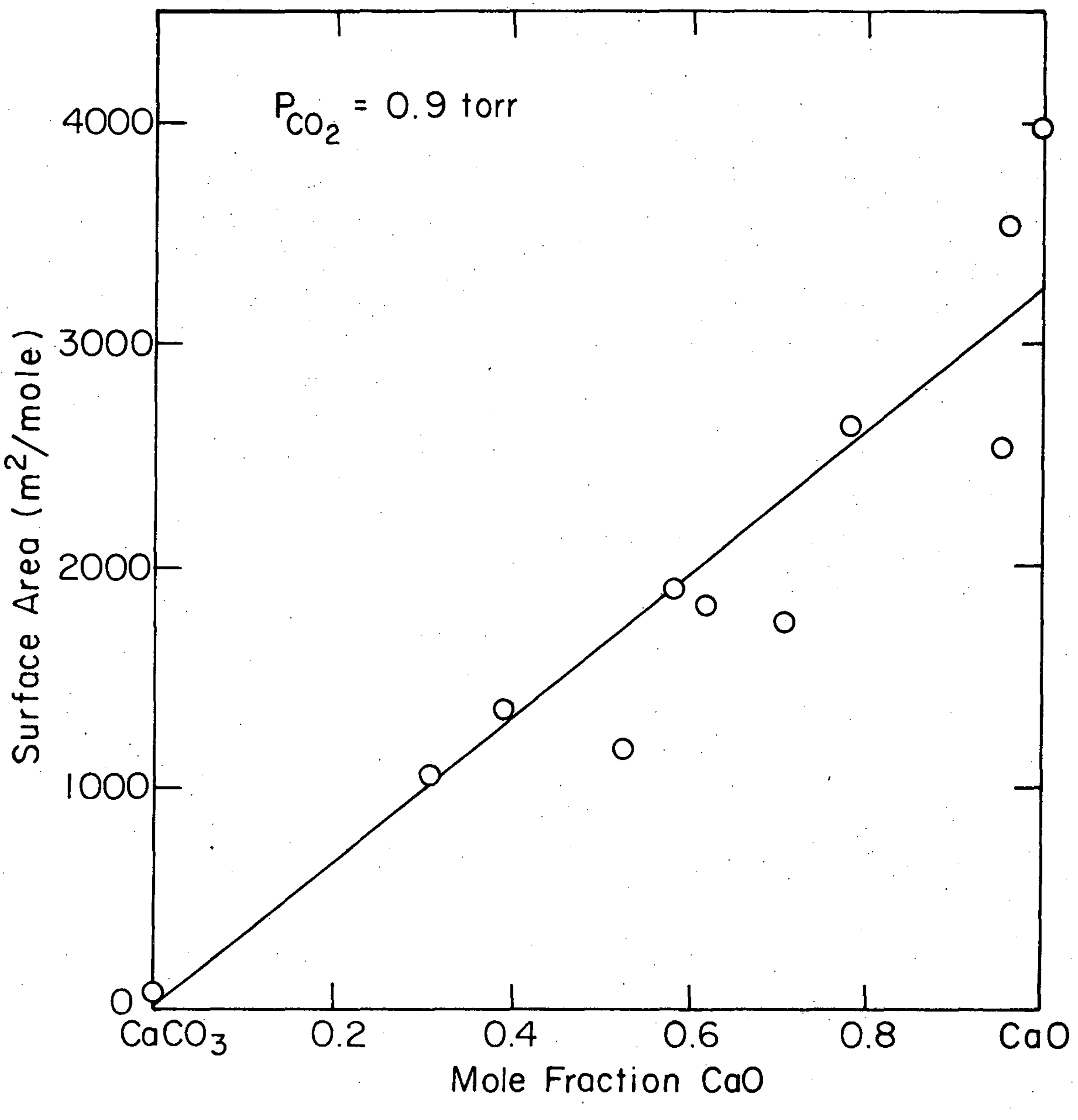

Vacuum
Surface Area (m²/mole)
5000
4000
3000
2000
1000
0
CaCO₃
0.2
0.4
0.6
0.8
CaO
Mole Fraction CaO
XBL 784-4839

Fig. 4



XBL 784-4836

Fig. 5



XBL 784-4837

Fig. 6

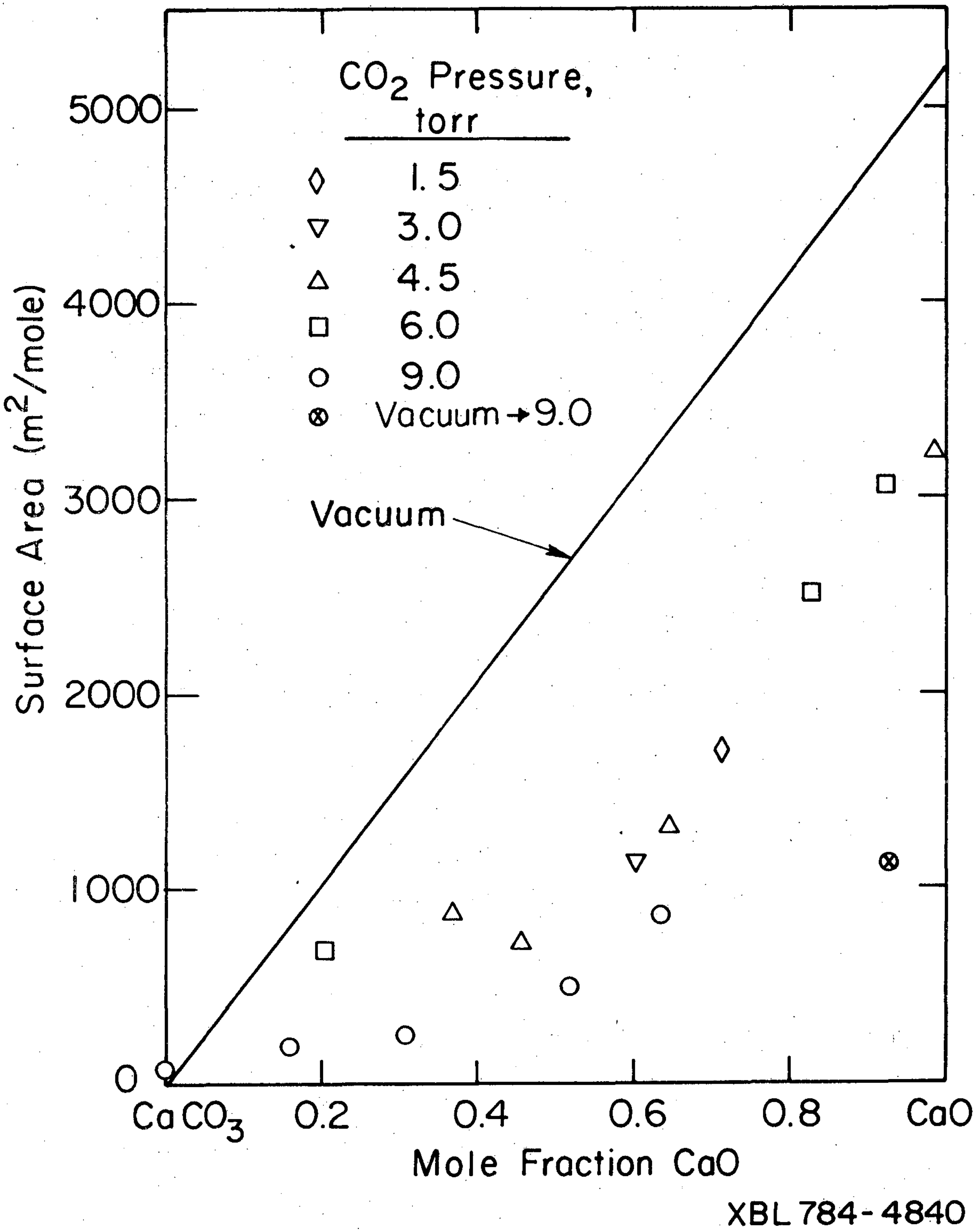

CO_2 Pressure, torr
◊ 1.5
▽ 3.0
△ 4.5
□ 6.0
○ 9.0
⊗ Vacuum → 9.0
Vacuum
Surface Area (m^2/mole)
5000
4000
3000
2000
1000
0
$CaCO_3$
0.2
0.4
0.6
0.8
CaO
Mole Fraction CaO
XBL 784-4840

Fig. 7

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720