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Publication Date

1979-08-01

UC-25

LBL-9713 c. 1
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BY DECOMPOSITION OF $CaCO_3$ AND $Ca(OH)_2$ IN VACUUM

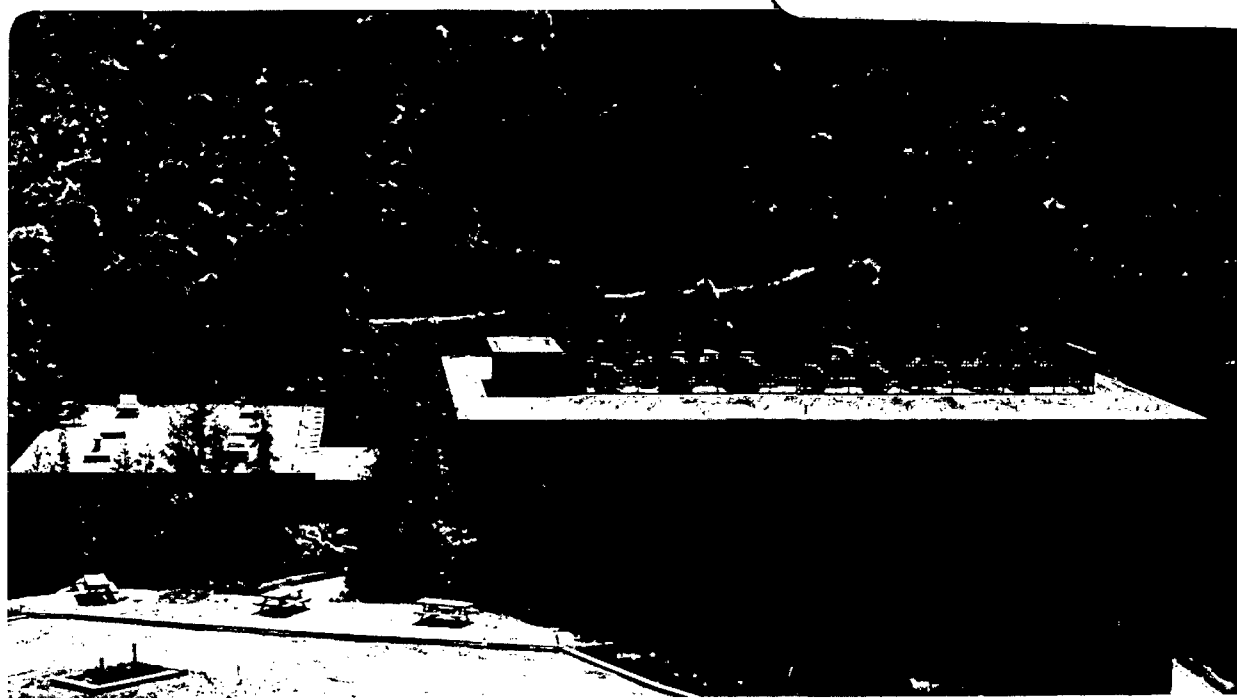Dario Beruto, Alan W. Searcy, Luigi Barco, and Giorgio Spinolo

August 1979

DISCLAIMER

CHARACTERIZATION OF THE POROUS CaO PARTICLES
FORMED BY DECOMPOSITION OF $CaCO_3$ AND $Ca(OH)_2$ IN VACUUM

Dario Beruto,[*] Alan W. Searcy,[†] Luigi Barco,[*] Giorgio Spinolo[**]

ABSTRACT

Scanning electron microscope observations show that the solid products of decomposing $CaCO_3$ powder in vacuum at 510°C (called sr-CaO) and of decomposing $Ca(OH)_2$ powder at 320°C in vacuum (called h-CaO) are particles which have approximately the same exterior dimensions as the parent $CaCO_3$ or $Ca(OH)_2$ particles. N_2 adsorption and desorption isotherms show sr- and h-CaO to have high internal surface areas, which for sr-CaO have cylindrical symmetry with the most common diameters being about 100Å, and for h-CaO are slit shaped, with the most common slit width being about 27Å. The conclusions reached in earlier investigations — that these decomposition reactions in vacuum initially yield a form of CaO which has the same unit cell dimensions as the parent solid — were in error, probably because sr-CaO and h-CaO are converted to poorly crystalline $Ca(OH)_2$ before the presence of small amounts of CaO could be detected by XRD. From the volume of N_2 adsorbed by the porous powders when the N_2 pressure is infinitesimally below its saturation value, the porosity of h-CaO is calculated to be 36 ± 5% and of sr-CaO, to be 41.5 ± 5%. Comparison of these porosities with the relative molar volumes of $Ca(OH)_2$, $CaCO_3$ and CaO shows that the linear dimensions of the 1 to 20μm particles of h-CaO and sr-CaO are about 5% smaller than those of the parent particles. Because XRD data show that no significant crystal growth occurs during decomposition or annealing for up to 15 hours at the decomposition temperatures, this shrinkage must occur by cooperative, diffusionless movement of crystallites of sr-CaO or h-CaO as they form.

INTRODUCTION

For an endothermic decomposition reaction that can be described by the general equation

$$AB(s) \rightarrow A(s) + B(g)$$
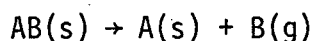
the reaction kinetics and the properties of the solid reaction product are interrelated. Unless the rate limiting step is highly irreversible, the decomposition rate may be limited by the thermodynamic stability of the — often metastable[1] — solid product of the reaction,[2] and may become limited by the diffusion of the gaseous product through the porous solid product layer.[3] If, as seems often to be the case, the solid product grows by a cooperative, diffusionless transformation[4,5] rather than by diffusion, the forward and reverse reaction rates cannot be described by the kind of interrelated rate constants which are familiar in chemical reaction kinetics.

As part of an effort to better understand the kinetics of $CaCO_3$ decomposition, a study of the properties of the CaO which is formed by decomposition of $CaCO_3$ powder in vacuum was initiated.[6-9] This porous product of $CaCO_3$ decomposition in vacuum, called sr-CaO, has a surface area which is much greater than previously reported[10,11] for CaO produced from $CaCO_3$ and reacts more rapidly with water vapor than is apparent from the earlier literature.[9]

Because of its high reactivity, further characterization of the properties of sr-CaO is of potential practical, as well as theoretical importance. CaO is used or is being considered for removal of sulfur from steels, from petroleum, and from coal and its gaseous products of oxidation. A CaO of higher reactivity may be a more effective reagent in these applications.

The properties of CaO produced by decomposition of $Ca(OH)_2$ in vacuum are also of interest: first because the layer structure of $Ca(OH)_2$ is likely to cause diffusion to occur in two dimensions as found for $Mg(OH)_2$,[12] second because CaO from $Ca(OH)_2$ decomposition in vacuum has a higher surface area[13] than does sr-CaO, and third because the initial CaO formed when $Ca(OH)_2$ is decomposed is reported to have a pseudo-$Ca(OH)_2$ structure.[13] The reported formation of a pseudo-calcite form of CaO from $CaCO_3$ decomposition[10] has been shown to be inconsistent with the changes in surface area during the reaction.[8]

In the present paper are reported x-ray diffraction peak line broadening measurements, measurements of gas absorption and desorption isotherms, and scanning electron microscope (SEM) observations for sr-CaO, for CaO from decomposition of $Ca(OH)_2$ powder in vacuum (called h-CaO),[9] and for CaO produced by carrying out these decomposition reactions in an atmosphere of N_2 gas. From the data are deduced minimum crystal dimensions and the probable shapes and dimensions of the pores in the CaO formed of sr-CaO and h-CaO. Implications of the data to the probable mechanism of CaO formation from the parent solid are discussed.

EXPERIMENTAL

The $CaCO_3$ and $Ca(OH)_2$ used in this research have x-ray diffraction patterns in good agreement with those in the J.C.P.D.S. files (A.S.T.M. index). Chemical analyses are summarized in Table 1. The $CaCO_3$ was formed of sharp edged, rhombohedral blocks of 3 to 10μm dimensions (Fig. 1). The $Ca(OH)_2$ contained particles which had shapes rather like those of the calcite powder, but with rough surfaces and less sharp edges (Fig. 2). Most of these particles had dimensions of 6 to 20μm; some had dimensions of the order of 1μm.

To obtain h-CaO, 37 mg samples of $Ca(OH)_2$ were placed in a Pt crucible of 0.72 cm diameter and 0.82 cm height hung from a Sartorium microbalance in a Pyrex tube inserted in a resistance furnace. This furnace was connected with an adsorption apparatus so that the h-CaO need not be exposed to air before adsorption isotherms were measured. The decomposition was carried out under vacuum of about 5×10^{-4} torr and at a furnace temperature of 593 K.

Because higher temperatures were required for $CaCO_3$ decompositions, 50 mg samples of $CaCO_3$ were heated at 10°C/min in a Netszch STA 409 thermobalance under a vacuum of 5×10^{-5} torr to a temperature of 783 K. No significant decomposition was observed before reaching that temperature, which was maintained until the reaction was completed. The sr-CaO was transferred as quickly as possible from the thermobalance to the thermogravimetric adsorption apparatus. Because of the high reactivity of sr-CaO to water vapor[9] between 15 and 18% of the sample was converted to $Ca(OH)_2$ during the transfer from one apparatus to the other. This $Ca(OH)_2$ was decomposed in vacuum at 593 K in the adsorption apparatus.

The surface areas reported for sr-CaO in Table 2 are corrected for the higher areas that result from the $Ca(OH)_2$ formation and decomposition. Adsorption and desorption isotherms of the CaO samples were determined using N_2 as the adsorbate at 78 K. X-ray diffraction patterns were obtained using a Philips powder diffractometer with a proportional detector and a Cu fine focus tube with an Ni filter. $CaCO_3$ and $Ca(OH)_2$ samples were heated in a homemade hot stage chamber,[14] and the decomposition reaction was followed at the same temperatures used for preparing samples for the adsorption-desorption studies by continuously recording the most prominent reflections of the reactant and the (111), (200) and (220) reflections of the CaO. The pressure was always lower than 10^{-3} torr.

SEM investigations were made on fresh samples of CaO powders dropped directly on a carbon coated surface. Some samples were then covered with a thin layer of gold and others were not. These methods gave results in fairly good agreement; however, it should be pointed out that because of the high reactivity of both sr-CaO and h-CaO to water vapor some $Ca(OH)_2$ formation must have occurred on the particle surfaces. It has been shown that the basic shape of the particles is little effected by complete conversion to $Ca(OH)_2$,[15] but the form of the crystallites that make up the porous particles probably are markedly changed by the reaction.

RESULTS AND DISCUSSION

Particles of sr-CaO and h-CaO show essentially the same exterior shapes as the parent particles of $CaCO_3$ or $Ca(OH)_2$. The pores of these types of CaO are too small to resolve with the available scanning

electron microscope (SEM) and interpretations of the SEM data must be cautiously made because reactions with water vapor is rapid enough to transform the exterior of the particles to $Ca(OH)_2$ during the time required to transfer the samples to the SEM. The features described here for sr-CaO, however, are not found on particles after complete conversion to $Ca(OH)_2$ and must, therefore, reflect at least in part the features of the porous CaO particles.

In some SEM photographs it is possible to discern terraces arranged along the bisector of the obtuse angle of the rhombohedral face of the parent $CaCO_3$ crystals and spaced some 0.1μm apart (Fig. 3). These terraces probably are formed of ordered arrays of the 0.01μm diameter needle-shaped crystals of CaO which Towe has observed to be produced when $CaCO_3$ is decomposed by electron beam heating in a transmission electron microscope.[16]

On a few sr-CaO particles, pits can be seen with diameters of about 0.1 to 0.3μm (Fig. 4). These pits may be the ends of tubular pores, but they are too large to account for the high surface area of sr-CaO. Smaller pores must also be present. Obst, et al.[11] were recently able to observe 0.02μm CaO crystallites separated by pores of smaller dimensions and arranged in relatively well ordered rows. Their samples were prepared at 1270 K which probably resulted in larger crystallites and lower porosities than were produced at the lower temperatures used in the present study.

Figure 5 shows h-CaO which was prepared not from the $Ca(OH)_2$ shown in Fig. 2, but from what appeared to be small single crystals of $Ca(OH)_2$ grown from an acqueous solution. Cracks develop in this h-CaO that

appear to be perpendicular to the c-axis of the $Ca(OH)_2$ crystallites. There is clear evidence that when $Mg(OH)_2$, which has the same crystal structure as $Ca(OH)_2$, is decomposed, water diffuses from the solid in the plain perpendicular to the c-axis to yield sheets of MgO crystallites separated by slit-shaped pores.[12] Figure 5 suggests that $Ca(OH)_2$ may decompose by a similar process.

In earlier studies of $CaCO_3$ and $Ca(OH)_2$ decomposition, only the diffraction pattern of $CaCO_3$ or $Ca(OH)_2$ was observed until a large fraction of the CO_2 present in the sample had been evolved.[10,13] These results led to the hypothesis that the initial solid products of the decomposition reactions are metastable CaO phases which have the same cation-anion spacings as the original $CaCO_3$ or $Ca(OH)_2$ and which only later transform to the normal (NaCl-type) modification of CaO. But for $CaCO_3$ decomposition in vacuum, Ewing, Beruto and Searcy showed that the surface area is a linear function of the extent of reaction.[8] This result, as they pointed out, indicates that there is no time delay in formation of a CaO phase of molar volume close to that of NaCl-type CaO.

In the present study the use of the hot stage x-ray diffraction unit made possible observation of the evolution of the intensities of the peaks of the CaO diffraction pattern during $CaCO_3$ or $Ca(OH)_2$ decomposition in vacuum. No induction period was observed, and the peak heights increased with a roughly parabollic dependence on time from the beginning of decomposition. This result shows that the normal crystallographic modification of CaO is produced by both reactions from the time that decomposition commences. The earlier results were undoubtedly misleading because water vapor in the atmosphere at room temperature converts most

of a small sample of either sr-CaO or h-CaO to a poorly crystalline Ca(OH)$_2$ within one to two minutes.[9]

The integrated breadths of the CaO diffraction peaks, evaluated as the ratio of the peak area to the peak height, were essentially constant through the course of either decomposition reaction, except in one doubtful experiment with sr-CaO. Evidently the pressures of CO$_2$ or H$_2$O generated by the decompositions are too low to catalyze significant crystal growth or annealing of crystal imperfections during the course of the reactions. Some samples were kept under vacuum at the temperature of decomposition for at least 15 hours after the diffraction peak of the reactant had disappeared. This treatment also caused no measureable change in the diffraction pattern of any of the CaO samples, either at the decomposition temperature or at room temperature, indicating that in vacuum the crystallites of sr-CaO and h-CaO have low rates of annealing and crystal growth.

Insufficient appreciation of the hydrolysis error led two of us to conclude[7] that sr-CaO differs more in crystallinity from ordinary CaO than it actually does, but the present study still shows the crystallinity of sr-CaO to be less than that for CaO formed in vacuum from large CaCO$_3$ crystals instead of from powder. Table 2 lists the crystallinities of sr-CaO, h-CaO and of CaO prepared in air or dry N$_2$, as measured by the ratio of the breadth of the major x-ray diffraction peak at half height to the peak height. The size of the crystals of CaO can be estimated from the line broadening if the contribution of internal strains to the line broadening is assumed to be negligible. For h-CaO, sr-CaO, and CaO from the decomposition of   CaCO$_3$ crystals in dry N$_2$ the average

crystal dimensions are calculated to be about 120Å, 150Å, and 380Å, respectively.

Surface areas for CaO produced from $CaCO_3$ and $Ca(OH)_2$ were measured by the BET method and the t-method[17] (see Table 3), and the adsorption and desorption isotherms were used to deduce the probable shapes and dimensions of the pores. The isotherms for h-CaO were of Brunauer's classification Type II.[18] The sloping shapes of the adsorption and desorption isotherms (curve a of Fig. 6) are of a kind which De Boer[19] predicts for capillary systems of planar symmetry, and planar symmetry is consistent with the expectation that H_2O probably escapes from $Ca(OH)_2$ crystals by preferential diffusion in the plane normal to the crystallographic c-axis.

The adsorption isotherms of sr-CaO were all of Type IV, and the steeply sloping loop for sr-CaO (curve b of Fig. 6) is consistent with De Boer's predictions for pores of cylindrical symmetry. The fact that the pores are formed by arrays of CaO needles which probably align in bundles with their axes parallel[16] make cylindrical symmetry probably for sr-CaO.

Application of the t-method to the isotherm data for both oxides gives the results shown in Fig. 7. In this method the statistical thickness t of multilayers of the adsorbed gas must be known, or estimated, as a function of P/P_0 on surfaces for which capillary condensation does not take place.[20,21] In the present study, the dependence of t on P/P_0 was estimated from the value of the constant C derived from the BET measurements.[22] The surface areas derived by the t-method are in very good agreement with those obtained by the BET method.

For h-CaO the volume of N_2 adsorbed increased almost linearly as a function of N_2 layer thickness at low coverages, but when layer thicknesses exceeded about 10Å, the volume of N_2 adsorbed increased much less rapidly with t (curve a of Fig. 7). This result is consistent with the conclusion that capillary condensation does not take place during adsorption in h-CaO. For sr-CaO the upward curvature of the plot of adsorbed N_2 versus layer thickness (curve b of Fig. 7) indicates the beginning of capillary condensation.

The conclusions that have so far been reached from the N_2 adsorption measurements do not depend upon a model for the shapes of the pores. The fact that capillary condensation occurs during adsorption in sr-CaO supports the conclusion that sr-CaO has pores of cylindrical symmetry, as suggested also by the facts that its crystallites are needle-shaped and that its isotherm is of Type IV. The fact that capillary condensation does not occur during adsorption in h-CaO supports the conclusion that h-CaO has slit-shaped pores, as suggested by analogy with MgO formed by decomposing $Mg(OH)_2$ and by the fact that h-CaO has an isotherm of Type II. In order to use the adsorption data to estimate the uniformity of pore dimensions and the pore size distributions by two means[23,24] that are model-dependent, the assumptions will be made that sr-CaO has cylindrical pores and that h-CaO has slit-shaped pores.

If pores in sr-CaO are of nearly uniform cylindrical symmetry and open at both ends, the surface area calculated for the desorption branch of the isotherm S_{cum}^{des} should be approximately equal to S_{BET}.[25] The discrepancy (Table 3) implies that some pores may be of the "ink-bottle" type. For h-CaO the slit-shaped model gives poor agreement

with experiment, probably because the pore structure is in fact complex in the h-CaO particles tested.

The $Ca(OH)_2$ particles used as a source for h-CaO had rounded rhombohedral shapes (Fig. 2) such as can result if the $Ca(OH)_2$ is produced by the sequence $CaCO_3 \rightarrow sr\text{-}CaO \rightarrow Ca(OH)_2$ rather than shapes like those shown in Fig. 5. The surface area of the $Ca(OH)_2$ used in the adsorption-desorption studies was about 6.6 m^2/g instead of 1 m^2/g as expected for pore-free particles. If, as these observations suggest, the h-CaO samples used in the adsorption-desorption study were formed from polycrystalline and porous $Ca(OH)_2$, the test $S_{cum}^{des} \cong S_{BET}$ should fail. Figure 8 shows the pore size distribution calculated from the two sets of t-method data. For h-CaO most of the pores are calculated to be near 27Å in width, but a large fraction of the pore volume is accounted for by considerably larger pores, as already suggested by the value calculated for S_{cum}^{des}. The pores in sr-CaO (curve b) have a more concentrated range of diameters that peak near 100Å.

The porosity of particles of sr-CaO and of h-CaO can be estimated from the assumption that they have exactly the same exterior dimensions as the $CaCO_3$ or $Ca(OH)_2$ particles from which they were formed. From the relative molar volumes of the two reactants and of CaO the predicted porosities of sr-CaO particles is ~55% and of h-CaO particles is ~50%. The actual porosities of the two types of CaO particles can be calculated from the volume of N_2 that they absorb when the N_2 pressure is infinitesimally below the equilibrium vapor pressure of N_2 at 78 K. By this means, the porosity of sr-CaO is found to be 41.5 ± 5%, and that of h-CaO is 36 ± 5%.

These results indicate that although the porous particles of sr-CaO and h-CaO appear in SEM pictures to be unchanged in shapes and dimensions from the parent particles of $CaCO_3$ and $Ca(OH)_2$, the decomposition reactions are accompanied by some particle shrinkage. For individual crystallinities of $Ca(OH)_2$ the shrinkage is probably almost entirely along the c-axis of the $Ca(OH)_2$ crystallites, but most of the SEM observations of the present study were of h-CaO produced from what were probably polycrystalline $Ca(OH)_2$ particles for which particle shrinkage would be essentially isotropic. The linear changes in particle dimensions, assuming isotropic shrinkage are calculated from the difference between theoretical and measured porosities to be ~5% for both sr-CaO and h-CaO.

The fact that the x-ray diffraction measurements showed the crystal dimensions of sr-CaO and h-CaO to be unchanged during the course of the decomposition reactions and for periods up to 15 hours at the reaction temperature after the reactions were completed indicates that the aggregation of the CaO into small crystallites probably occurs mainly by a cooperative process rather than by diffusion. A further test of this conclusion could be obtained by measuring the porosity of the powders as a function of annealing time. Cooperative, diffusionless processes normally occur instantaneously when a critical level of stress has been applied. Any decrease in porosities with time of annealing would almost certainly be a consequence of diffusion.

ACKNOWLEDGMENT

-13-

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Table 1.   Spectrographic Analysis of Starting Materials

Calcium carbonate powders

Impurity	Percent	Impurity	Percent
(NH_4)	0.003	Pb	0.0005
Ba	0.005	Na	0.1
(Cl)	0.005	K	0.01
Fe	0.002	(SO_4)	0.005
(NO_3)	0.1		

Calcium hydroxide powders

Impurity	Percent	Impurity	Percent
$CaCO_3$	3	(Cl)	0.001
(NO_3)	0.01	(SO_4)	0.005
Pb	0.001	Al	0.001
Mg	0.5	Fe	0.001
Ba	0.01	K	0.01
Na	0.1	Sr	0.1
Cu	0.0005	Zn	0.002

Table 2. Surface Areas and Crystallinities of CaO from Various Sources

Material	Source of Material	Surface Area (m^2/g)		Integral Breadth of Major x-ray Diffraction Peak $(200)_3$ (rad. X 10^3)
		Starting Material	Oxides	
CaO	Decomposition Ca(OH)$_2$ granular block 1-10µm powder, dry N$_2$, 400°C	6.6	2-3	5.5
h-CaO	Decomposition same Ca(OH)$_2$ powder <u>in vacuo</u>, 320°C	6.6	133	13.1
CaO	Decomposition CaCO$_3$ 1-10 m powder in air at 900°C	less than 1	1-2	4.1
sr-CaO	Decomposition same CaCO$_3$ powder <u>in vacuo</u>, 510°C	less than 1	78	9.8
sc-CaO	Decomposition calcite single crystal <u>in vacuo</u>, 580°C	~7 x 10^{-4}	89	7.44

Table 3. Surface Areas and Porosities for Porous CaO Powders

Material	Specific Surface S_{BET} S_t (m^2/g)		Cumulative Surface from desorption data (m^2/g)		Volume ads. at the saturation point (cm^3/g)	Cumulative volume from desorption data (cm^3/g)		Porosity	
	S_{BET}	S_t	Cylinder	Slit-shape		Cylinder	Slit-shape	Calculated for 0% shrinkage	Experimental
h-CaO	133	127	–	90.5	0.213	–	0.190	≈50%	36%
sr-CaO	78	77	92	–	0.269	0.268	–	≈55%	41.5%

FIGURE CAPTIONS

1. SEM photograph of $CaCO_3$ particles used in decomposition studies.

2. SEM photograph of $Ca(OH)_2$ particles used in decomposition studies.

3. SEM photograph of ordered terraces on some sr-CaO particles.

4. SEM photograph of pits present in a few sr-CaO particles.

5. SEM photograph showing cracks formed in h-CaO parallel to probable hexagonal planes of the original $Ca(OH)_2$ crystals ($1\mu m$ = 2.5 cm).

6. N_2 adsorption-desorption isotherms at 78°K for h-CaO (curve a) and sr-CaO (curve b).

7. Volume of N_2 adsorbed as a function of the statistical thickness for h-CaO (curve a) and sr-CaO (curve b).

8. Pore distributions as functions of the relative pressure of N_2 (P/P_o) and of pore slit width d for h-CaO (curve a) and of pore radius r for sr-CaO (curve b).
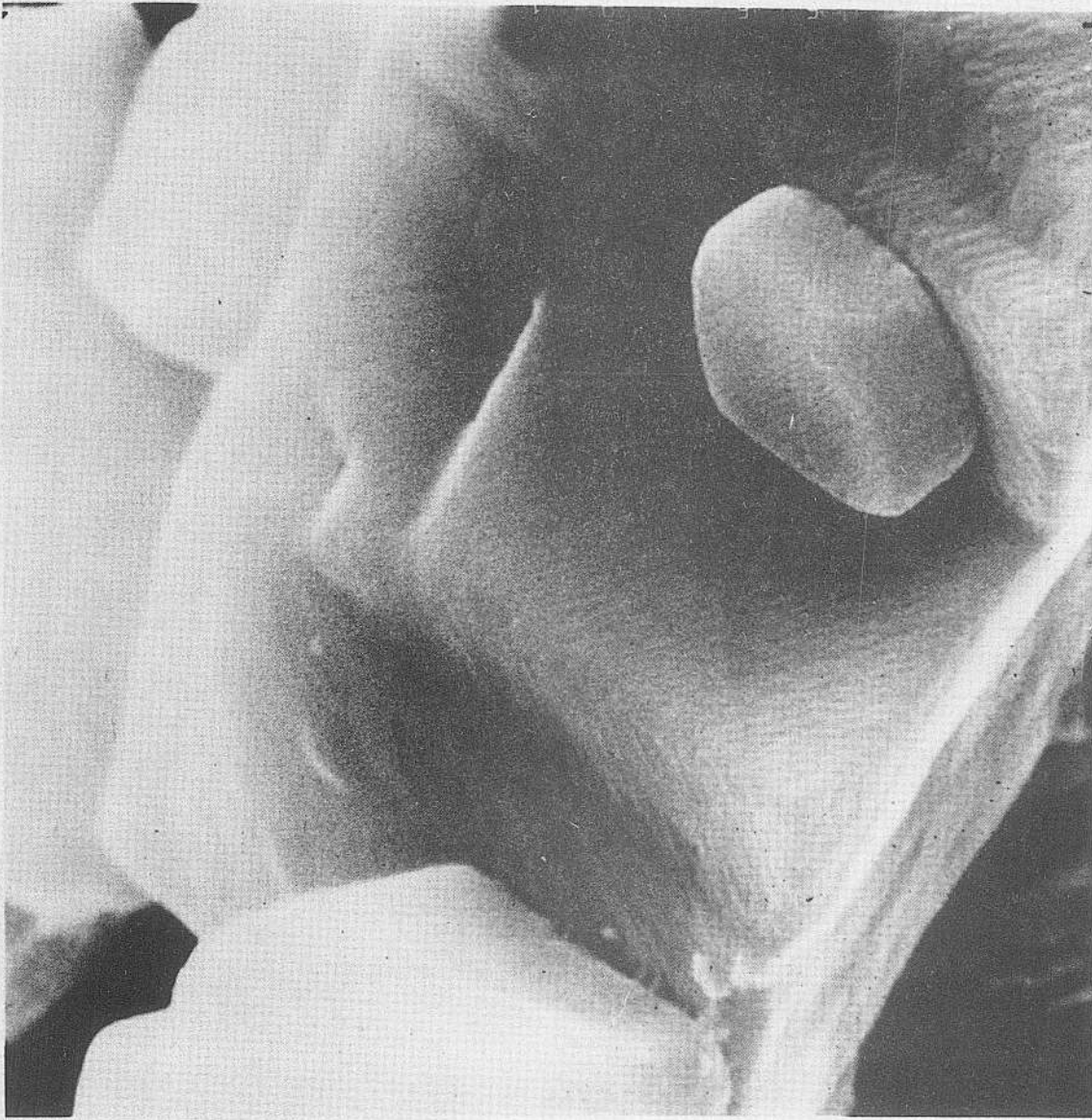
1μm

LBL766-5106

Fig. 1

XBB798-10982

Fig. 2
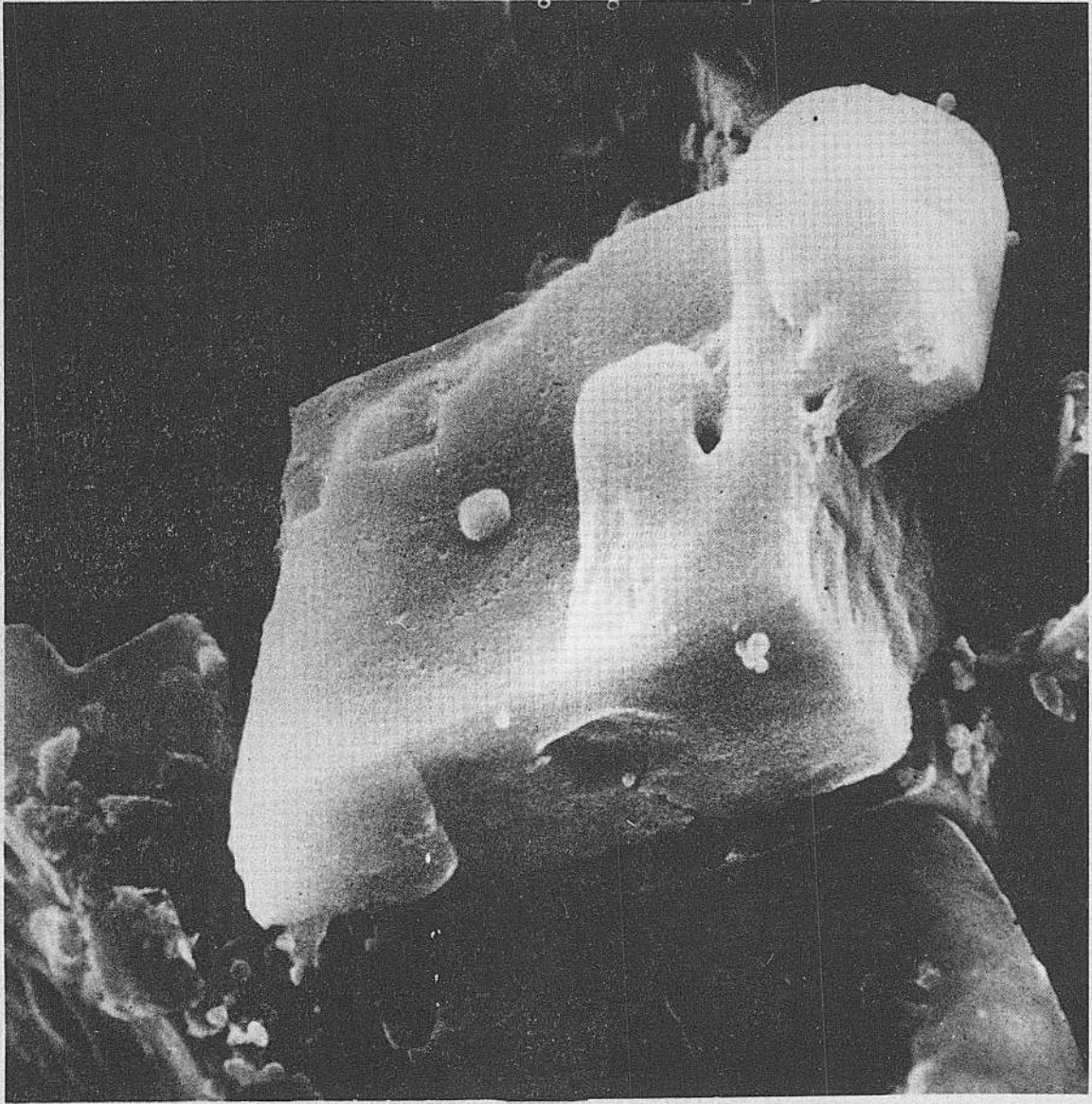
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1 μm
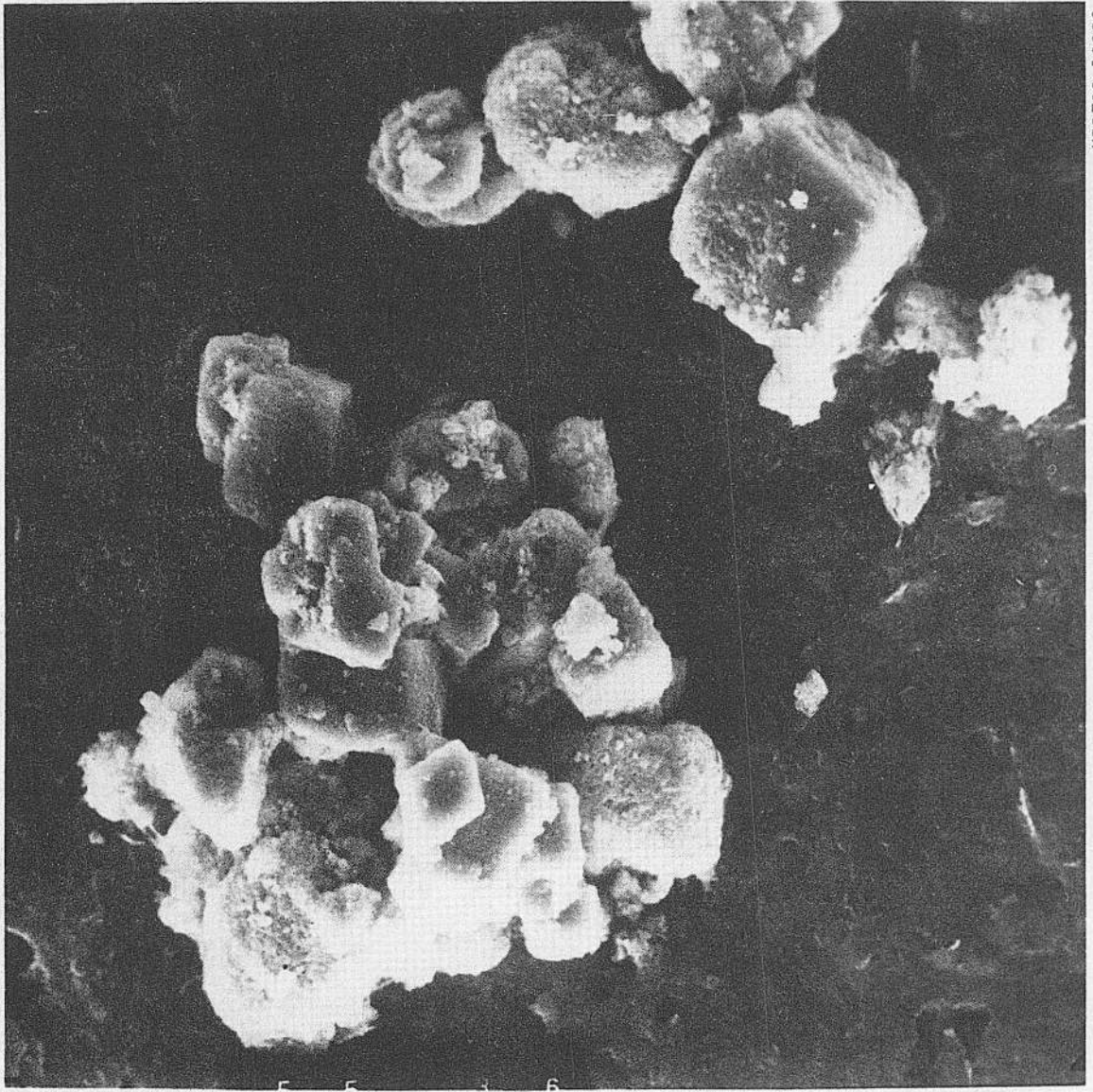
Fig. 3

XBB798-10981

1 μm

XBB798-10980
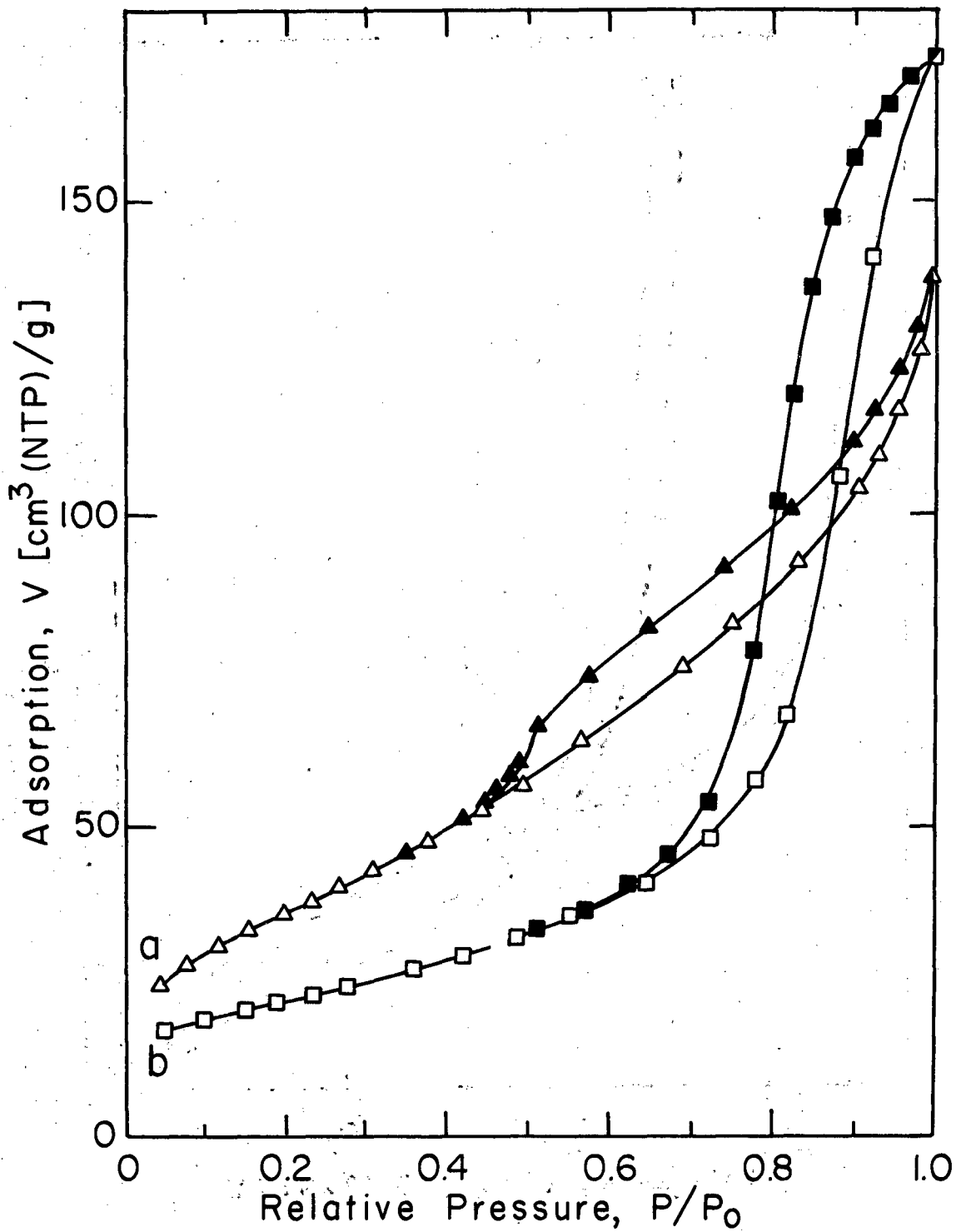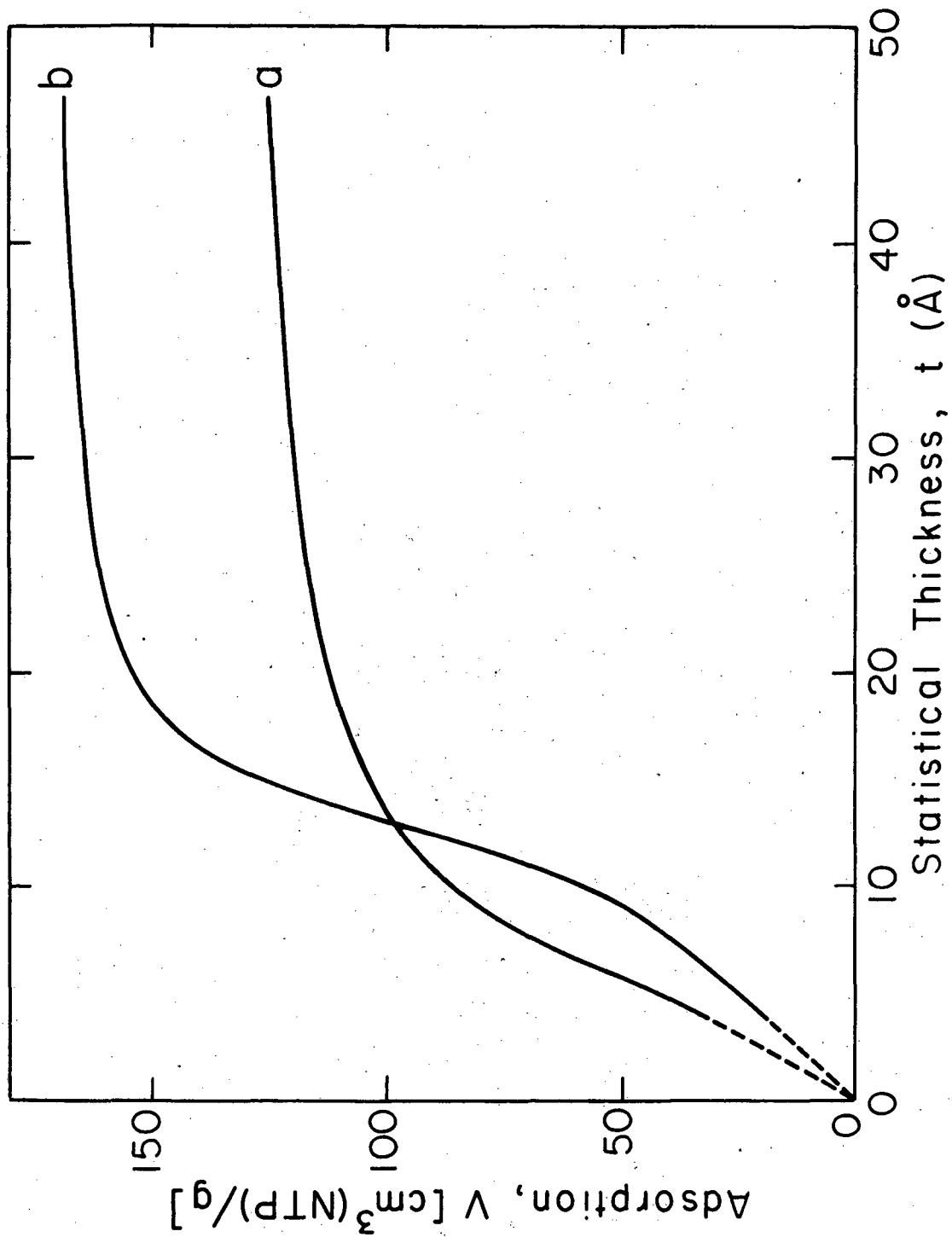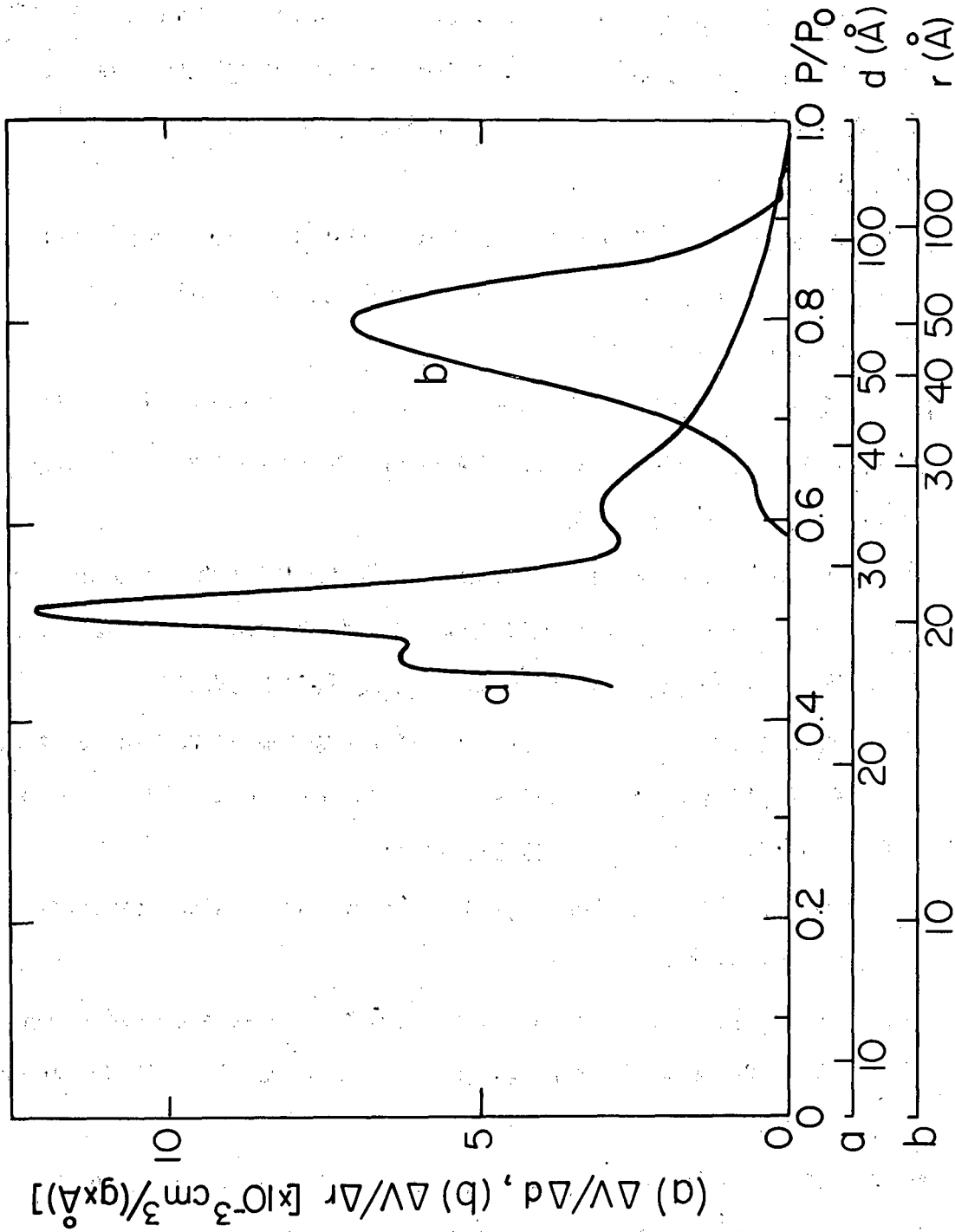
Fig. 4

Fig. 5

XBL 7 98-6893

Fig. 6

Fig. 7

XBL 798-6895

Fig. 8

XBL798-6894

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