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Mun Gyu Kim
(M.S. Thesis)

November 1982

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This work was supported by the Director, Office of Energy Research,
Office of Basic Energy Sciences, Materials Sciences Division of the
U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

TABLE OF CONTENTS

	Page
ABSTRACT	v
I. INTRODUCTION	1
II. EXPERIMENTAL	7
A. N ₂ Adsorption-Desorption at 78°K	9
B. X-ray Analysis	9
C. Morphology Analysis.	10
III. RESULTS.	11
A. Kinetic Data	11
B. N ₂ Adsorption-Desorption Data.	12
C. X-ray Analysis	13
D. SEM Observations	13
IV. DISCUSSION.	15
V. REFERENCES.	27
ACKNOWLEDGEMENT.	29
TABLES	30
FIGURE CAPTIONS.	35
FIGURES.	37

Sintering of product solid CaO from CaCO_3 is catalyzed during the decomposition by a CO_2 pressure which is only about 10^{-4} times the thermodynamic equilibrium CO_2 pressure.

Morphological studies of product CaO made by high resolution scanning electron microscope (SEM) and N_2 adsorption measurements showed the dimensions of pores in CaO from CaCO_3 powder to be greater than those from larger single crystal, but the dimensions of CaO crystallites were smaller when produced from the powder.

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ABSTRACT

Calcite of different particle sizes ranging from about 3 μm to 4 mm in cross sectional distance was decomposed isothermally at 610°C and 670°C in vacuum with variation of sample amount, sample bed depth and packing density, all of which may influence the decomposition rate and the product solid properties.

The effective initial flux of CO_2 from powder samples (~ 3 to 20 μm) and the true initial flux of CO_2 from larger single crystals (0.5 to 4 mm) were constant at $(8.0 \pm 1.0) \times 10^{-5} \text{ g/cm}^2\text{sec}$ and $(2.3 \pm 0.4) \times 10^{-6} \text{ g/cm}^2\text{sec}$ at 670°C, respectively. While the decomposition rate of a powder sample was limited by a metastable equilibrium CO_2 pressure which gave a reaction gradient in the powder bed, an irreversible chemical step of decomposition was rate limiting for larger single crystals.

The conventional kinetic model of contracting surface area was not applicable for calcite powder decomposition and was doubtful for larger crystal decomposition because the assumptions of the kinetic model did not accord with the calcite decomposition.

I. INTRODUCTION

The decomposition product, CaO, of CaCO_3 has been widely used in industry for production of such materials as cements, soda-lime-silica glasses, refractories, and getters of stack gases in steel manufacturing processes. Many investigators²⁻¹⁵ have studied the reaction, $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$, because of the importance of CaO in industry. However, there have been many discrepancies in previous results of CaCO_3 decomposition, particularly in conclusions about the rate limiting step of the reaction,^{6,7,8} kinetic data,^{2,5} and properties of the product CaO.^{4,10} Particle size differences of CaCO_3 have been suggested to be one of the causes of these discrepancies.^{5,8,12}

Kinetic data for decomposition reactions are still most commonly reported in terms of plots of the fraction of weight lost, α as a function of time.¹⁷ Mechanisms are often inferred from the exponent of the time terms of these plots without any supporting evidence that the conditions assumed in deriving a predicted time dependence are appropriate. For example, if a plot fits a curve of the form, $1-(1-\alpha)^{1/n}=kt$ where n is 1, 2, or 3 and k is a reaction rate constant, the data are usually interpreted in terms of a decreasing surface area model.^{16,17} Among the decreasing surface area models, the so-called contracting volume model, $1-(1-\alpha)^{1/3}=kt$, is obtained from the particles of 3 nearly equal dimensions such as a cube or sphere, and the contracting area model, $1-(1-\alpha)^{1/2}=kt$, from the particles of 2 nearly same dimensions and one much larger dimension such as a cylinder or column-shaped prism. Derivation of these models implicitly assumes the reaction to

be so irreversible that the probability is negligible that a gas molecule will be reabsorbed by the reactant surface or will react with the solid reaction product. One purpose of this thesis is to attempt to clarify the question of the reversibility of the decomposition of calcite powders.

Beruto and Searcy⁹ have shown that the inherent reversibility can be calculated by comparing the ratio of the rate of decomposition of single crystals in vacuum to the maximum possible decomposition rate calculated from the Hertz-Knudsen-Langmuir equation, $J_{\max} = P_{\text{eq}} / (2\pi MRT)^{1/2}$. Ewing et al.,¹⁰ Knutsen et al.,¹³ and Roche²⁸ have explored the applicability of this approach to the more complex problem of analysis of decomposition rates for powder beds. These studies yielded unexpected and, for calcite, seemingly internally inconsistent results. Under some conditions of calcite decomposition and of MgSO_4 decomposition, gas fluxes from a container which is open at the top are independent of bed depth. This result implies that equilibrium pressures are reached in the powder beds. But these apparent equilibrium pressures are for calcite only 3×10^{-4} times¹³ and for MgSO_4 only 10^{-3} times²⁸ the true equilibrium pressures.

Why such low apparent equilibrium pressure should be established is not understood. Single crystal decomposition does not appear to approach the same equilibrium state. Furthermore, it has been shown for calcite powder that the decomposition rate is not significantly reduced when a CO_2 pressure as much as 5×10^3 times the apparent bed CO_2 pressure is established in the apparatus. This observation, which implies that equilibrium is not attained between CO_2 gas and the reac-

tant calcite in the powder beds, can not be reconciled with the apparent equilibrium established in vacuum by means of any known model.

Earlier studies of calcite decomposition often did not provide information about sample size, particle size, and particle packing densities, all of which may influence the decomposition rates. The most pertinent previous studies appear to be those of Britton et al.,² those of Gallagher and Johnson,⁵ and those made in this laboratory.

Britton et al.² concluded from their experiments on calcite decomposition in vacuum with three pieces weighing together 0.5 g and on 0.5 g of -10 +12 mesh natural calcite that the reaction proceeds at an interface which advances from the outside of each lump, or perhaps of the whole sample for a finely divided material, towards the interior at a constant linear velocity. They also concluded that the decomposition of CaCO_3 is reasonably consistent with a contracting volume model, $1-(1-\alpha)^{1/3} = kt$. They mentioned four factors which cause a slight deviation of n from 3; self-cooling, recombination at the interface, restricted escape of CO_2 , and slow rate of nucleation. Researches^{9,14,15} in this laboratory confirm the advancing interface model for large crystals but show the process to have an apparent activation enthalpy of 50 ± 3 kcal/mol, instead of 41.6 ± 2.9 kcal/mol, as reported by Britton et al.

Gallagher and Johnson⁵ reported the effects of sample size and heating rate on the kinetics of CaCO_3 decomposition. For isothermal experiments at $880^\circ - 981^\circ\text{K}$ in a stream of oxygen ($60 \text{ cm}^3/\text{min.}$), they used sample sizes in the range of 1-32 mg with a 20-44 μm particle size. They fitted their data to a contracting area equation, $1-(1-\alpha)^{1/2} = kt$,

for $\alpha = 0.05$ to $\alpha = 0.07$. They reported the activation enthalpy to vary from 49.7 kcal/mole for a 1 mg sample to 45.3 kcal/mole for a 32 mg sample, a decrease with increase in sample size. They suggested that four factors influence the rate constant: particle geometry, geometry of the sample bed, self-cooling, and the partial pressure of CO_2 inside the sample. They concluded that heat transfer due to self-cooling limited the observed decomposition rates.

Beruto and Searcy⁹ studied the decomposition of calcite single crystals of constant reaction interfaces by the use of the Langmuir method. They reported the activation enthalpy of the reaction to be 49 kcal/mol, and defined and applied for the first time the decomposition coefficient, i.e., the ratio of the measured flux to the maximum possible flux, to correlate and predict decomposition reaction rates. From the measured decomposition coefficient, 10^{-5} , they concluded that the decomposition of calcite single crystals is a highly irreversible process.

Powell and Searcy⁸ studied the rate and activation enthalpy of decomposition of CaCO_3 in vacuum with single crystals 0.94 to 1.1 cm in length, 0.48 to 0.56 cm in width, and 0.14 to 0.18 cm in thickness. They demonstrated that heat transfer is not rate limiting under conditions used by them or by Beruto and Searcy⁹ and reported the enthalpy of activation to be 50 ± 3 kcal per mole.

Darroudi and Searcy¹⁵ used the Langmuir method to study the effect of CO_2 pressure on the rate of decomposition of calcite single crystals. They found that the decomposition rates were essentially independent of CO_2 pressures corresponding to as much as 10^3 times the

flux that leaves the CaCO_3 in vacuum. They suggest that in this CO_2 pressure range, the rate limiting process is a solid state diffusional step or surface step of CO_2 , Beruto and Searcy^{19,20} reached similar conclusions from the application of their theoretical model to measurements of calcite decomposition rates in vacuum.

Knutsen et al.¹³ measured the decomposition rate in vacuum of calcite powder (2 to 5 μm average particle size) in Knudsen effusion cells and in open crucibles. The open crucible experiments gave an apparent equilibrium CO_2 pressure, $\sim 3 \times 10^{-4}$ times the known pressure for the reaction. This apparent equilibrium pressures could result for CaCO_3 decomposition if the solid decomposition product is unstable by $\sim RT \ln 3.3 \times 10^3 \approx 14$ kcal, which is unlikely. They believed it to be more probable that during decomposition in vacuum calcite is close to equilibrium with CO_2 but is not at equilibrium with the CaO , which is probably formed by a cooperative process such as twinning or shear.

The surface area of CaO produced in calcite decomposition, like the decomposition rate, depends on reaction conditions. Glasson^{3,4} studied the surface area of CaO produced from the decomposition in vacuum and air of calcite powder and crystals. He found that the surface area of CaO produced in vacuum at 700°C from a 2.5 cm sphere of natural calcite was not constant with the mole fraction of CaO produced, but decreased from about $32 \text{ m}^2/\text{g}$ to about $20 \text{ m}^2/\text{g}$ as the reaction proceeded. He suggested that the CO_2 which diffused from the reaction interface to outward was chemisorbed at the surface of the porous CaO and that this chemisorbed CO_2 catalyzed CaO surface diffusion to decrease the surface area. He tested this thesis that CO_2 causes

sintering of CaO by exposing a fully decomposed sample for 5 hours in approximately half of the equilibrium CO_2 pressure at 750°C and found that the CaO surface area was decreased from $31 \text{ m}^2/\text{g}$ to $16 \text{ m}^2/\text{g}$.

Ewing et al.¹⁰ studied the surface area of CaO during the isothermal decomposition of a powder sample of $\sim 3 \mu\text{m}$ average particle size. They showed that the surface area of the sample varied linearly with the mole fraction of CaO, which indicates the specific surface area of CaO is constant throughout the decomposition when the background pressure of CO_2 is low. They also found, in agreement with conclusions of Glasston, that CO_2 catalyzed the sintering of CaO. They considered that this sintering of CaO might result from bulk diffusion of $\text{CO}_3^{=}$ (formed by the reaction $\text{O}^{=} + \text{CO}_2$) in the CaO lattice.

The present study reports the influence of particle size, powder bed depth, and packing densities on the flux of CO_2 and the surface area of CaO produced from CaCO_3 decomposition. The measurements indicate that decomposition mechanisms are different for large particles and powders. High resolution scanning electron microscope (SEM) observations show the pore and crystallite systems of the porous CaO produced by CaCO_3 decomposition. The overall reaction mechanism and product solid properties which the data suggest are compared with previous reports and are discussed in terms of the kinetic and morphological data.

II. EXPERIMENTAL

A natural calcite single crystal was cut and ground to make samples of 74–90 μm , 0.5–0.6 mm, 1.0–1.4 mm, and 4 mm average particle size using standard sieves. To avoid contamination during grinding, the finely divided samples, consisting of particles 5–10 μm and 10–20 μm in size, were obtained from Baker analytical reagent CaCO_3 , low in alkali, using an ultrasonic fine sieve. For powder of about 3 μm particle size Mallinckrodt analytical reagent CaCO_3 was used. Calcite particles from these different sources have nearly the same rhombohedral shape, as shown in SEM micrographs (Fig. 1–6). Spectrographic analyses showed the total impurities in the samples were 1% or less (Table 1). Surface areas of the calcite powders measured by the BET method were all less than 1 m^2/g (Table 3).

For isothermal decomposition at 670°C in vacuum, a 179 ± 1 mg sample of each particle size was placed in an alumina sample cell of thickness, inner diameter and height; 0.10 cm, 0.98 cm and 2.44 cm, respectively. In order to minimize possible effects of different cell geometries, alumina sample cells with heights of 1.05 to 2.44 cm were used in isothermal experiments at 610°C and 670°C in vacuum. The distance between the top of a sample and the top of a cell was held at 1 cm for all the runs except for the run with 1.05 cm cell.

The sample cell was fitted into a platinum basket which was suspended from a 1.0 mm diameter quartz rod into an alumina tube. The rod is connected to a Cahn 1000 recording microbalance that measures the continuous weight change at a full scale sensitivity of 1.0 mg

during thermogravimetric reactions. A detailed description of the apparatus and the back pressure control system was given by Knutsen.¹³

A tube furnace wound with Kanthal wire was used to heat the sample hung in the alumina tube. The temperature was measured with a chromel alumel thermocouple which was placed near the sample cell and connected to a digital readout device. The sample was hung in a 15 cm long uniform temperature zone to avoid a temperature gradient between thermocouple and sample. Sample weight changes were measured continuously on a strip chart recorder at a scale of 10 mg, or 100 mg full scale. For vacuum experiments, a silicone oil diffusion pump maintained the pressure below 5×10^{-5} torr initially and at 1×10^{-3} to 1×10^{-4} torr during the decomposition. The temperature was increased to 400°C slowly, and to 610°C or 670°C at a rate of about 20°C/min. This speed of temperature increase limited the decomposition to less than 3% before the desired temperature was reached. When a desired fraction of decomposition was achieved, the furnace power was turned off to cool the sample.

When the sample was near room temperature, the vacuum system was closed and dry N_2 was introduced to fill the apparatus to atmospheric pressure. CaO reacts rapidly with atmospheric moisture and CO_2 ; therefore the sample was quickly removed, and either transferred as rapidly as possible to the appropriate apparatus for other experiments such as surface area measurements, XRD and SEM observation, or was stored in a small sealed bottle in a desiccator dried by anhydrous $CaSO_4$.

A. N₂ Adsorption-Desorption at 78°K

An N₂ adsorption-desorption isotherm was obtained with the BET apparatus 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 a liquid N₂ bath. A thermal conductivity detector measures the amount of N₂ which is desorbed when the sample is warmed to ambient temperature. The pressure of N₂ is controlled by adjusting the ratio of flow rates of He and N₂.

Each point of an N₂ adsorption plot was obtained by adsorption at successively measured relative pressures. A desorption branch was obtained by adsorbing N₂ at $P/P_0 = 1.0$, and desorbing at successively lower N₂ pressures at the temperature of the liquid N₂ bath. From each N₂ adsorption-desorption isotherm, surface area, pore volume and pore size distribution were obtained.^{23,24} The plot of absorbed volume vs. t (adsorbed liquid N₂ layer thickness) is used to obtain S_t (the surface area obtained by t -method²⁷) and to check capillary condensation of liquid N₂.

B. X-Ray Analysis

For the XRD measurements, the CaO produced from larger crystals were ground, but the CaO from CaCO₃ powders were used without grinding. Samples were packed in a plastic sample holder and irradiated in a Picker X-ray diffractometer using K α_1 radiation (wave length 1.54050 Å). The operating conditions were: 14 mA, 40 KV, 2 degrees 2 θ /min., and 1,000 counts/sec. Samples were scanned from 2 θ = 28° to 2 θ = 45°. This scan

range includes the major peaks of the three possible phases; CaO -37.4°, CaCO_3 -29.4°, and Ca(OH)_2 -34.1°.

C. Morphology Analysis

While some samples were stored in a desiccator, others were dispersed immediately in CCl_4 to prevent hydration and agglomeration of CaO . For an SEM observation, the dispersed sample was dropped in a carbon coated sample holder using an eyedropper, and a layer of gold was coated on the sample to prevent electron charging in the sample. Samples stored in a desiccator were prepared by the same method. The SEM used for this study is ISI-130 which can resolve to about 3 nm.

III. RESULTS

A. Kinetic Data

Weight losses were measured as a function of time and examined in three ways; 1) in terms of the conventional plots of α (= fraction decomposed) vs. time (Fig. 8), 2) in terms of the flux of CO_2 calculated by the equation $J_{tr} = \Delta w / A \Delta t$, where J_{tr} is the flux per unit area of the total CaCO_3 surface (A) obtained by the BET method, and 3) in terms of $J_{ef} = \Delta w / A_e \Delta t$ where A_e is the effective surface area, i.e., cross sectional area of the alumina cell. Values of $\Delta w / \Delta t$ reported in the tables and figures are for weight loss in the time of the initial 20% decomposition.

J_{ef} was nearly independent of particle size for the powder samples (5 μm to 20 μm) and J_{tr} was nearly independent of particle size for larger crystal samples (0.5 mm to 4 mm) (Table 2). During the isothermal experiments at 670°C, powder samples were often partially blown out of the crucible when the decomposition had proceeded about 10–30%. One example is shown in figure 12. Possible reasons for this behavior are suggested in section IV. At 610°C, powder samples did not blow out. Accordingly, this temperature was used for studies of the effects of different sample sizes, cell sizes, and packing densities on weight losses.

Total decomposition times and surface areas of CaO formed in the top of the sample cells are shown as a function of sample height in figures 13 and 14, respectively. For large crystals, total decomposition times and surface areas of CaO are independent of sample heights

but for powder samples, total decomposition times increase linearly and surface areas of CaO decrease linearly with increasing sample heights.

From the plot of effective flux of CO_2 versus packing density (Fig. 10), the flux of CO_2 is shown to be nearly independent of particle size, sample size, and packing density for at least these two powders of about $3\text{ }\mu\text{m}$ and $10\text{--}20\text{ }\mu\text{m}$ particle sizes. Though some powder samples of greater packing densities showed slightly lower fluxes and took longer times for complete decomposition than those of smaller packing densities, the values were within standard deviations.

B. N_2 Adsorption-Desorption Data

For the $10\text{--}20\text{ }\mu\text{m}$ and 4 mm size particles, N_2 adsorption-desorption isotherms were obtained (Fig. 18). These isotherms are Brunauer's classification type IV and De Boer's classification type E, which implies that the pores are of open ended cylindrical or tubular shapes.^{23,25} From both branches of the isotherms, cumulative surface areas, cumulative pore volumes and average pore diameters were obtained (Table 5).²⁴ The adsorption branch data were more consistent with the BET surface areas and with the pore volumes obtained at the relative pressure, $P/P_0 \approx 0.97$ than were desorption branch data. These results suggest that the pores are not of uniform but of rather complex shapes, such as "ink bottles"²⁴ as De Boer²⁶ predicted. The surface areas obtained by the t -method were reasonably consistent with S_{BET} , and the t -plots showed no evidence of pores smaller than 2 nm in diameter (Fig. 20).

C. X-ray Analysis

XRD patterns showed no line broadening for CaO from either powder or single crystal calcite decomposition and no calcite peaks for completely decomposed samples. To test whether the extent of reaction depends on the distance from the top of the powder beds, XRD patterns were obtained for the top and bottom portions of the sample (Figs. 15 and 16). Though quantitative analysis is difficult, comparison of the two XRD patterns indicates that the reaction proceeded more rapidly near the exposed upper surface. It was difficult to compare the crystallinities because the particle sizes for XRD measurements were not uniform, and grinding induces rapid hydration with water vapor in air.

D. SEM Observations

CaCO_3 particles are block-like and relatively uniform in dimensions (Figs. 1-6). The external shapes of the particles were not changed after decomposition (Figs. 21 and 22). In interpreting the SEM pictures it must be remembered that surfaces are coated with layers of gold of thicknesses comparable with the pore and CaO crystallite dimensions which are inferred from the BET measurements. The structure observed reflects the spacing and order of CaO crystallites and pores but the true dimensions of the crystallites are smaller and of the pores larger than seen in the SEM pictures (Figs. 21-26). CaO crystallites produced from powder samples are not plainly visible, but appear much smaller than those produced from single crystals (Figs. 23 and 24). Small cracks (about $1\text{ }\mu\text{m}$ size) are present in CaO produced

from large single crystals (Fig. 25), but not in CaO from powder samples. Cleavage surfaces of CaO from large calcite crystals show that the shapes of pores are not uniform, but very complicated (Fig. 26).

IV. DISCUSSION

Initially some isothermal decompositions of CaCO_3 samples of the same weight, 179 ± 1 mg, were made at 670°C in vacuum without consideration of packing density and sample height. Later measurements were made with a constant distance (1 cm) between the top of the sample cell and the top of the sample. The average effective flux of CO_2 for powder samples of 10–20 μm particle size was nearly the same in both studies within the standard deviation of $\sim 1 \times 10^{-5} \text{ g/cm}^2\text{sec}$ (Fig. 10, Table 2).

If the reaction is irreversible, variation in height of the cell above the sample surface should have no effect on the rate of decomposition; but if the reaction is reversible, CO_2 molecules that collide with the cell wall may return to the sample and be reabsorbed in it. The rate is then reduced by a factor calculated first by Clausing. If the transmission of CO_2 is governed by a Clausing correction factor, the flux of CO_2 from the 12.5 mm cell should be about 1.6 times greater than that from the 24.4 mm cell for the same sample file of 2.5 mm in height.

Sandry and Stevenson²² have derived an equation for the unit flux, J that will escape from a cylindrical tube of Clausing correction, C when the source of vapor is a surface of condensation coefficient, α_c (or vaporization coefficient, α_v ¹⁸). Beruto and Searcy²⁰ used the Sandry and Stevenson equation to study the effects of a porous solid product on endothermic decomposition reactions. The equation is $J/J_0 = C/[C + (1-C)\alpha_d]$, where J_0 is the unit flux that would escape from the

surface if no tube impeded the Knudsen flow, C is the Clausing correction factor, and α_d is the decomposition coefficient, $\alpha_d = J_0/J_{eq}$ where J_{eq} is calculated by introducing the standard free energy change of the reaction,¹ ΔG° into the Hertz-knudsen-Langmuir equation, $J_{ef} = P_{eq}/(2\pi MRT)^{1/2} = \exp(-\Delta G^\circ/RT)/(2\pi MRT)^{1/2}$. From the experimental flux of CO_2 in vacuum, α_d of large calcite crystal decompositions is found to be about 10^{-5} (Table 2) which agrees with previous results^{8,9,15} from the Langmuir method. Substituting $\alpha_d = 10^{-5}$ into the Sandry and Stevenson equation gives $J \approx J_0$ because C is much greater than α_d . Thus, the flux of CO_2 is nearly independent of channel distance for CO_2 escape from the top of the sample to vacuum.

The less complex kinetic results obtained for the large crystals (0.5 to ~ 4 mm) will be discussed first. For the large crystals, the true initial flux of CO_2 is constant at $(2.3 \pm 0.4) \times 10^{-6}$ g/cm²sec at 670°C (Table 2), a value reasonably consistent with previous studies^{9,9,15} in this laboratory. Total decomposition time is inferred to be nearly proportional to the particle size from Table 2 and independent of sample bed depth (Fig. 13). These results imply that the CO_2 pressure within the sample cell does not affect the decomposition rate and that the reaction interface advances with constant velocity.

Possible rate limiting steps are heat transfer to a reaction interface, CO_2 escape from a reaction interface through the porous solid product, and a solid state chemical step as shown schematically in figure 17, which illustrates the movement of solid molecules (or equivalent pairs of ions) A, and gas molecules B that must occur in physical space to separate AB(s) into A(s) and B(g).

Effusion of CO_2 through CaO pores can not be rate limiting because the total decomposition time is directly proportional to particle size. If the CO_2 effusion were rate limiting, the flux should be proportional to a/ℓ , where a is the average cross sectional distance of the pores through the CaO and ℓ is their length.²⁰ Roberts et al.²¹ also showed that the decomposition rate of calcite single crystals was not affected by the formation of a CaO product layer up to 1 mm in thickness. Powell and Searcy⁸ have shown that heat transfer is not rate limiting for decomposition of large calcite crystals with dimensions in the range 0.94 to 1.1 cm in length, 0.48 to 0.56 cm in width and 0.14 to 0.18 cm in thickness under conditions like those used in the present study.⁸ Therefore, a solid state chemical step must be rate limiting, as concluded in the previous studies^{8,15} in this laboratory.

For the isothermal decompositions at 670°C in vacuum, J_{tr} , the true initial flux of CO_2 from powder samples (~ 3 to $20\ \mu\text{m}$) is about 40 times smaller than that from single crystals (0.5 to $\sim 4\ \text{mm}$) (Table 2). These results are essentially consistent with findings of other investigations^{10,12} on calcite decomposition. Since the effective initial flux is nearly independent of powder bed depth (Fig. 10), the largest quantity of powder sample gives the lowest true flux of CO_2 per quantity of CaCO_3 present (Fig. 11). Thus, the solid state chemical step is not rate limiting because the reaction rate is independent of surface area. A self-cooling effect in the endothermic reaction can not account for the decrease in true flux because the temperature difference would have to be $\sim 110^\circ\text{C}$ if self-cooling were respons-

ible. Temperature differences in this study are less than 10°C and were small in other similar investigations.^{10,12} For the measurements of temperature differences between reference thermocouple and sample, a CO_2 pressure, which is ~ 10 times higher than the equilibrium pressure and prevents the decomposition of CaCO_3 , was maintained at 670°C for more than 3 hours. A lower temperature was measured by the thermocouple put in the calcite powder. The temperature drop could be attributed to self-cooling because a temperature drop was not observed with the thermocouple located just above the sample cell. Thus, the reasonable conclusion from the data is that, although back reaction of the CO_2 is negligible for single crystal decomposition,⁹ an equilibrium CO_2 pressure is established inside the powder. This (metastable) equilibrium CO_2 pressure, P_{meq} will limit the decomposition rate to $J_{\text{ef}} = P_{\text{meq}} / (2\pi\text{MRT})^{1/2}$ and give the linear plot of total decomposition time versus powder bed depth (Fig. 13).¹⁸ The equilibrium must be a metastable one because the measured value of P_{meq} is $\sim 4.5 \times 10^{-4} P_{\text{eq}}$.

If a metastable equilibrium pressure is established in the powder beds, three questions are raised: 1) Can the activity of CaO really be as high as $\sim 2.2 \times 10^3$ as implied by the thermodynamic relation, $a_{\text{CaO}} a_{\text{CO}_2} = 1$? (Here $a_{\text{CO}_2} = P_{\text{meq}}/P_{\text{eq}}$ and a_{CaO} is the activity of CaO .) 2) How can the decomposition rate be independent of introduced background CO_2 pressures up to 10^3 times P_{meq} ? 3) Why does the sample blow out at 670°C after seemingly constant, low CO_2 pressures are established in the powder beds?

A CaO activity of 2.2×10^3 implies that a form of CaO metastable by $RT \ln 2.2 \times 10^3 \approx 14.4$ kcal/mole is the reaction product. XRD measurements show only normal CaO to be produced. The surface free energy of the CaO can be estimated from the surface area with the assumption that the surface tension is the same as that reported for MgO, 1200 erg/cm^2 , to be about 1.3 kcal per mole. Even if the lattice is strained, the strain energy is very unlikely to account for the discrepancy. Thus, the observed CaO almost certainly does not have a high enough activity to account for the low measured CO_2 pressure. Dai²⁹ recently showed by TEM that a highly metastable solid solution of CaO in CaCO_3 is formed in very small volume elements of the original CaCO_3 before CaO diffraction spots suddenly appear. It is possible that the measured CO_2 pressures are equilibrium pressures for decomposition of CaCO_3 to a transient CaO- CaCO_3 phase.

Searcy (private communication) suggests that the hypothesis that a transient, metastable phase is formed is consistent with the observation that powder samples sometimes blow out of the crucible after steady state conditions have been established. The CO_2 fluxes measured before blow-out indicate that a low and constant CO_2 pressures in the Knudsen flow range has been established. There is no obvious mechanism for trapped CO_2 gas to build to pressures higher than the pressure corresponding to the measured CO_2 flux; the independence of flux on powder bed depth indicates that back reaction of the CO_2 holds its pressure to that level. If, however, a CaO- CaCO_3 phase unstable by ~ 14.4 kcal/mole is present, its exothermic transformation, $\text{CaO}(\text{CO}_2)_n(\text{s}) - \text{CaO}(\text{s}) + n\text{CO}_2(\text{g})$, on the surface of one particle might sometimes pro-

vide enough heat to trigger the same reaction throughout the powder bed with a sudden release of the CO_2 in the CaO-CaCO_3 which causes the blow-out.

The question of how background pressures of CO_2 more than two orders of magnitude higher than apparent equilibrium pressures in a powder bed can fail to reduce the reaction rate significantly remains unanswered. It is hoped that a planned search by TEM for the hypothesized intermediate CaO-CaCO_3 phase in CO_2 pressures comparable to those established in the powder bed and higher may suggest an explanation of the conflicting data.

The weight loss data of 10-20 μm particle size powder and of a 4 mm size single crystal are plotted in figure 9 and compared with contracting area and volume models. The reaction rate constants, k of the decreasing surface area models are not constant but decreased slowly as the decomposition proceeded. The reaction rate constants for the illustration were chosen to fit at $\alpha = 0.20$ and $\alpha = 0.05$, respectively. The choice of a so-called "reasonable rate constant" may give a better fit for the plots of the kinetic models.

However, the kinetic equations of decreasing surface area models assume that extremely rapid nucleation occurs on all faces and rapid surface growth follows, then the rate of decomposition is determined by the progression of the reaction interface into the center of a decomposing material with a constant velocity.¹⁷ The constant velocity would only be obtained, however, if the reaction is so irreversible that back reaction is negligible, as described in the introduction. Since the reaction interface seemed to move with a constant velocity

for the decomposition of large single crystals (Table 2), the decreasing surface area model might be applicable. But the reaction rate constant of the kinetic model for ~ 4 mm particle size was not constant during the decomposition, probably due to the slight effects of CO_2 escape from the reaction interface or to a smaller interface area than that of the assumed model because of rapid decomposition of corners and edges of the CaCO_3 crystal.

Britton et al. applied the contracting volume model from $\alpha = 0$ to $\alpha = 0.33$ for their calcite decomposition of three "lumps". They also obtained an activation enthalpy (41.6 ± 2.9 kcal/mole) for the reaction by Arrhenius plots. Since they did not specify the surface area of the calcite "lumps", the flux of CO_2 per unit area could not be obtained. Probably their scattered experimental data and lower activation enthalpy, compared to values^{8,9,15} from the Langmuir method, resulted from variation of the surface area of CaCO_3 .

Though Gallagher and Johnson⁵ used relatively small samples, only 1 to 32 mg, with 20-44 μm particle size range, their kinetic data showed a definite effect of CO_2 pressure inside their sample. They used the contracting area model to describe the weight loss data from $\alpha = 0.05$ to $\alpha = 0.7$, where a plot of $[1-(1-\alpha)^{1/2}]$ vs. time showed linear behavior. They obtained activation enthalpies, ΔH^* from Arrhenius plots, that varied systematically from 49.7 kcal/mole for the 1 mg sample to 45.3 kcal/mole for the 32 mg sample, and they concluded that their decomposition rates were controlled mainly by heat transfer due to self-cooling. The activation enthalpy for the 1 mg sample is consistent with values^{8,9,15} obtained for single crystals in vacuum. Ap-

parent heats of decomposition for larger samples approached the equilibrium heat of decomposition, perhaps because the inert atmosphere in which the samples were heated caused CO_2 pressures in the larger samples to approach their equilibrium values. There is no clear reason from the sample geometry to assume that $(1-\alpha)$ should vary with a $1/2$ power dependence on time. That formulation implies the reaction proceeds preferentially in two dimensions.

BET surface area measurements (Table 4) support the conclusion from the kinetic data that an equilibrium was approached in the powder beds. The surface areas of partly decomposed powder samples differ greatly between the top and bottom portion of the powder samples. These results imply that the reaction was in a mixed control regime³⁰ in which some reaction proceeded throughout the sample, but the decomposition proceeded preferentially from the top to the bottom of the powder beds because a metastable equilibrium CO_2 pressure was approached in the powder beds. If each particle of a powder sample decomposed at the same rate, as expected if the reaction is far from equilibrium, the surface areas of the top and bottom portion of partly decomposed sample should be the same.

A weight loss and XRD experiment was performed to corroborate this result. A 470 mg sample of CaCO_3 of about $3\text{ }\mu\text{m}$ particle size was 52% decomposed. The top portion of the sample was removed, and the weight loss which was then measured by decomposing the remaining part showed it to contain 65 mole % CaCO_3 . The XRD patterns obtained from the top and bottom parts of the 52% decomposed powder also showed the de-

composition to proceed preferentially in the top part of the sample (Figs. 15 and 16).

Ewing et al. had concluded that a powder sample decomposed at essentially the same rate throughout the sample. This was based on their finding that the surface areas were about the same for the top and bottom portion of 50 decomposed powder calcite sample of the same 3 μm cross section CaCO_3 powder used in this study. These different results of surface area for partly decomposed powder sample may result from differences in the sample cell or from differences in temperature gradient. Ewing et al. used a platinum bucket of 2 x 2 cm^2 cross sectional area. From the weight of CaCO_3 used by Ewing et al. and from the minimum obtainable packing density found in this study, about 0.25 g/cm^3 , the height of the sample in the platinum bucket would be no more than 0.7 cm. It is difficult to obtain a good separation of top and bottom portions of the sample from a cell with such a large cross sectional area and shallow sample depth.

Because decomposition pressures increase exponentially with temperature, a small difference in temperature distribution within the two samples also could account for the differences in the influence of distance from the exposed sample surface on decomposition rates. The high thermal conductivity of the platinum could cause the calcite close to the cell bottom to be slightly higher in temperature than the calcite near the surface. This gradient would cause a distillation from the bottom to the top of the sample which would neutralize, or even reverse, the preferential decomposition from top to bottom that would otherwise occur.

Ewing et al. also reported the effect of CO_2 background pressure on the surface area of CaO produced from CaCO_3 decomposition. They found that CO_2 catalyzed the sintering of CaO and decreased the surface area of product solid CaO .

In this study, one additional point about CO_2 effects on the sintering of porous CaO was observed; the surface area of CaO produced from CaCO_3 powder decomposition was decreased in proportion to the total time required to complete decomposition (Fig. 14). This means that sintering of CaO was catalyzed by even the very low CO_2 pressures in the powder beds because the surface area of CaO is not changed with long time annealing in vacuum after complete decomposition.^{10,14} The longer exposure to CO_2 can also explain the fact that surface area of CaO from 0.5–0.6 mm crystals of CaCO_3 is greater than that from 4 mm crystal CaCO_3 (Table 3).

One experiment was made to test the effect of low CO_2 pressure on sintering of CaO . The CaO obtained from 1.0–1.4 mm CaCO_3 at 670°C in vacuum was exposed for 26 hours CO_2 at $P_{\text{CO}_2} = 0.12$ torr, which is about 9×10^{-3} the thermodynamic equilibrium pressure, and $\sim 10^3$ times greater than the observed decomposition pressure. During the exposure, there was no measurable weight change with the microbalance set at 10 mg full scale sensitivity. The resultant surface area was $75 \text{ m}^2/\text{g}$, which is $\sim 30 \text{ m}^2/\text{g}$ smaller than that of CaO not exposed in P_{CO_2} , but heated at the same temperature.

Different explanations were advanced for the CO_2 catalyzation of sintering of porous CaO by Glasson⁴ and by Ewing et al.¹⁰ as mentioned in the introduction: These are surface diffusion by chemisorbed

CO_2 and bulk diffusion by solution of CO_2 as $\text{CO}_3^{=}$ ions in the CaO lattice, respectively. The CaCO_3 diffraction patterns observed by Glasson and by Ewing et al. in CaO heated in a CO_2 atmosphere supposedly below the decomposition pressure are probably the consequence of recarbonization.¹³ XRD measurement of CaO ($75 \text{ m}^2/\text{g}$) exposed in $P_{\text{CO}_2} = 0.12$ torr in this study did not show a CaCO_3 diffraction peak. Although the CO_2 effects of sintering of the active CaO from CaCO_3 decomposition in vacuum were shown, it is not possible from this or earlier studies to conclude whether sintering was catalyzed by CO_2 chemisorbed on CaO or CO_2 in solution in the CaO lattice.

N_2 adsorption-desorption isotherms (Fig. 18) of CaO for the present study are consistent with open-ended cylindrical or tubular pore shapes.^{24,25} The desorption branch is usually used to calculate pore size distribution whatever the shape of adsorption-desorption curve is,²⁴ but De Boer²⁶ suggested that for "ink bottle shape pores" S_{BET} should be smaller than $S_{\text{cum}}^{\text{des}}$ and approximately equal to $S_{\text{cum}}^{\text{ads}}$. Also, for slit shape pores S_{BET} should be smaller than $S_{\text{cum}}^{\text{ads}}$ and approximately equal to $S_{\text{cum}}^{\text{des}}$. Since the adsorption branch data is in better agreement with S_{BET} and the measured pore volume at the relative pressure, $P/P_0 = 0.97$ than is the desorption branch data (Table 5), the pore shape is predicted to be "ink bottle shape" or complex shape.

Pore shapes observed by SEM are not of uniform cylindrical or tubular shapes, but are of rather complicated shapes (Figs. 21-26). However, the "ink bottle" model predicts that $S_{\text{cum}}^{\text{ads}}$ can't be greater than S_{BET} , which is not consistent with this result. Another hypothesis²⁶ is introduced to explain that $S_{\text{cum}}^{\text{ads}}$ is slightly greater than S_{BET} : Pores

may be interconnected to give a S_{cum} greater than S_{BET} . Interconnected pores can give additional contributions to S_{cum} from interconnected pseudointerfaces between pores, which are not included in S_{BET} .

The SEM pictures reveal what appear to be rod shaped CaO particles, which is consistent with the conclusion from TEM studies²⁹ that the particles are needles of ~ 10 nm diameter. SEM data support the inference from the BET study that pore dimensions of CaO made from CaCO_3 powders is greater than that made from large single crystals (Fig. 19). In the figures 21-26, pore sizes are observed to be approximately 5-15 nm, which is reasonably consistent with the average pore diameter calculated from adsorption branch data (Fig. 19). CaO crystallite sizes made from 10-20 μm CaCO_3 particles are observed by SEM to be smaller than those made from 4 mm CaCO_3 particles (Figs. 23 and 24). Since the t-plot shows no evidence of pores smaller than ~ 2 nm and since the surface areas of CaO from 10-20 μm CaCO_3 particles are smaller than those from 4 mm particles, the crystallites from the 10-20 μm CaCO_3 must be partly aggregated into non-porous clusters.

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ACKNOWLEDGEMENT

I express my sincere gratitude from the bottom of my heart to Professor Alan W. Searcy for his guidance and help which he provided throughout the course of this research. I would also like to thank Dario Beruto who gave me the basic understanding of high temperature gas-solid reactions. Thanks to every member of the professor "Searcy Group", especially to Dr. David Meschi. They provided many helpful suggestions with kindness and patience.

I extend my appreciation to LBL technicians, without whom this work would have been impossible to complete.

This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

Table 1. Spectrographic Analysis of CaCO_3

<u>Sample Source:</u>	<u>Mallinckrodt AR</u>	<u>Baker AR</u>	<u>Natural Single Crystal</u>
Ca	<u>Principal Metallic Constituent</u>		
Sr	0.025 %	0.01 %	<0.002 %
Mg	0.02	<0.01	0.005
Fe	0.003	<0.0005	
Mn	0.002		
Ba	0.001	0.002	
Al	0.001		<0.0005
Cu	<0.001		<0.0003
K	<0.5	0.008	
Na	<0.05	0.007	
Si	<0.005		
Cl	0.001	0.001	
F		0.001	
SO_4		0.005	
Heavy metals (as Pb)		0.0005	

Table 2. Initial Fluxes of CO₂ and Total Decomposition Time*

Particle size	J _{true} initial (g/cm ² sec)	J _{eff.} initial (g/cm ² sec)	Total decomp. time
5-10 μ m	5.2, 5.8 (5.5 $\pm$ 0.4) $\times 10^{-8}$	8.5, 9.4 (9.0 $\pm$ 0.6) $\times 10^{-5}$	62, 70 66 $\pm$ 5 min
10-20 μ m	7.8, 8.4, 9.6 (8.6 $\pm$ 0.9) $\times 10^{-8}$	8.1, 8.4, 9.5 (8.7 $\pm$ 0.7) $\times 10^{-5}$	60, 65, 70 65 $\pm$ 5 min
74-90 μ m	4.3, 5.3, 5.7 (5.1 $\pm$ 0.7) $\times 10^{-8}$	5.2, 6.3, 6.8 (6.1 $\pm$ 0.8) $\times 10^{-5}$	100, 110, 120 110 $\pm$ 10 min
0.5-0.6 mm	2.2, 2.5, 2.7, 2.8 (2.5 $\pm$ 0.3) $\times 10^{-6}$	2.2, 2.5, 2.7, 2.9 (2.5 $\pm$ 0.3) $\times 10^{-5}$	4.8, 5.2, 5.5, 5.7 5.3 $\pm$ 0.4 hr
1.0-1.4 mm	1.7, 1.8, 2.2, 2.6 (2.1 $\pm$ 0.4) $\times 10^{-6}$	0.8, 0.8, 1.0, 1.2 (1.0 $\pm$ 0.2) $\times 10^{-5}$	9.0, 9.2, 9.3, 10.0 9.4 $\pm$ 0.4 hr
~ 4 mm	1.8, 2.3, 2.8 (2.3 $\pm$ 0.5) $\times 10^{-6}$	1.9, 2.8, 3.2 (2.6 $\pm$ 0.7) $\times 10^{-6}$	30, 32, 34 32 $\pm$ 2 hr

* Decomposition was made at 670°C in vacuum.
 Thermodynamic equilibrium flux of CO₂ at 670°C is 1.77×10^{-1} g/cm²sec
 Separate numbers are the experimental values of each run.

Table 3. Surface Areas and Pore Volumes*

Particle size	Calcite Surface Area (cm ² /g)		CaO properties		CaO ave. pore dia. (nm)	Theoretical meso-porosity (%)
	Calculated	Measured	S _{CaO} (m ² /g)	V _{m.p.} (ml/g)		
5-10 μ m	3.1×10^3	6.9×10^3	83 $\pm$ 1.0	0.262 $\pm$ 0.003	12.6 $\pm$ 0.2	39.8 $\pm$ 0.5
10-20 μ m	1.6×10^3	4.2×10^3	81 $\pm$ 2.0	0.258 $\pm$ 0.004	12.7 $\pm$ 0.4	39.2 $\pm$ 0.6
74-90 μ m	2.8×10^2	5.0×10^3	99 $\pm$ 2	0.256 $\pm$ 0.003	10.2 $\pm$ 0.3	38.9 $\pm$ 0.5
0.5-0.5 mm	42.3	-	114 $\pm$ 4	0.254 $\pm$ 0.002	8.9 $\pm$ 0.3	38.6 $\pm$ 0.3
1.0-1.4 mm	19.4	-	102 $\pm$ 2	0.251 $\pm$ 0.003	9.8 $\pm$ 0.2	38.2 $\pm$ 0.5
~ 4 mm	5.4	5.3 $\pm$ 0.3	102 $\pm$ 3	0.247 $\pm$ 0.003	9.7 $\pm$ 0.3	37.5 $\pm$ 0.5

*CaO was obtained from the CaCO₃ decomposition at 670°C in vacuum.

Table 4. Decomposition Data for Powder CaCO_3 at 610°C *

Particle size	Sample height (mm)	Packing density (g/cm^3)	Reaction time (min)	reaction	$J_{\text{eff. initial}}$ ($\text{g}/\text{cm}^2\text{sec}$)	S_{BET}^{**} (m^2/g)	
						top	bottom
$\sim 3 \mu\text{m}$	2.5	0.424	95 ± 5	100	$(2.20 \pm 0.08) \times 10^{-5}$	97	
$\sim 3 \mu\text{m}$	14.4	0.424	490 ± 15	100	$(2.10 \pm 0.07) \times 10^{-5}$	74	60
$\sim 3 \mu\text{m}$	14.4	0.424	115	40	2.04×10^{-5}	84	6.1
10-20 μm	2.5	1.008	180 ± 5	100	$(2.40 \pm 0.08) \times 10^{-5}$	95	
10-20 μm	14.4	1.008	1800 ± 120	100	$(2.05 \pm 0.08) \times 10^{-5}$	66	48
10-20 μm	14.4	1.008	225	29	2.13×10^{-5}	45	1.3

* Equilibrium flux of CO_2 at 610°C is $4.04 \times 10^{-2} \text{ g}/\text{cm}^2\text{sec}$.

**Top and bottom indicate the location of sample in the sample file chosen for BET measurements.

Table 5. N₂ Adsorption - Desorption Data of CaO*

Particle size	Surface areas**			Pore volumes***			Ave. pore radii****		
	S _{BET}	S _t	S _{ads.} cum.	S _{des.} cum.	V _{m.p.}	V _{ads.} cum.	V _{des.} cum.	$\bar{r}_p$	$\bar{r}_p^{\text{ads.}}$ $\bar{r}_p^{\text{des.}}$
10-20 μm	77	76	80	97	0.261	0.258	0.269	6.8	6.5 5.6
~ 4mm	104	101	111	143	0.245	0.246	0.267	4.7	4.4 3.7

* CaO was obtained from the calcite decompositions at 670°C in vacuum.

** S; Specific surface area (m²/g)

*** V; Specific pore volume (ml/g).

V_{m.p.}; Meso-pore volume obtained at a relative pressure, P/P₀ $\approx$ 0.97

**** $\bar{r}_p$; Average pore radius (nm)

$$\bar{r}_p \text{ (nm)} = \frac{2 \times 10^3 V \text{ (ml/g)}}{S \text{ (m}^2\text{/g)}}$$

FIGURE CAPTIONS

- Figure 1. Mallinckrodt AR CaCO_3 ($\sim 3 \mu\text{m}$).
- Figure 2. Baker AR CaCO_3 (5–10 μm).
- Figure 3. Baker AR CaCO_3 (10–20 μm).
- Figure 4. Natural calcite, magnification 400 (74–90 μm).
- Figure 5. Natural calcite, magnification 20 (0.5–0.6 mm).
- Figure 6. Natural calcite of magnification 20 (1.0–1.4 mm).
- Figure 7. Experimental apparatus.
- Figure 8. Decomposition rates of CaCO_3 with six different particle sizes at 670°C .
- Figure 9. α (= fraction decomposed) vs. time plot of 10–20 μm and $\sim 4 \text{ mm}$ particle size CaCO_3 compared with kinetic models of contracting area and contracting volume (sphere), respectively.
- Figure 10. Effective initial flux of CO_2 vs. packing density with a constant distance (= 1 cm) between the top of sample cell and the top of sample file.
- Figure 11. Effective initial flux of CO_2 vs. sample weight for $\sim 3 \mu\text{m}$ and 10–20 μm powder samples at 610°C .
- Figure 12. Weight lost vs. time for $\sim 3 \mu\text{m}$ powder sample (435 mg) at 670°C , an example of sample blow-out.
- Figure 13. Total decomposition time vs. sample height for $\sim 3 \mu\text{m}$ powder at 610°C and 1.0–1.4 mm single crystal CaCO_3 at 670°C .

- Figure 14. Surface area of CaO from the top portion of sample, plotted versus sample height for $\sim 3 \mu\text{m}$ powder at 610°C , and 1.0–1.4 mm single crystal CaCO_3 at 670°C .
- Figure 15. XRD pattern of top portion of 52% decomposed powder.
- Figure 16. XRD pattern of bottom portion of 52% decomposed powder.
- Figure 17. Schematic drawing of cross section for the reaction $\text{AB (s)} = \text{A (s)} + \text{B (g)}$ by Beruto and Searcy.
- Figure 18. N_2 adsorption-desorption isotherms at 78°K for product CaO from 10–20 μm (curve a) and $\sim 4 \text{ mm}$ CaCO_3 (curve b).
- Figure 19. Pore size distributions of CaO; curve a from adsorption branch of curve a in Fig. 18 and curve b from adsorption branch of curve b in Fig. 18.
- Figure 20. Adsorbed N_2 volume (V_a) vs. statistical thickness (t); curve a and b correspond to Fig. 18.
- Figure 21. CaO from 10–20 μm CaCO_3 located in the top portion of a sample of 14.4 mm height after decomposition at 610°C in vacuum.
- Figure 22. CaO located at the bottom of same sample as Fig. 21.
- Figure 23. CaO from 10–20 μm CaCO_3 at 670°C in vacuum.
- Figure 24. CaO from 1.0–1.4 mm CaCO_3 at 670°C in vacuum.
- Figure 25. CaO from 1.0–1.4 mm CaCO_3 at 670°C in vacuum.
- Figure 26. Cleavage plane of CaO from 1.0–1.4 mm CaCO_3 at 670°C in vacuum.

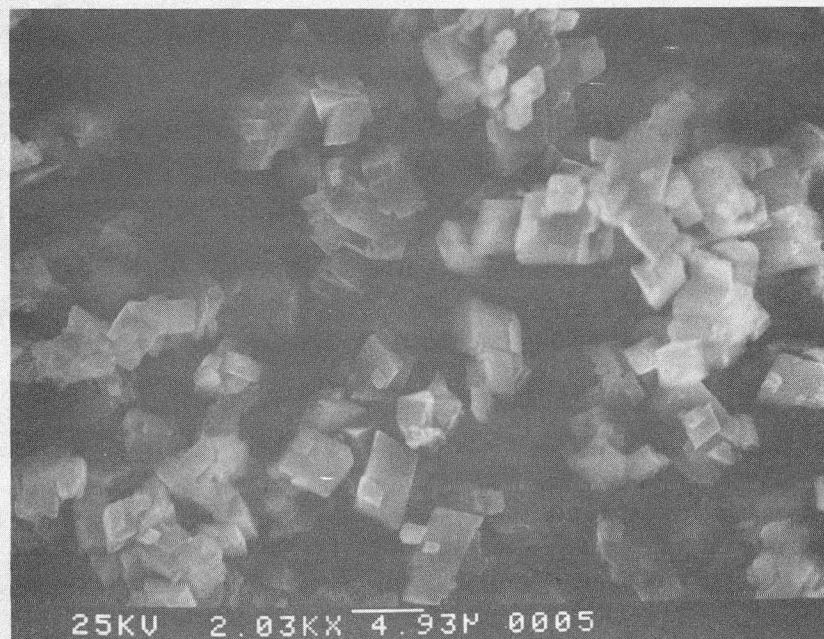


Fig. 1

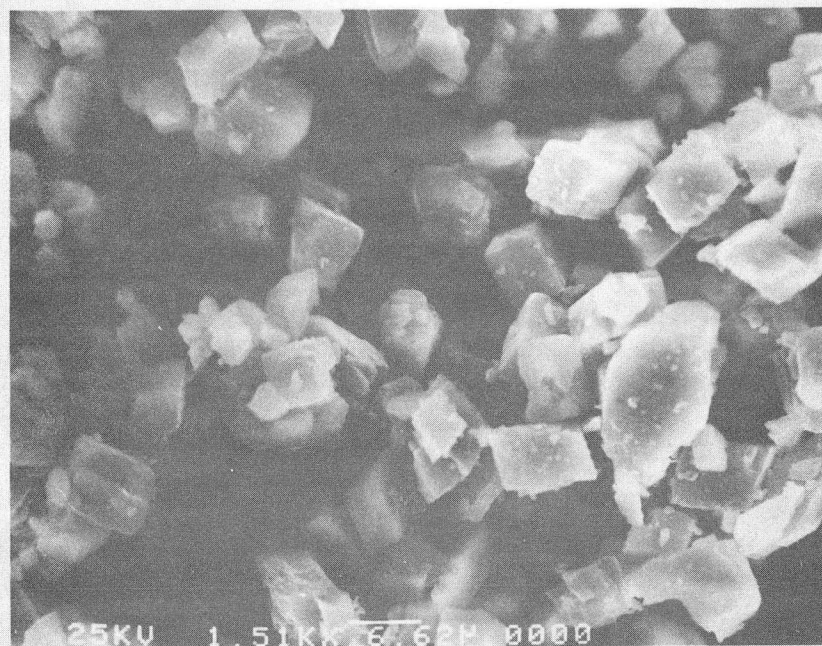


Fig. 2

XBB 825-4486

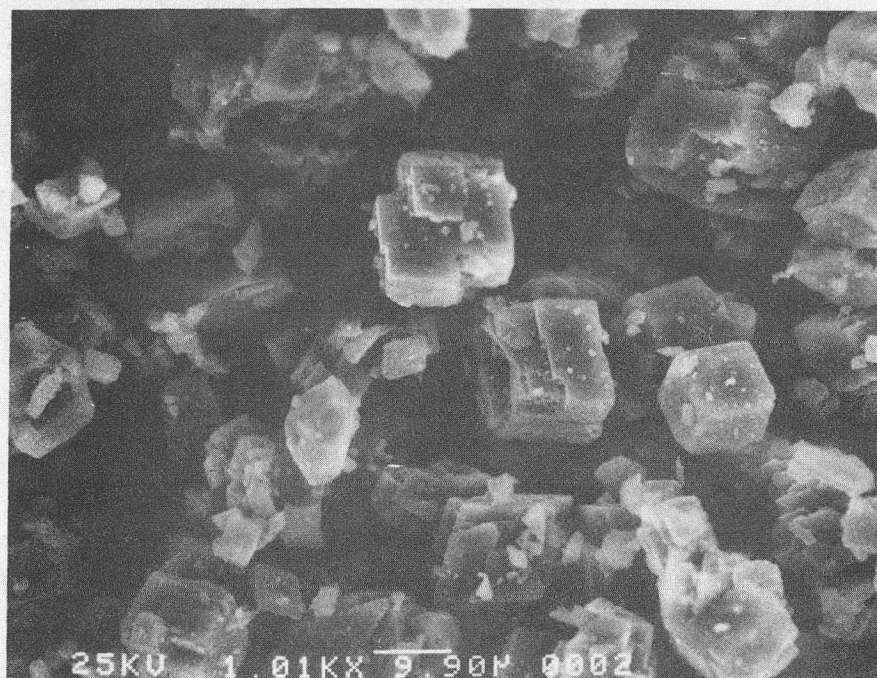


Fig. 3



Fig. 4

XBB 825-4485

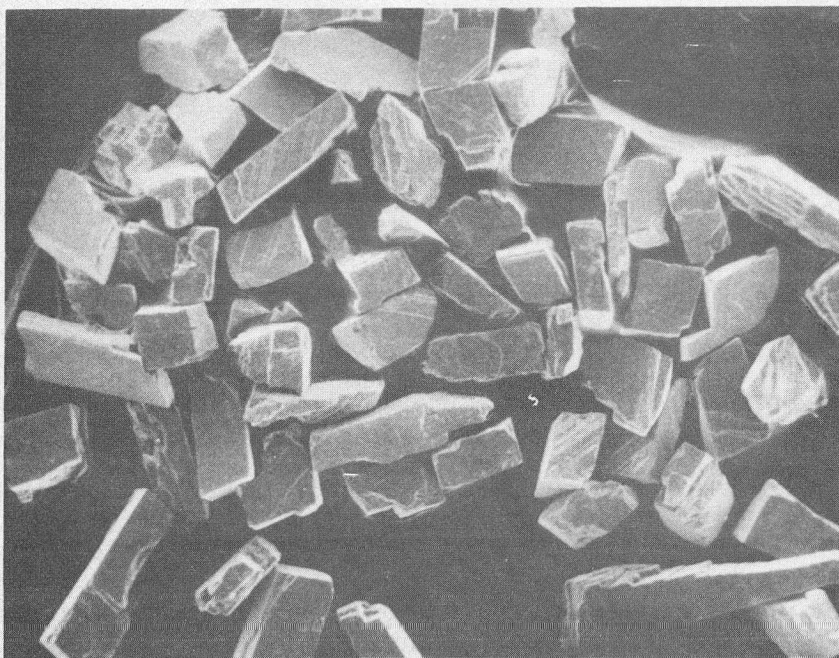


Fig. 5

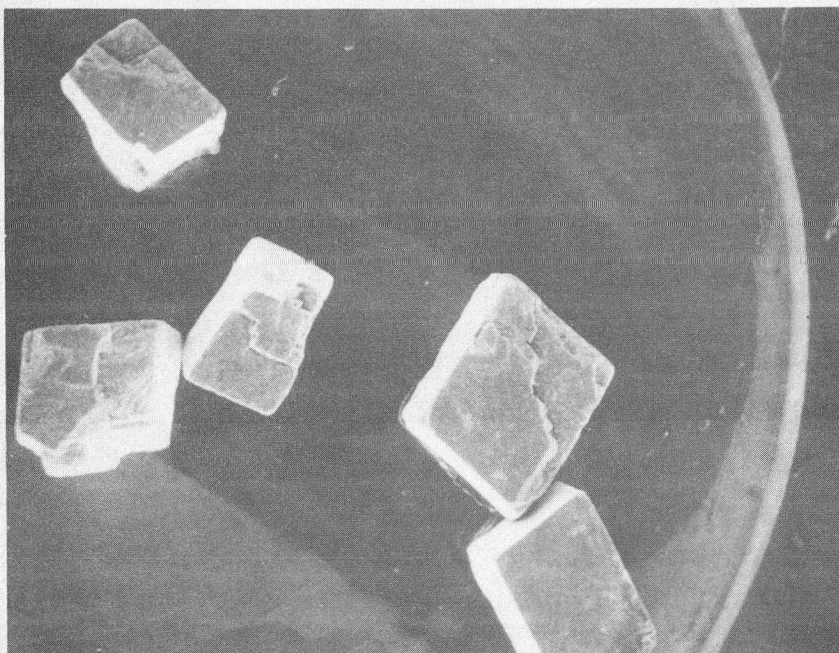
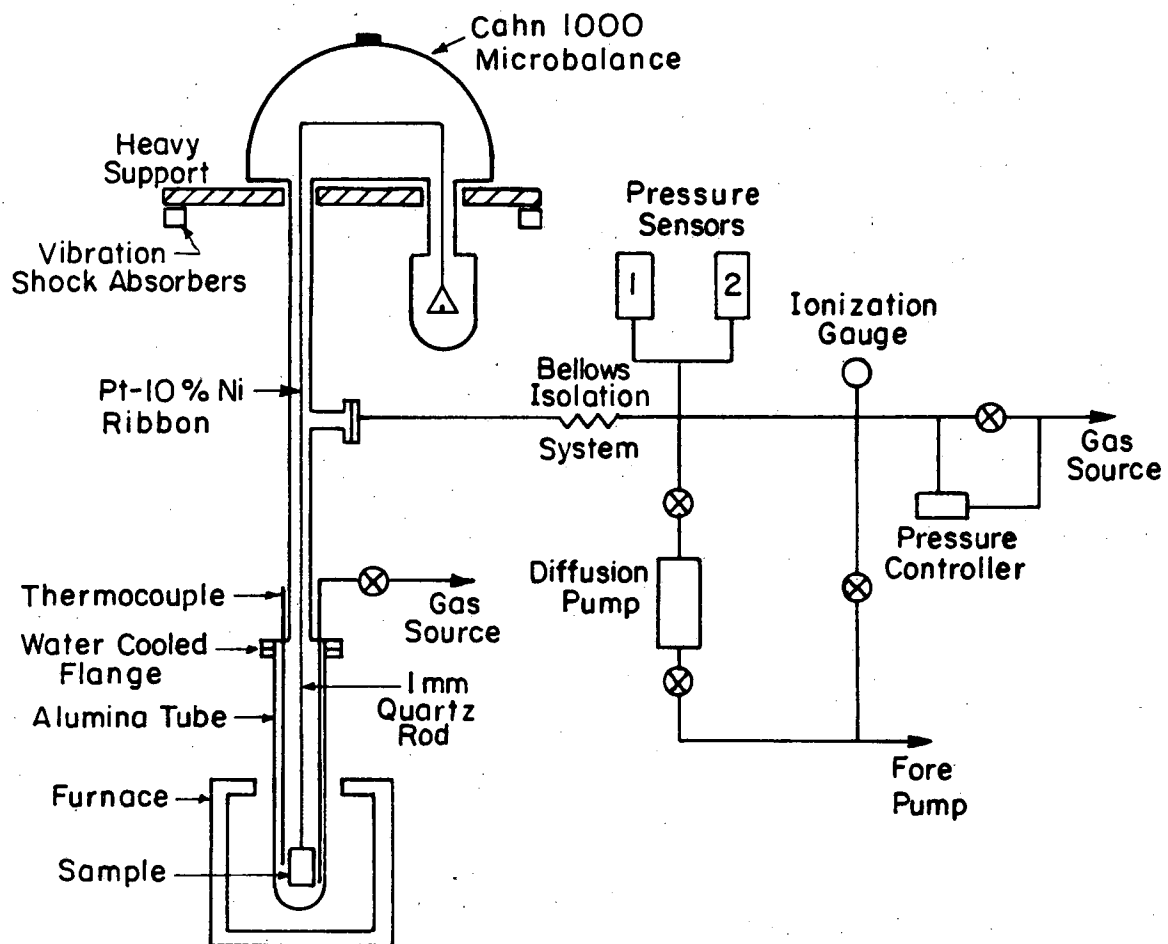


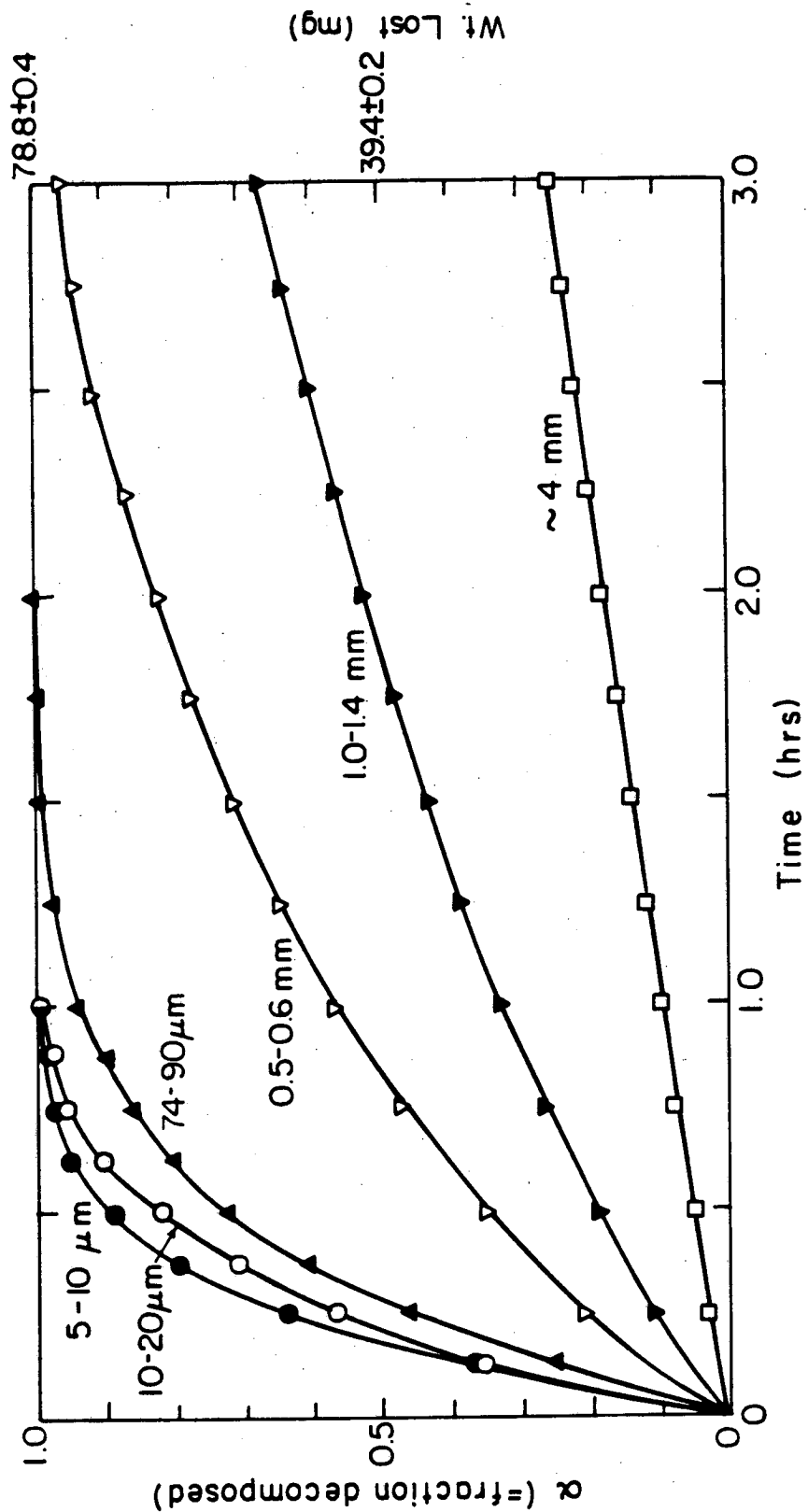
Fig. 6

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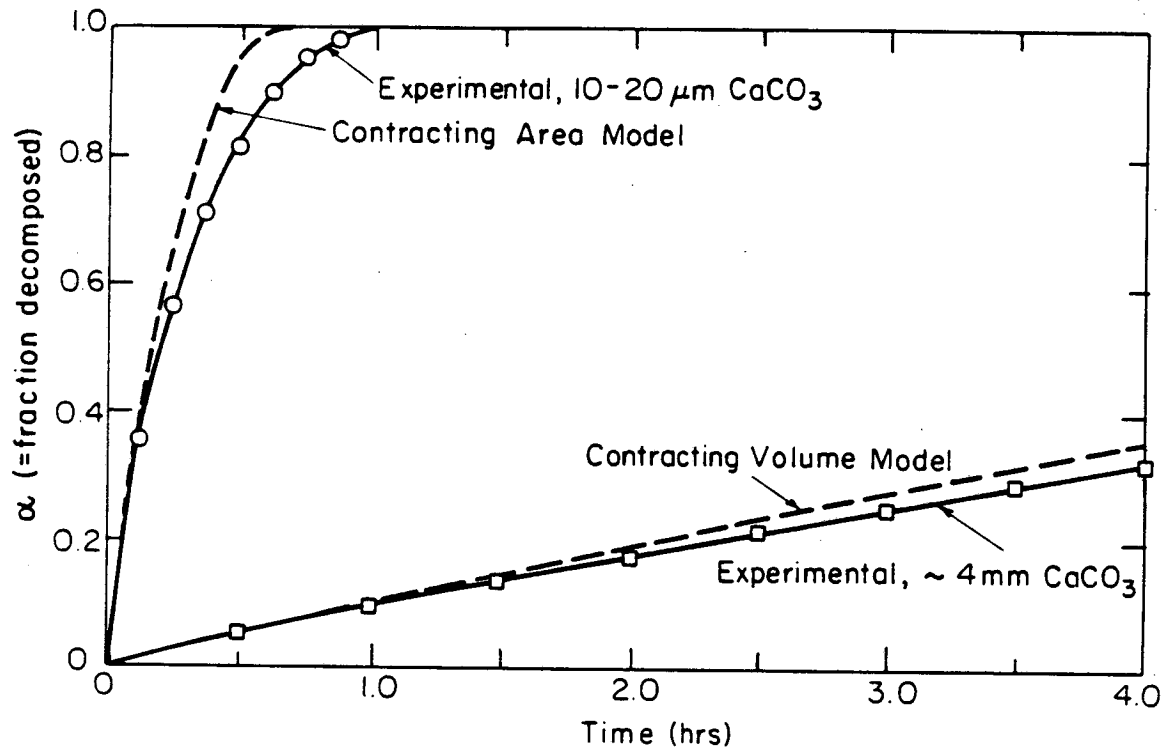
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Fig. 7



XBL 825-5760

Fig. 8



XBL 825-5763

Fig. 9

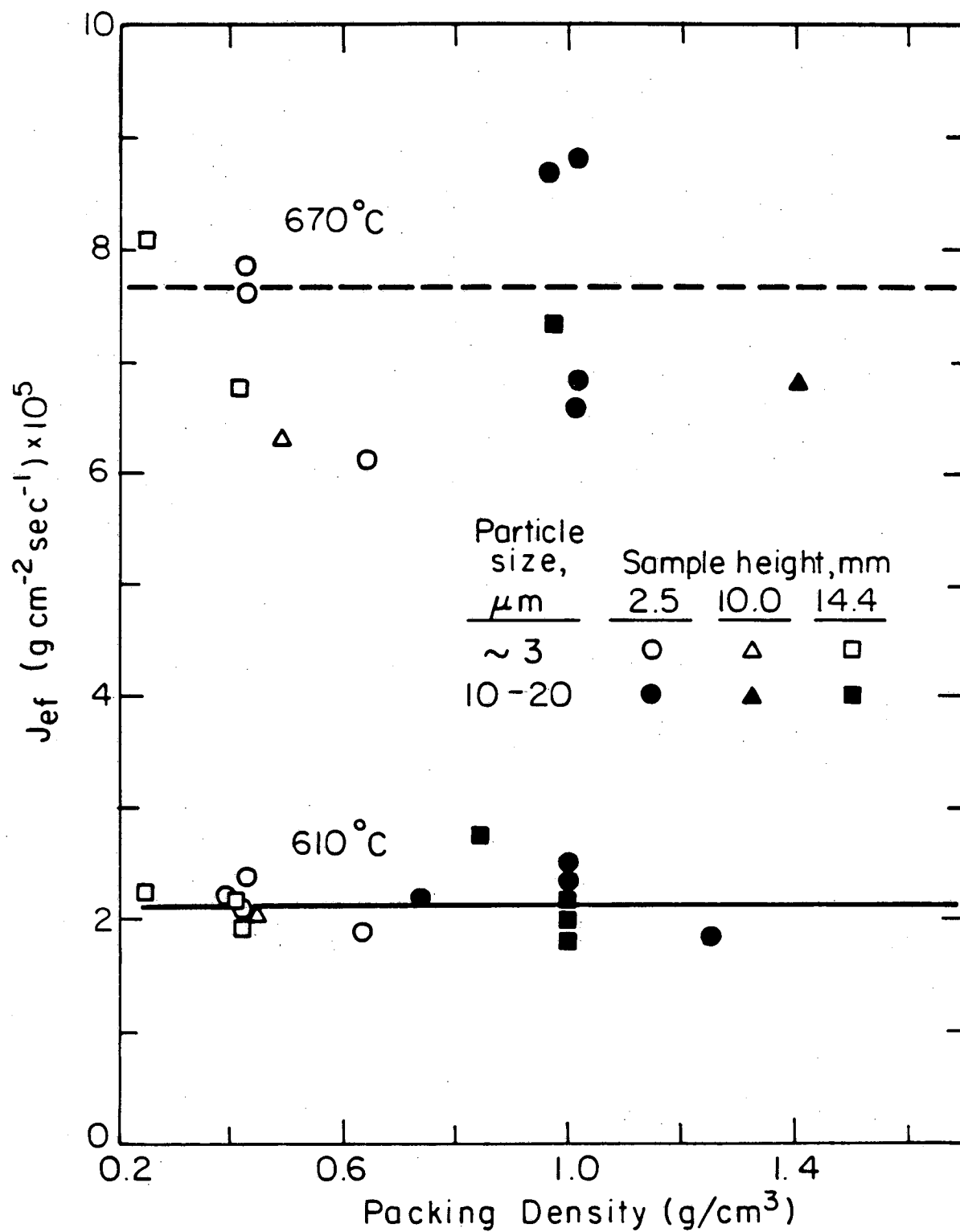
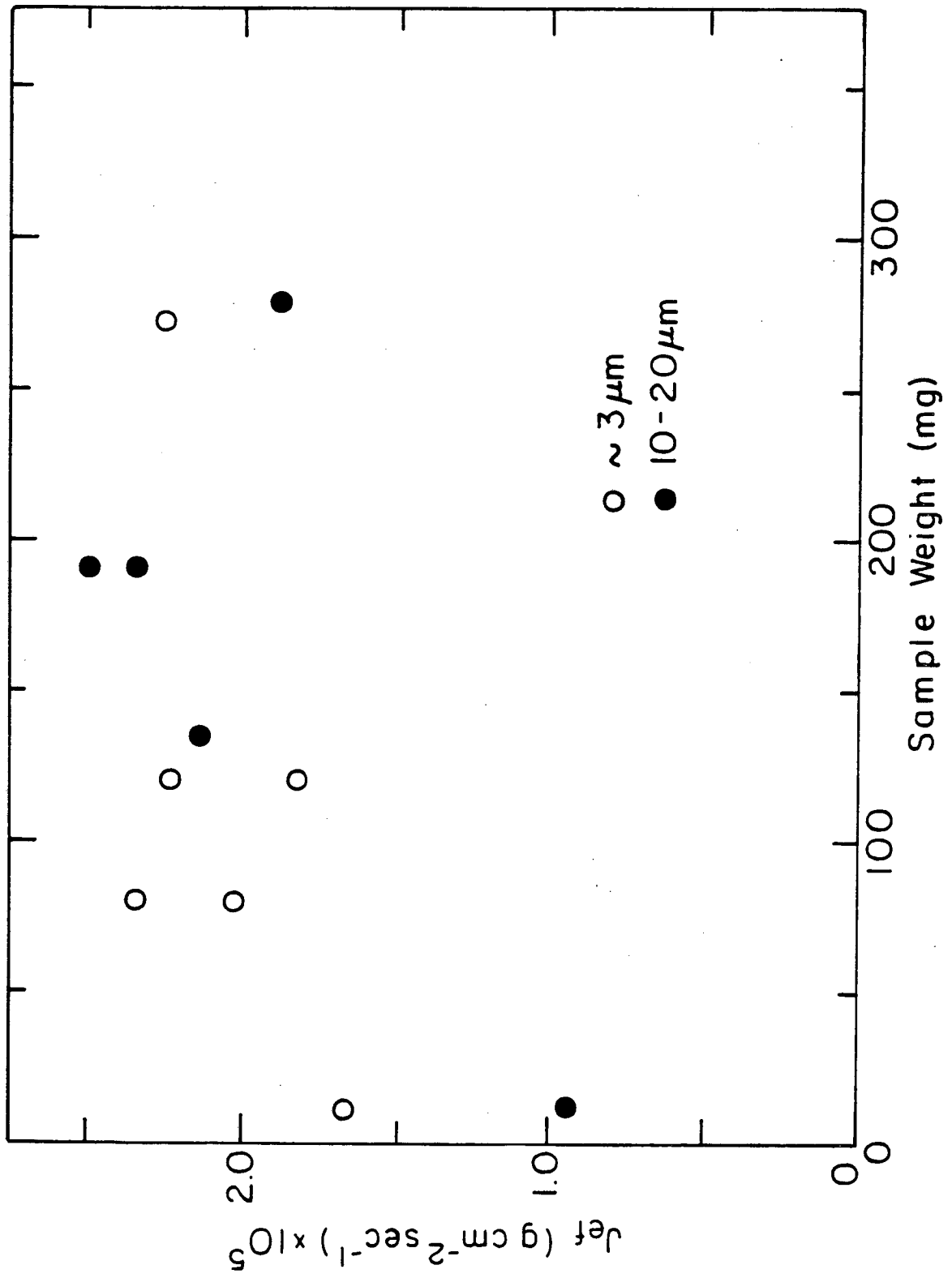


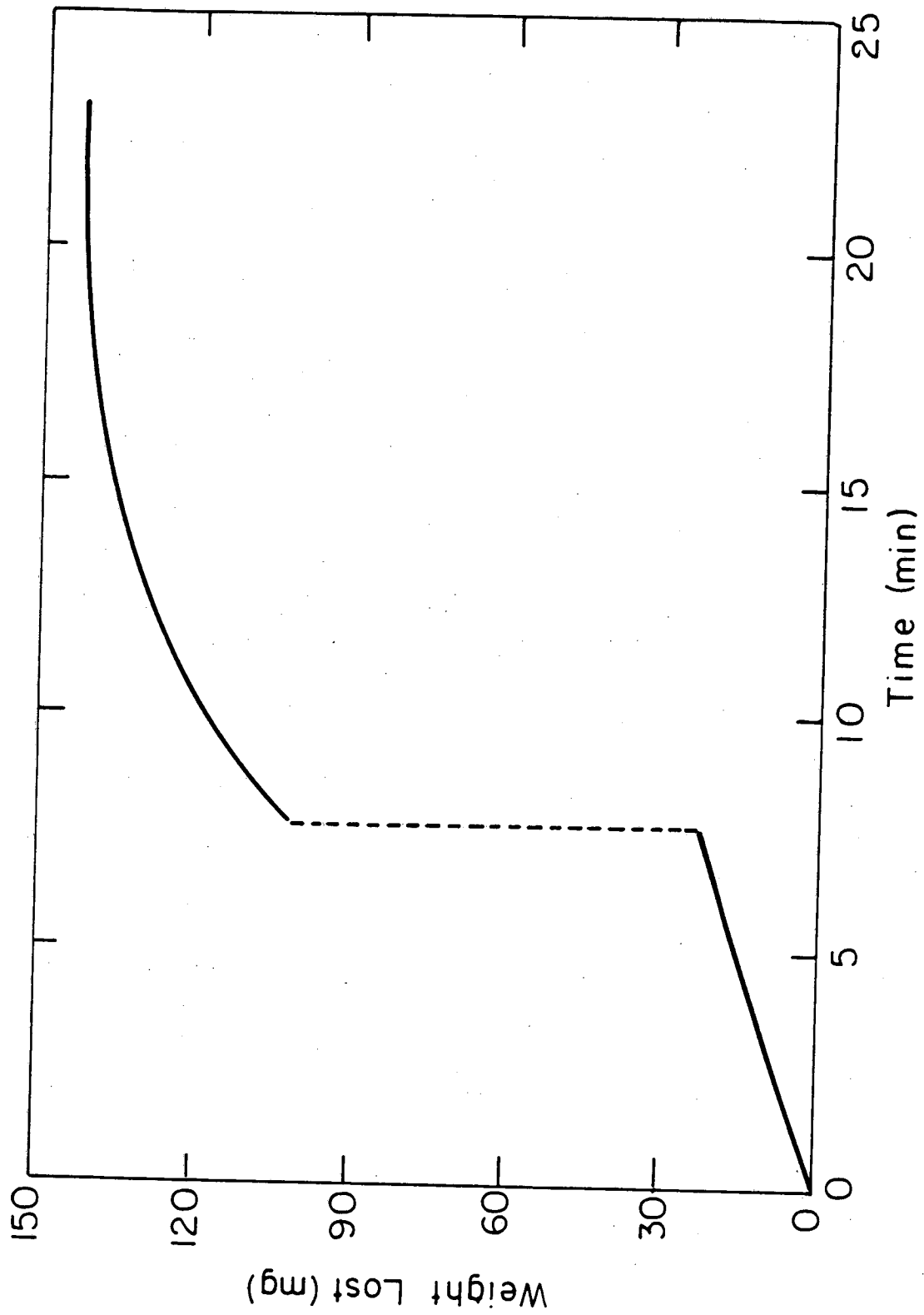
Fig. 10

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XBL 825-5765

Fig. 11



XBL 825-5766

Fig. 12

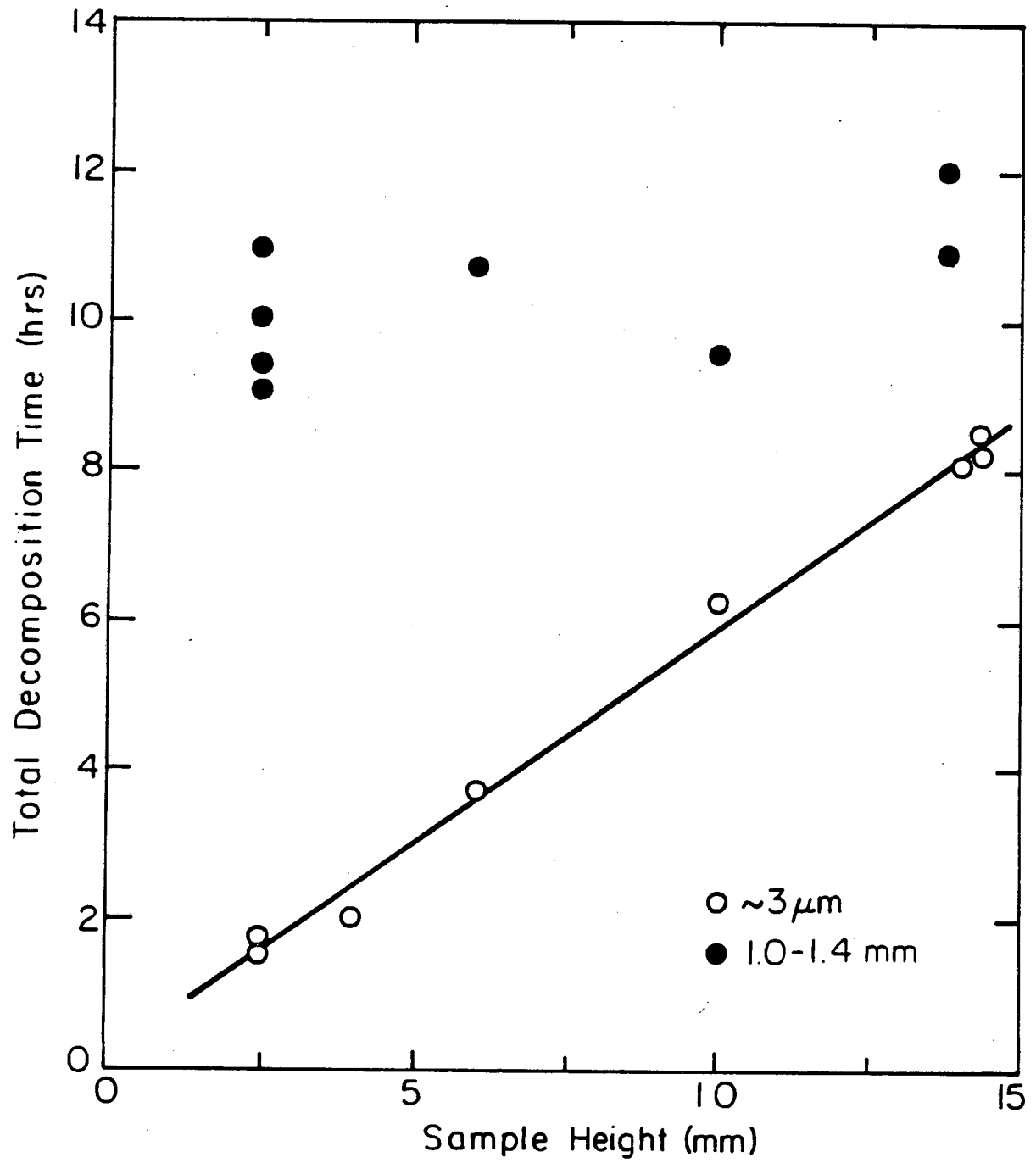


Fig. 13

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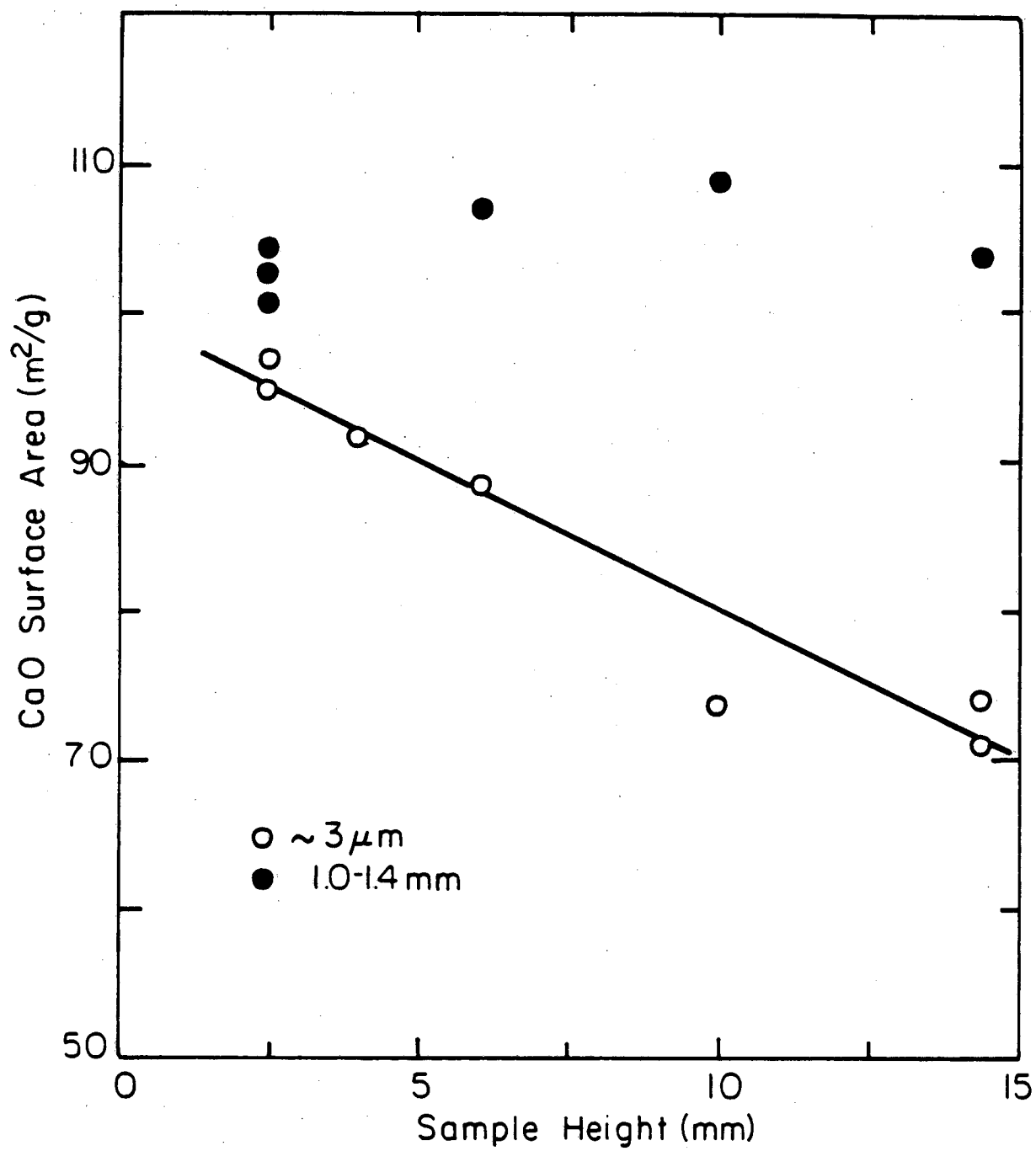


Fig. 14

XBL 825-5768

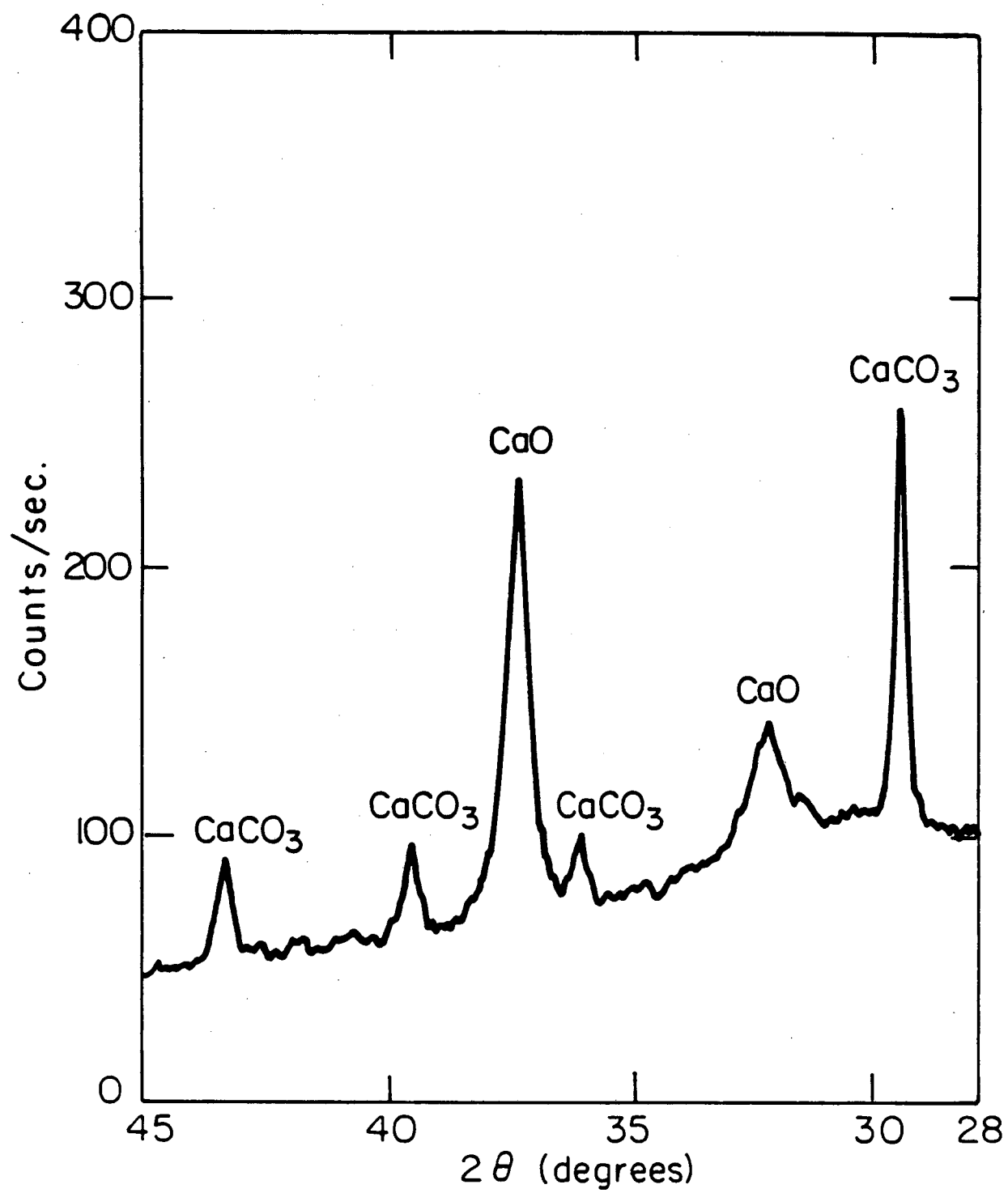


Fig. 15

XBL 825-5761

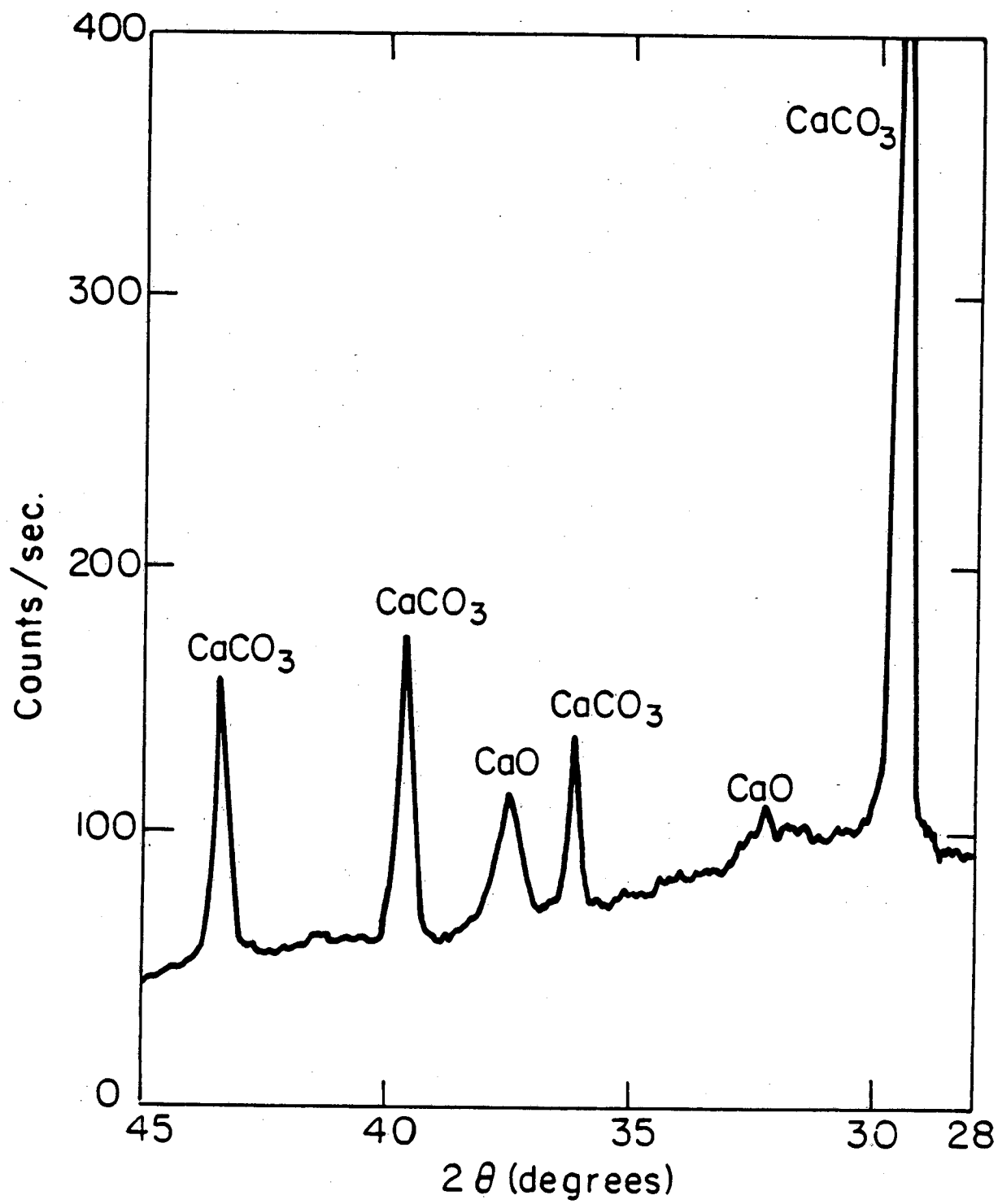


Fig. 16

XBL 825-5762

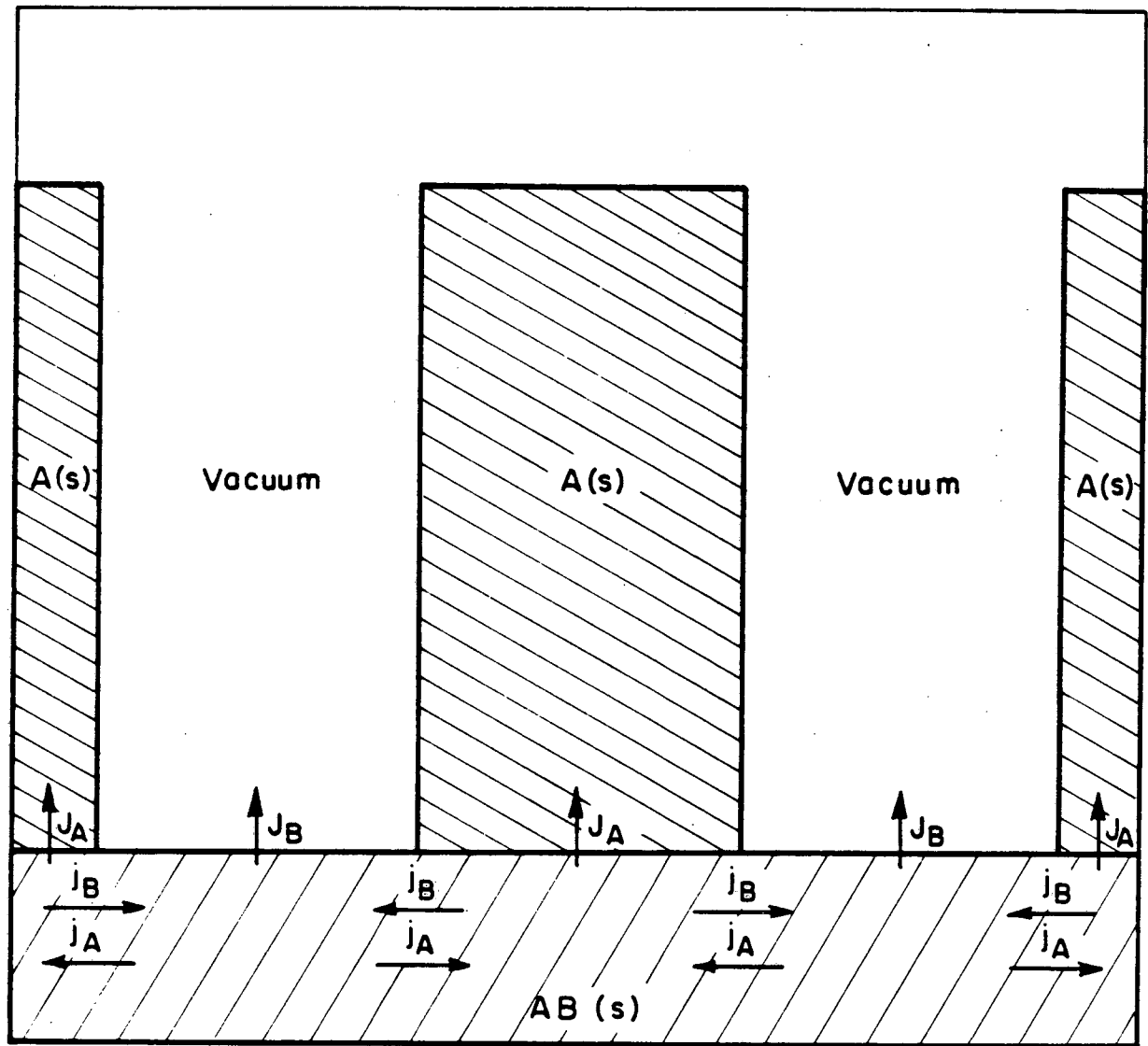


Fig. 17

XBL 748-6867

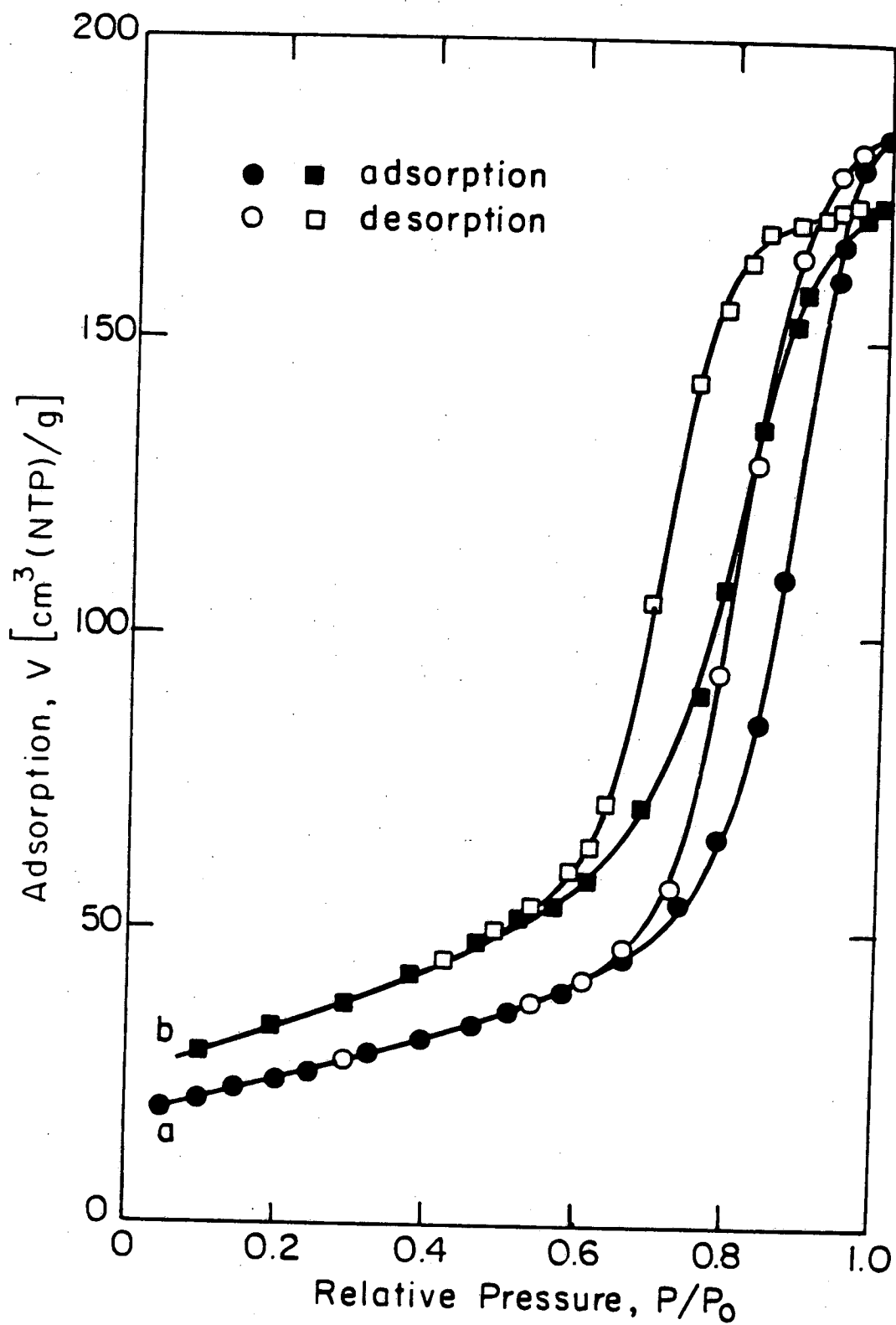
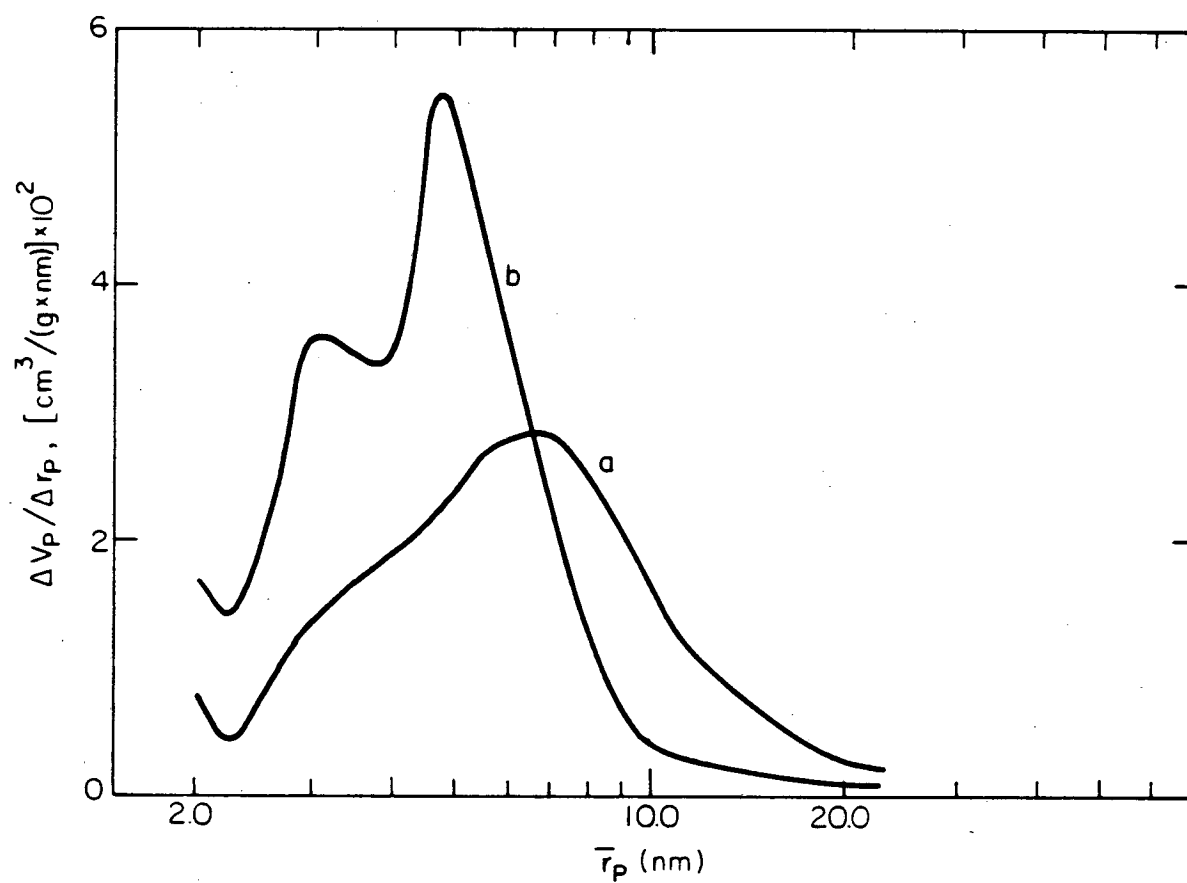


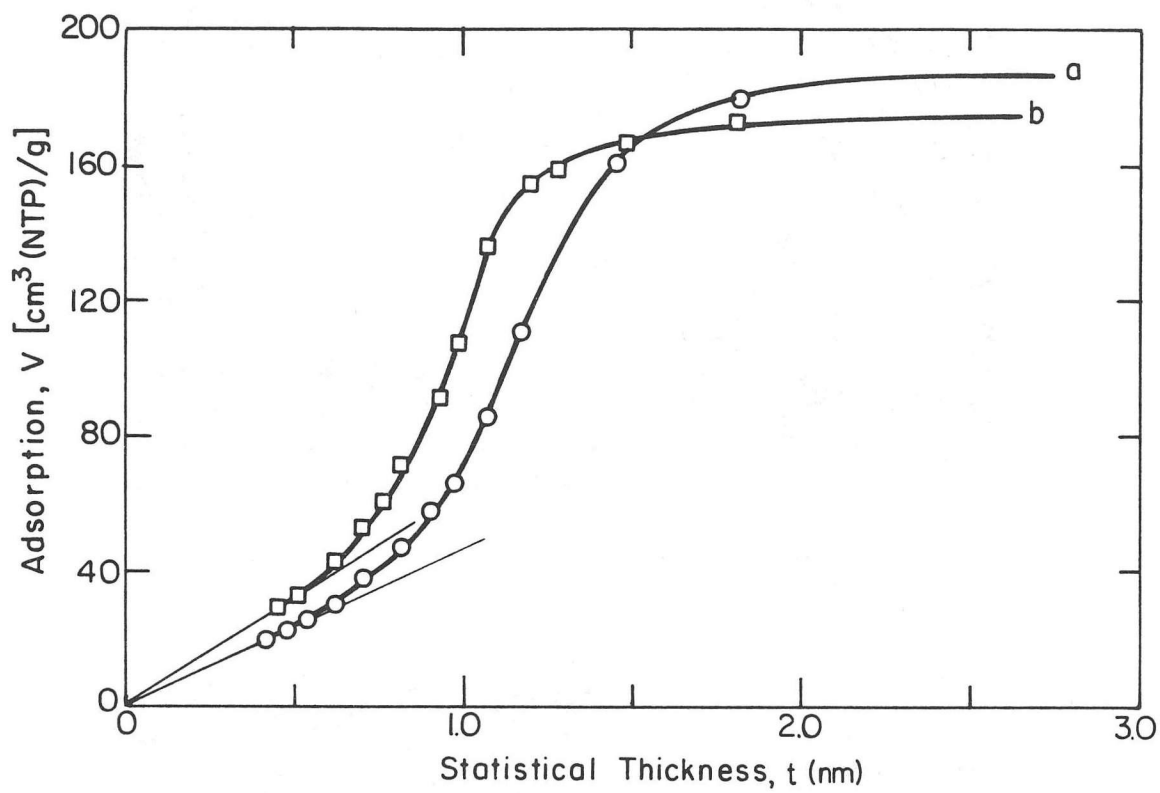
Fig. 18

XBL 825-5757



XBL 825-5758

Fig. 19



XBL 825-5759

Fig. 20

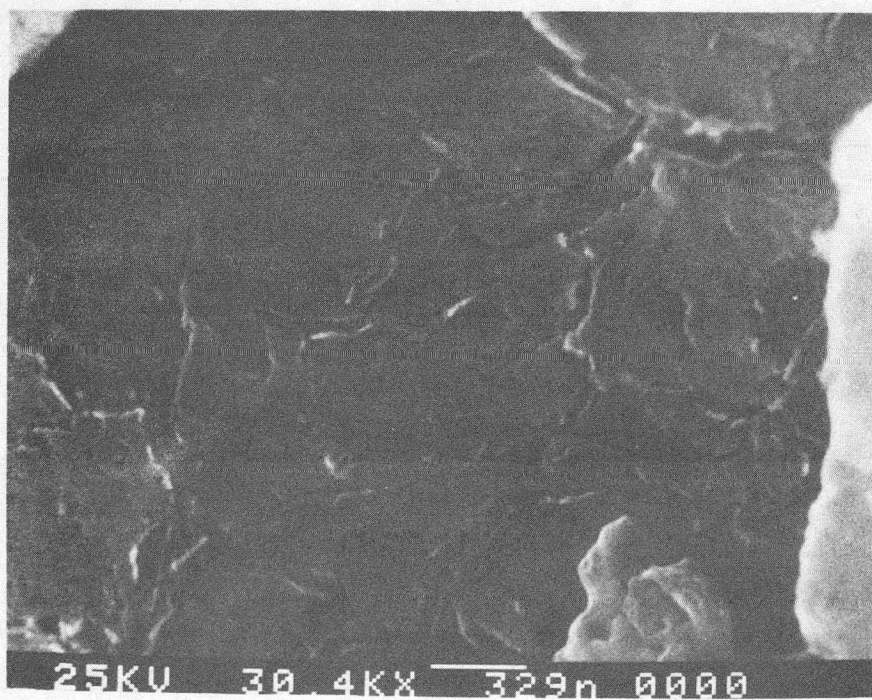
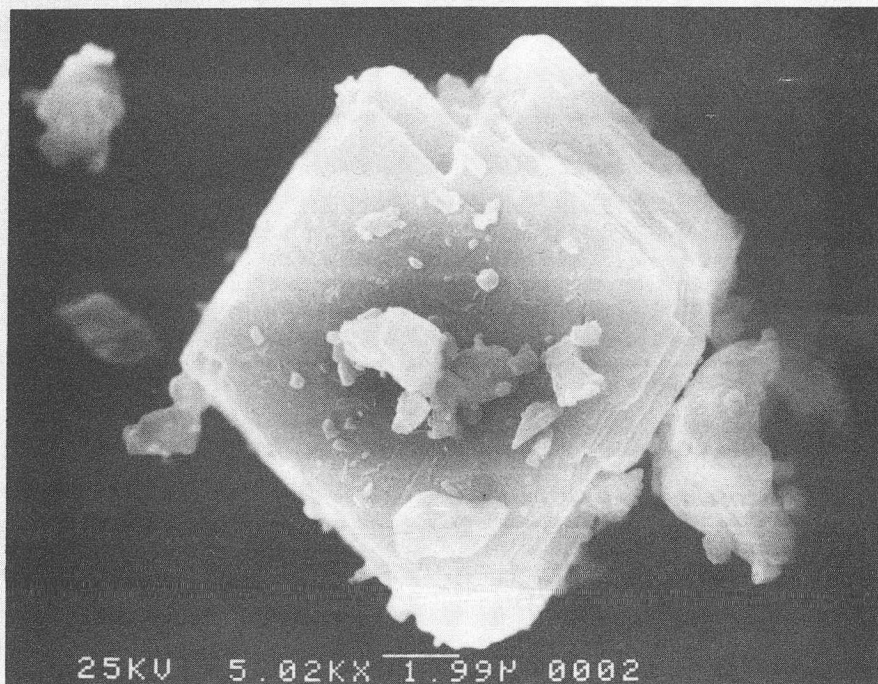


Fig. 21

XBB 825-4482

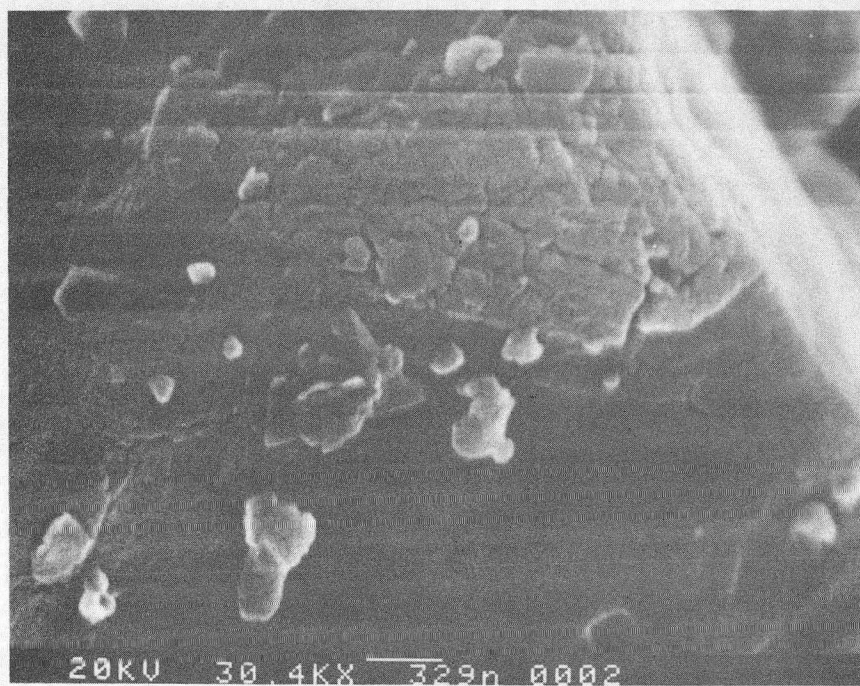
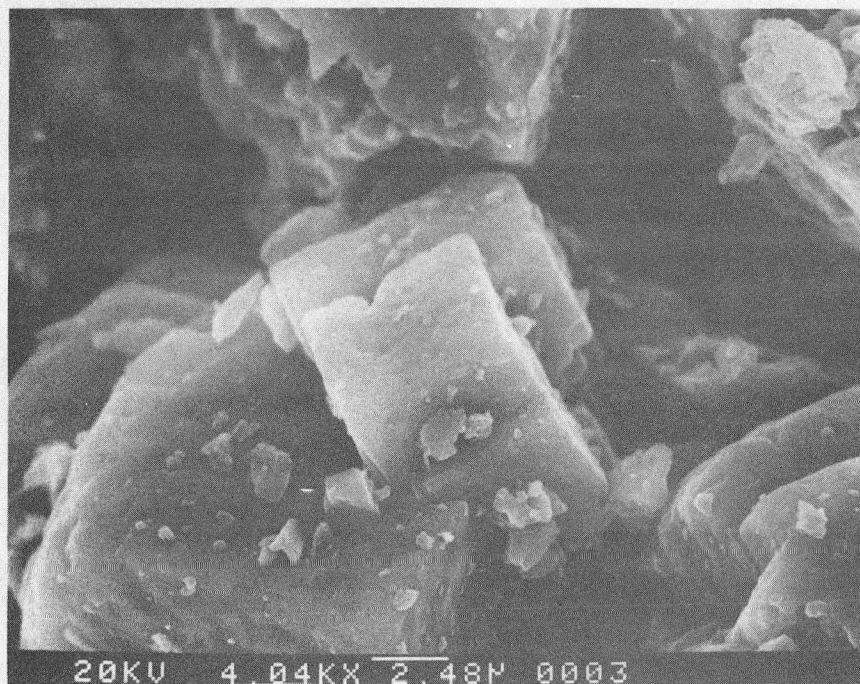


Fig. 22

XBB 825-4483

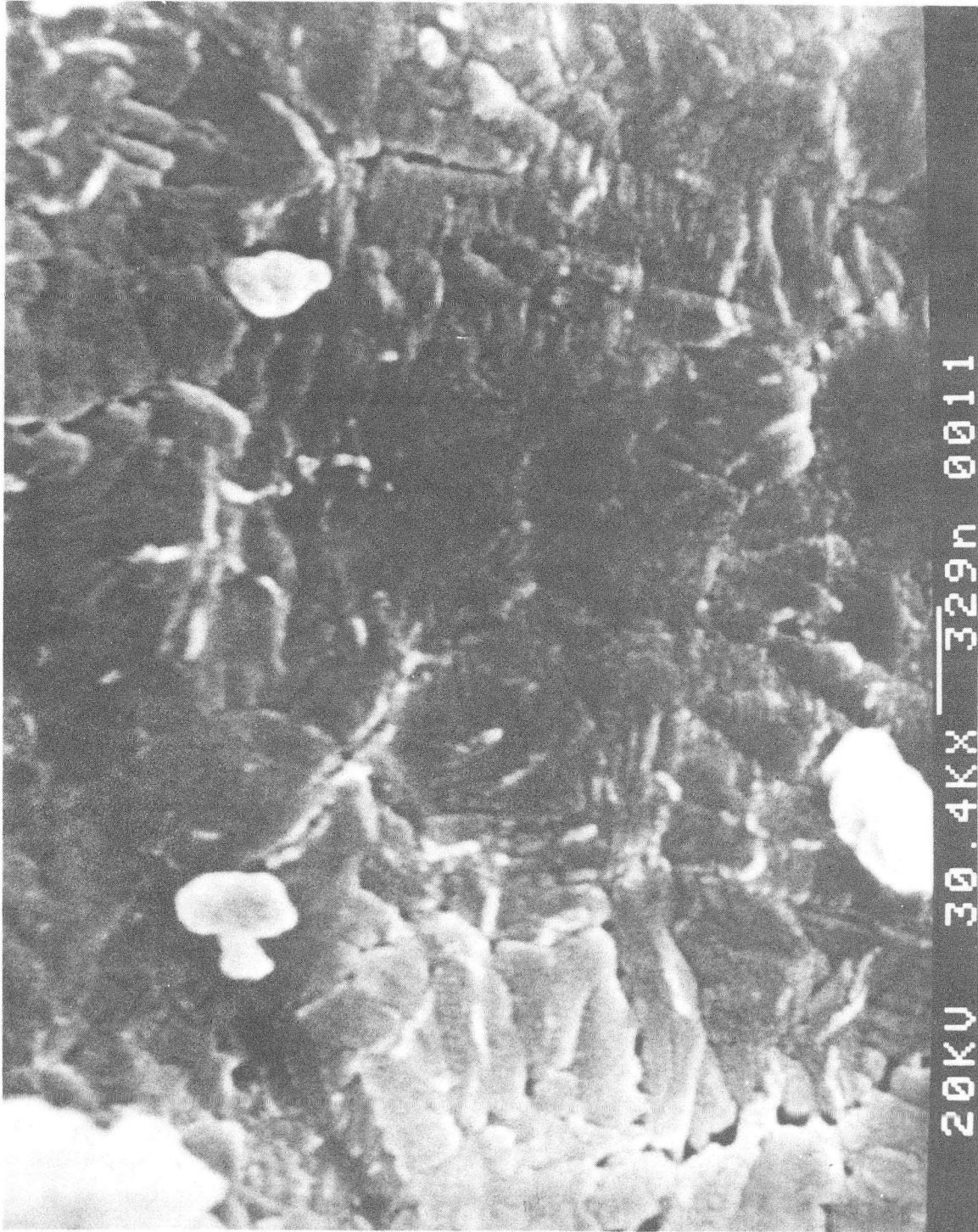
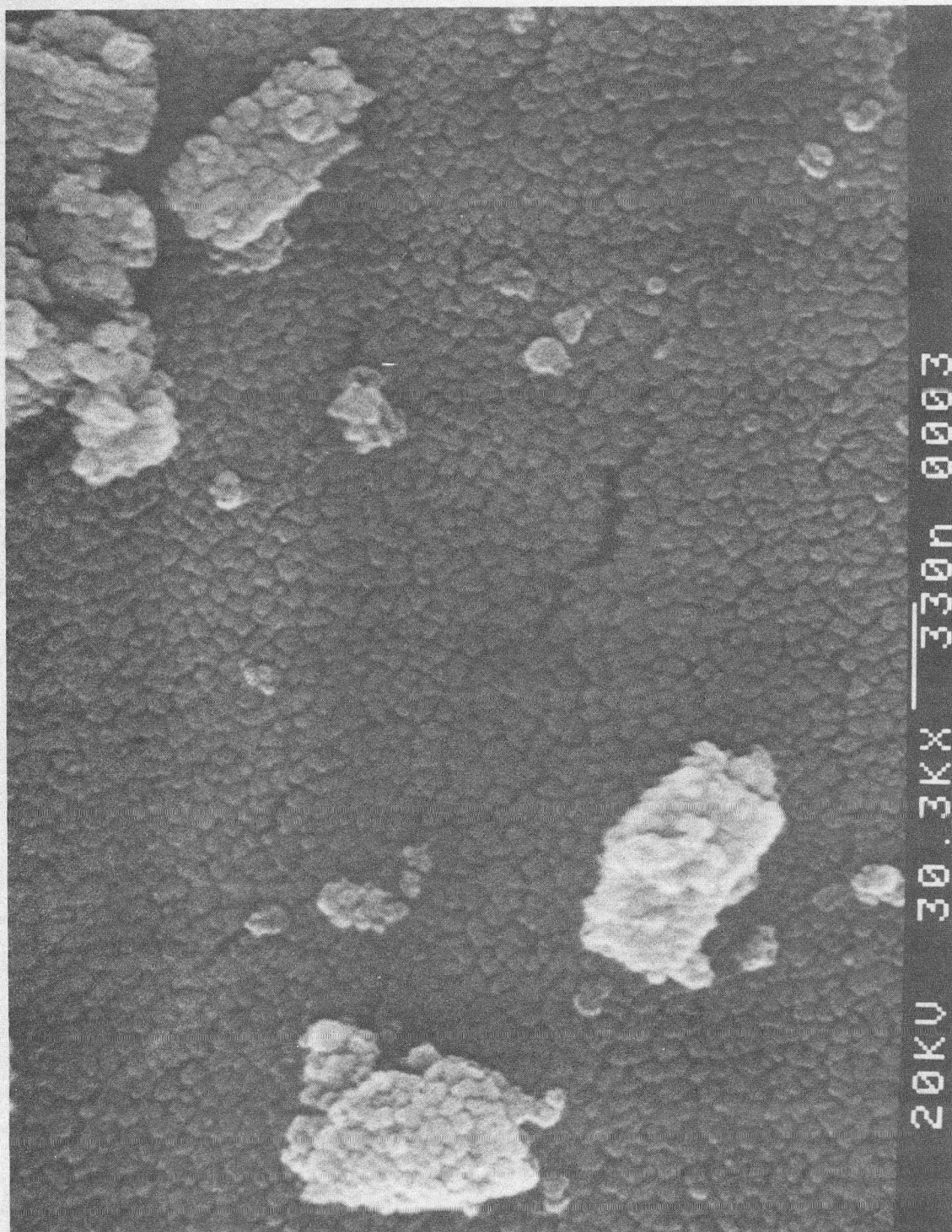


Fig. 23

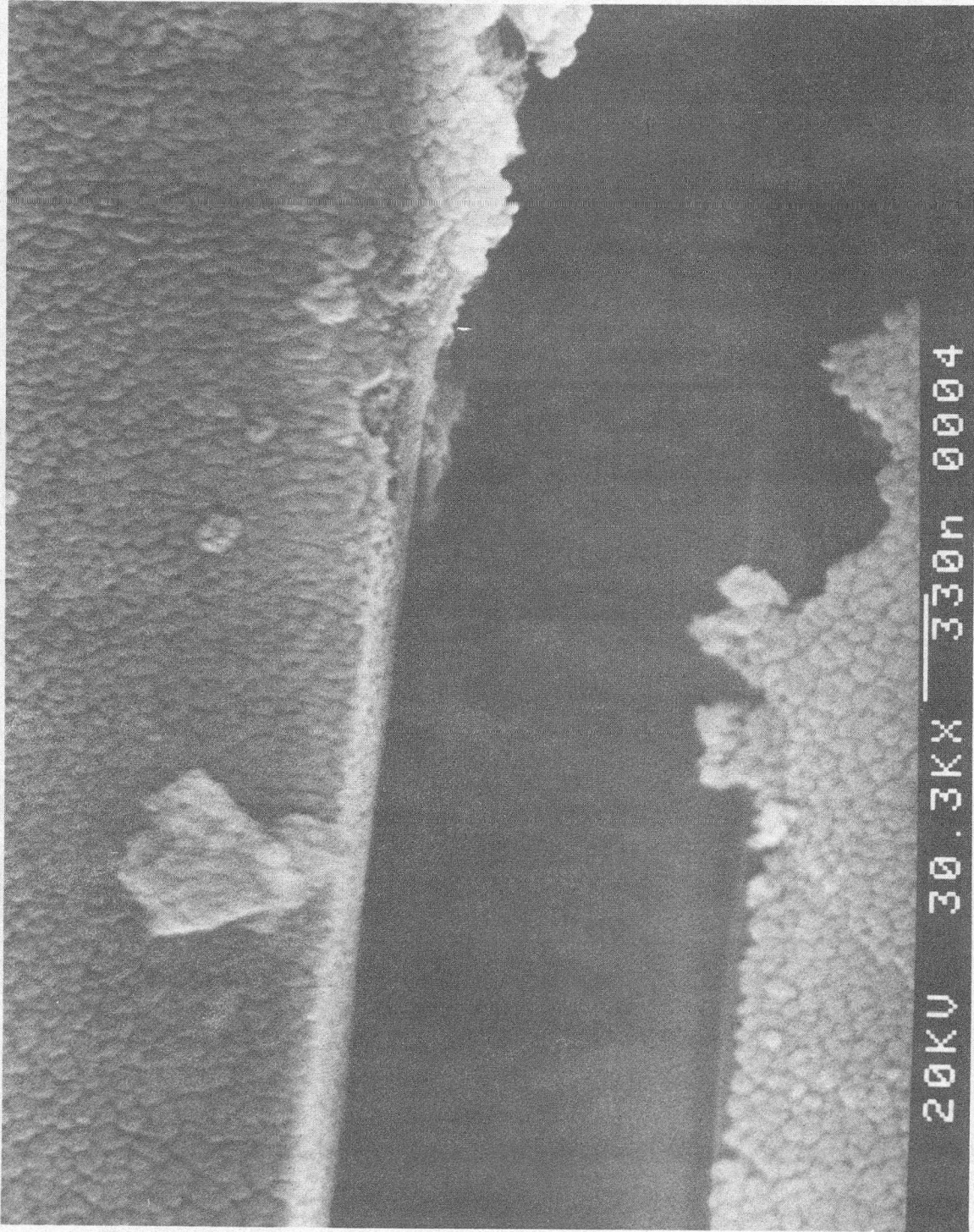
XBB 825-4479



20KV 30.3KX 330n 0003

Fig. 24

XBB 825-4480



20KV 30.3KX 330n 0004

Fig. 25

XBB 825-4481

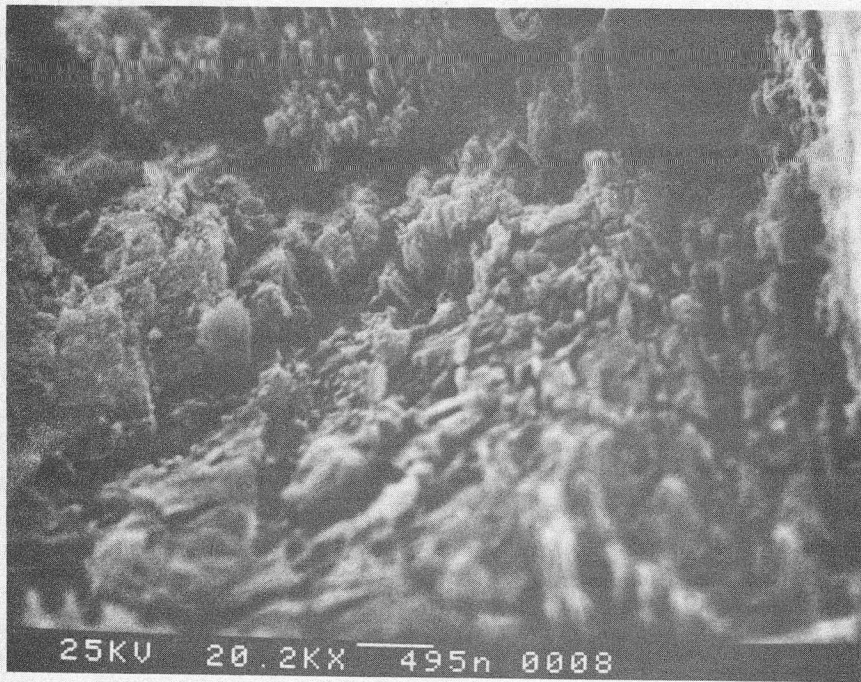
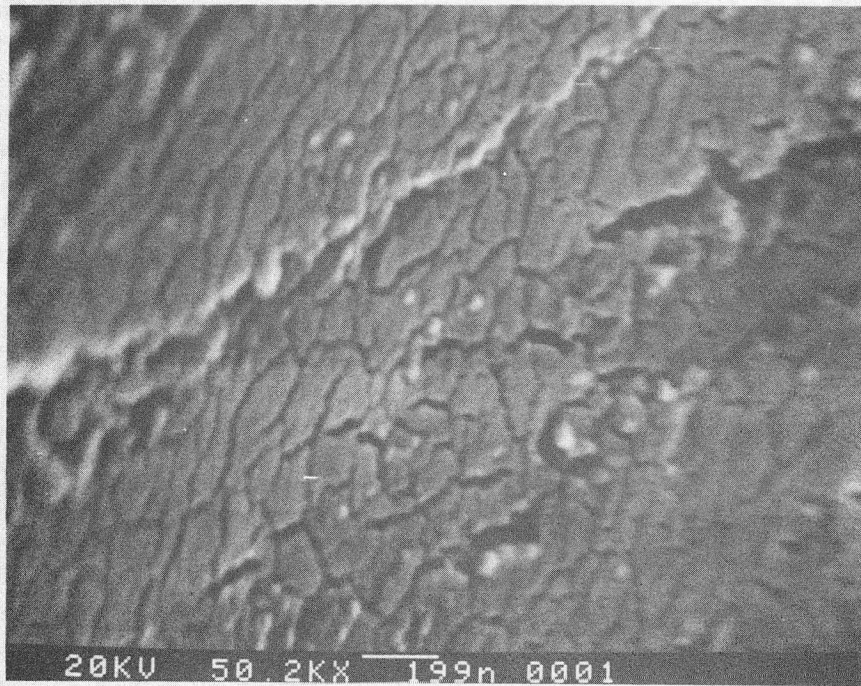


Fig. 26

XBB 825-4484

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