CHROM. 5209

THE DISTRIBUTION OF SUPPORT-BONDED SILICONES ON CHROMOSORBS*

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(Received December 23rd, 1970)

SUMMARY

Scanning electron microscopy was used to examine two types of support-bonded silicones. These phases, $(C_{18}H_{37}SiO_{3/2})_n$ and $[(CH_3)_2SiO]_n$, were chemically bonded to Chromosorbs of the W and G varieties in a fluidized bed polymerization, and exhaustively extracted to remove any non-support-bonded material. For scanning electron microscopy, particles were bisected and the countenance of the plane of fracture with its structural details compared to the outside surface. Most of the liquid phase covered the periphery rather than the interior of the support grains; and heat treatment, as could be expected, did not visibly alter this apparent polymer distribution. These results imply that the area covered by the visible liquid layer is much smaller than the BET surface, and that this layer is about ten times thicker than would be assumed from an isotropic distribution throughout the internal and external regions of the particle. The average thickness and the total area of support-bonded silicone films would therefore be functions of the support particle diameter at a given polymer load.

INTRODUCTION

The superior depth of focus of scanning electron microscopes makes these instruments a natural choice for the examination of various chromatographic supports (refs. 1–3 and others). The calcined diatomaceous earths, in particular, are impressive materials to examine. Several authors seem to concur that polymers coated onto these supports for subsequent use in gas–liquid chromatography (GLC) do not become apparent on the diatom structures until very high loadings are used.

In our investigation of support-bonded silicone phases[4,5], we had generally observed comparable behavior of support-bonded and "regular" GLC phases in terms

* Part of this research is a contribution from the Experiment Station Chemical Laboratories, University of Missouri, Columbia, Mo. 65201, U.S.A., Journal Series No. 6144. It has been supported by NSF grant GP-18616 and the Environmental Trace Substance Center, Columbia, Mo., U.S.A.

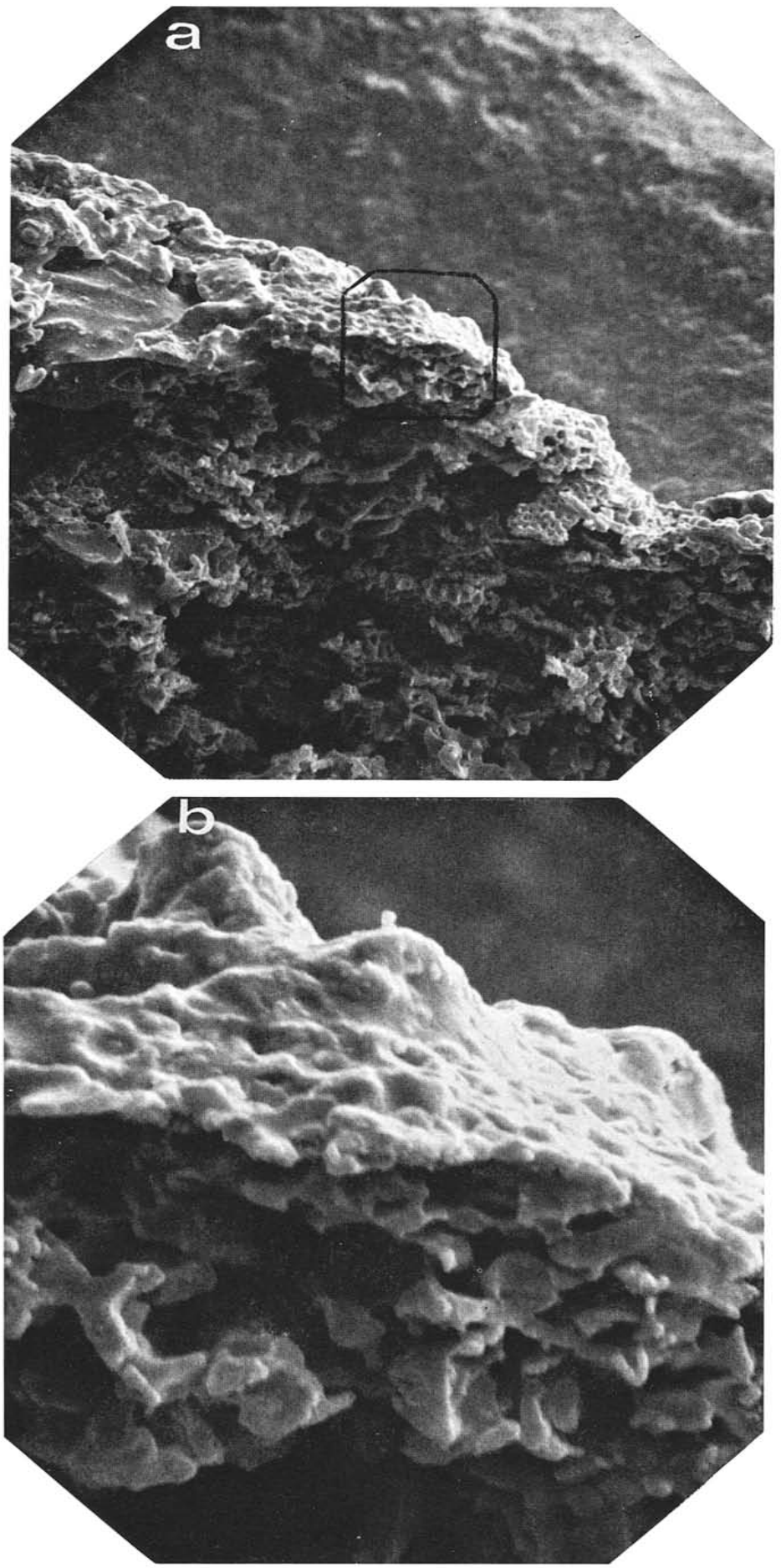


Fig. 1. 5.5% $[C_{18}H_{37}SiO_{3/2}]_n$ on Chromosorb G, after exhaustive extraction. (a) Line of fracture, 880 ×; (b) Line of fracture, detail, 4400 ×.

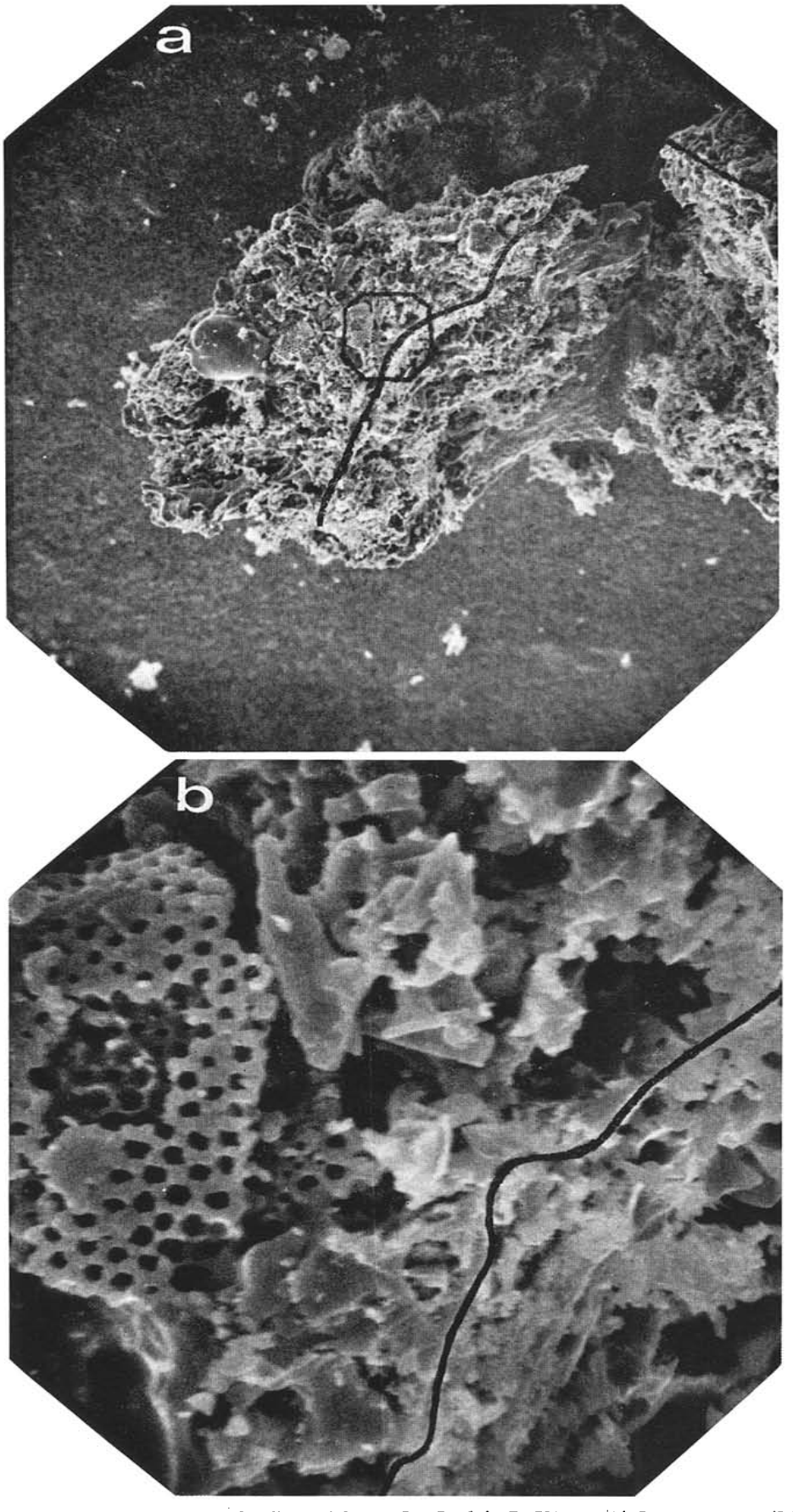
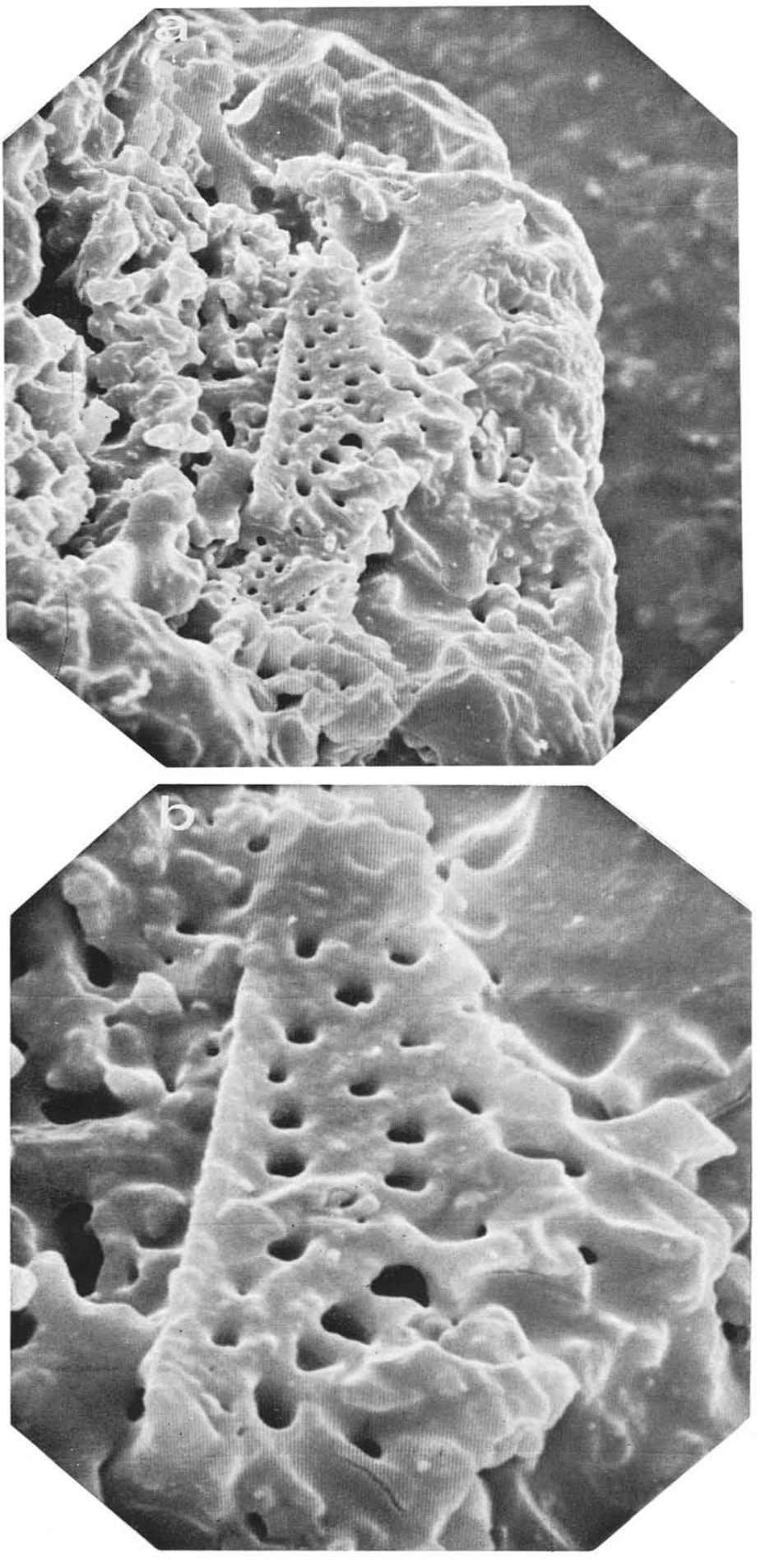


Fig. 2. Chromosorb G, acid washed. (a) Split particle, 150×; (b) Split particle, detail, 1500×.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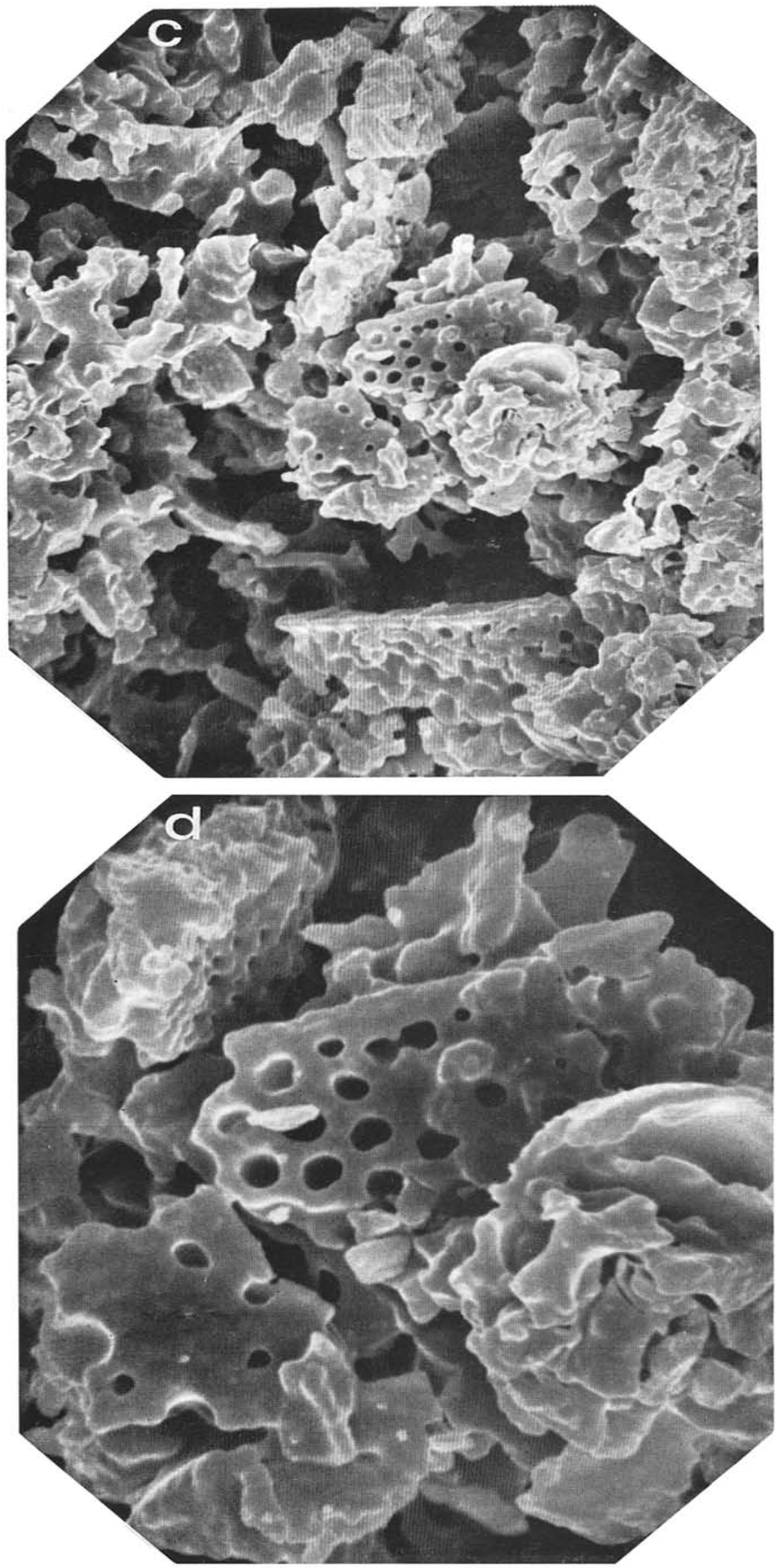


Fig. 3. 24 % $[(CH_3)_2SiO]_n$ on Chromosorb G, heat-treated, after exhaustive extraction. (a) Outside, 1500 × ; (b) Outside detail, 3750 × ; (c) Inside, 1500 × ; (d) Inside detail, 3750 × .

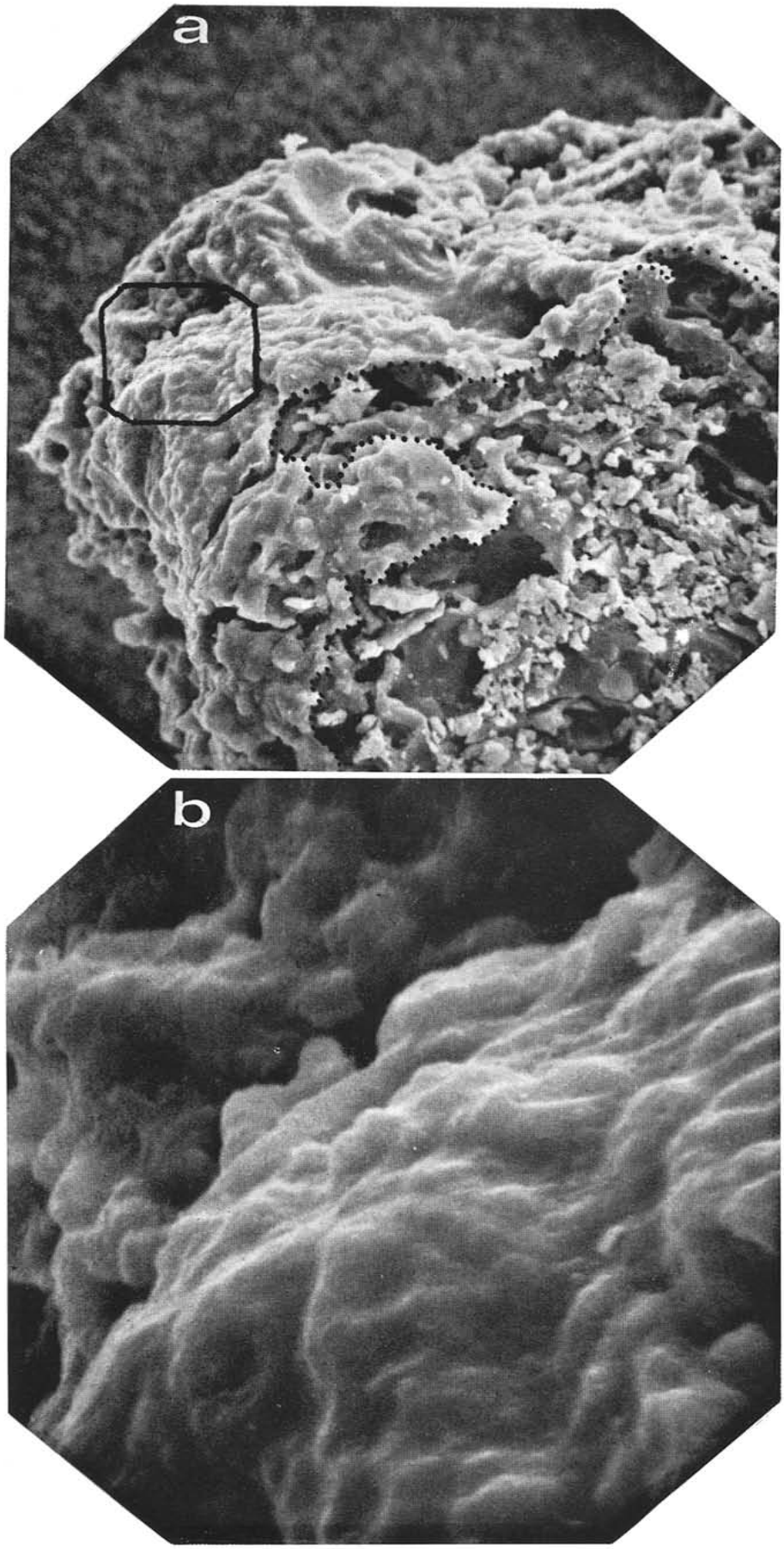


Fig. 4. 11% $[C_{18}H_{37}SiO_{3/2}]_n$ on Chromosorb G, after exhaustive extraction. (a) Line of fracture, 750×; (b) Outside, detail, 3750×.

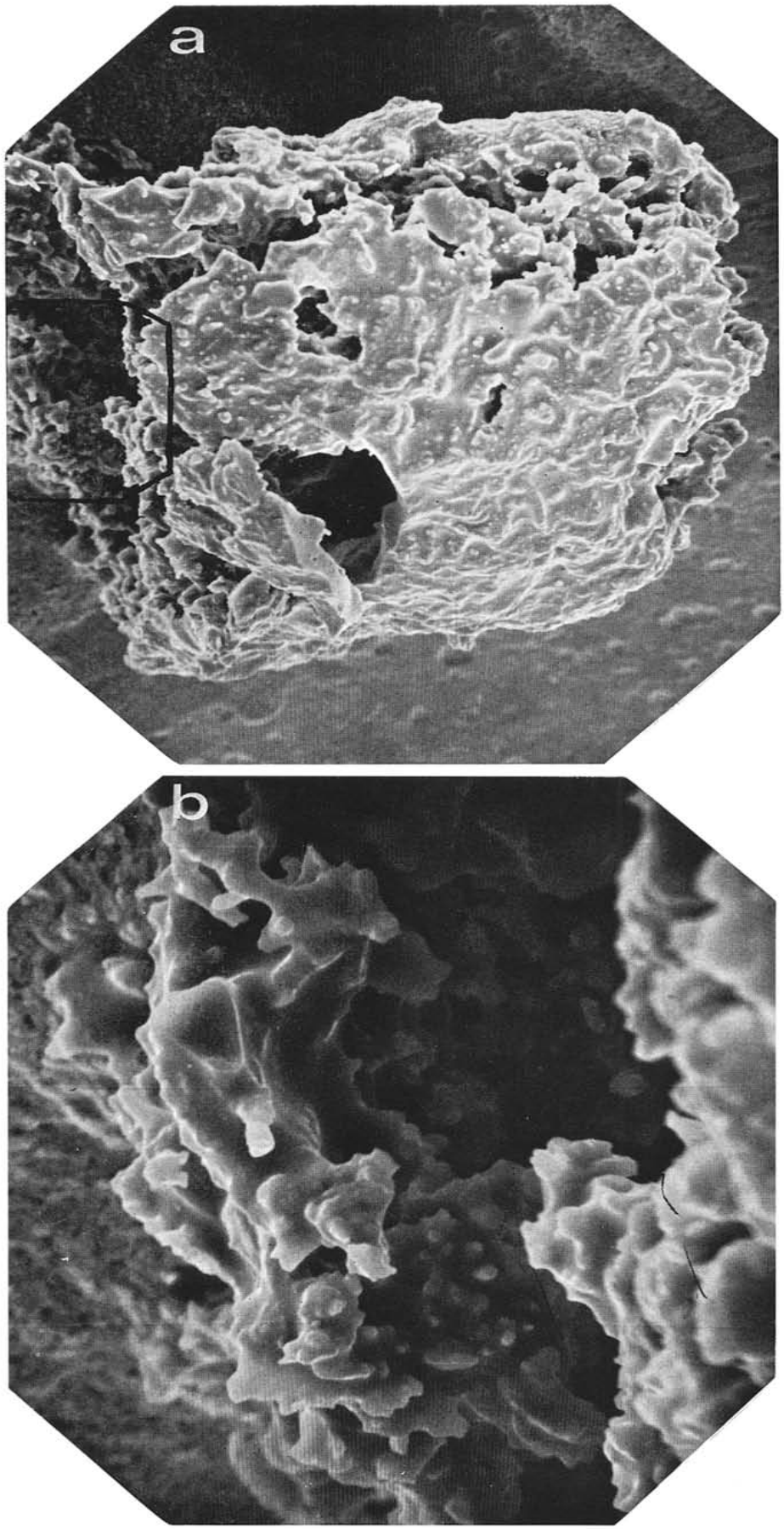
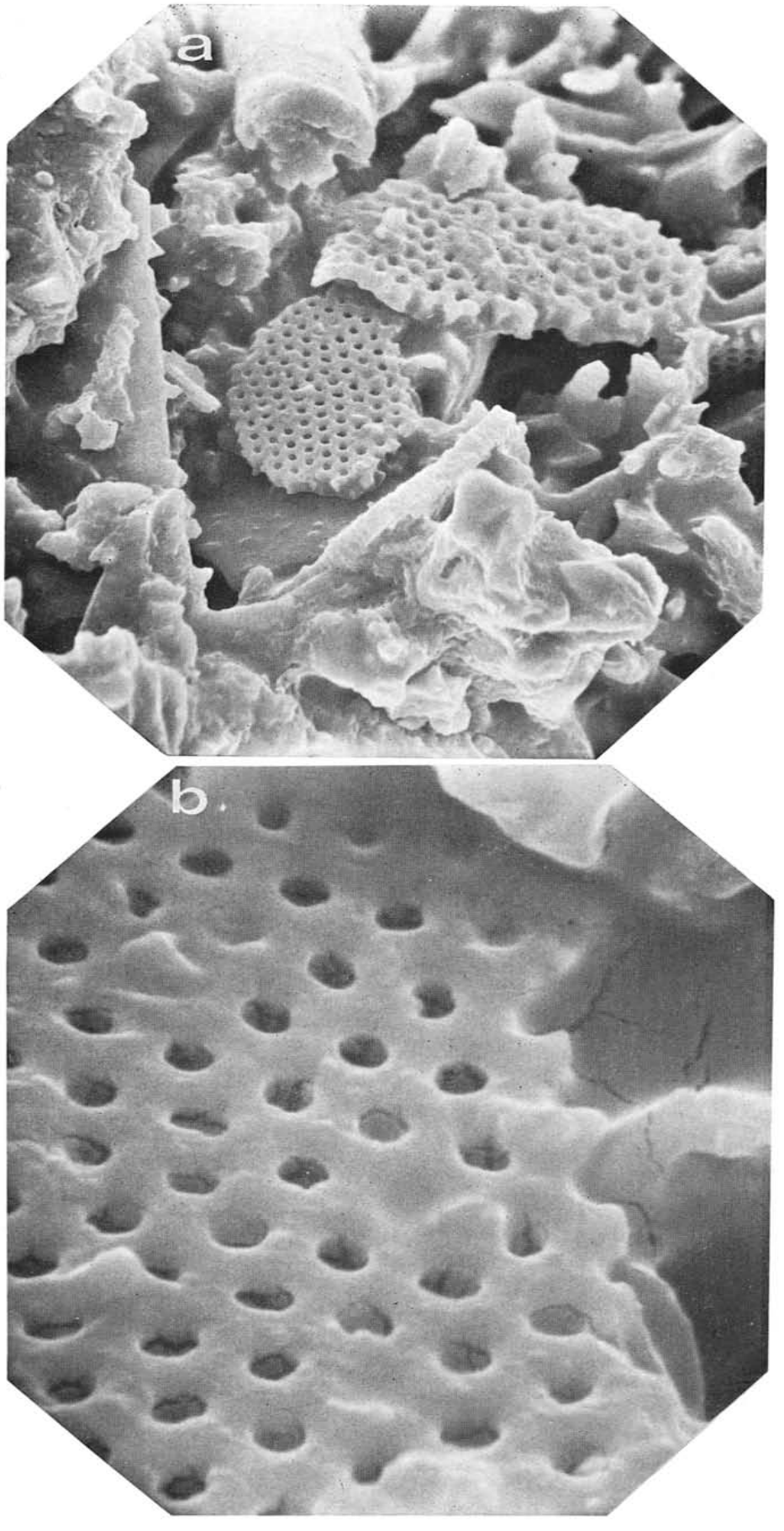


Fig. 5. 25% SE-30 on Chromosorb G, heat-treated. (a) Split particle, 375 × ; (b) Fracture region, detail, 1500 × .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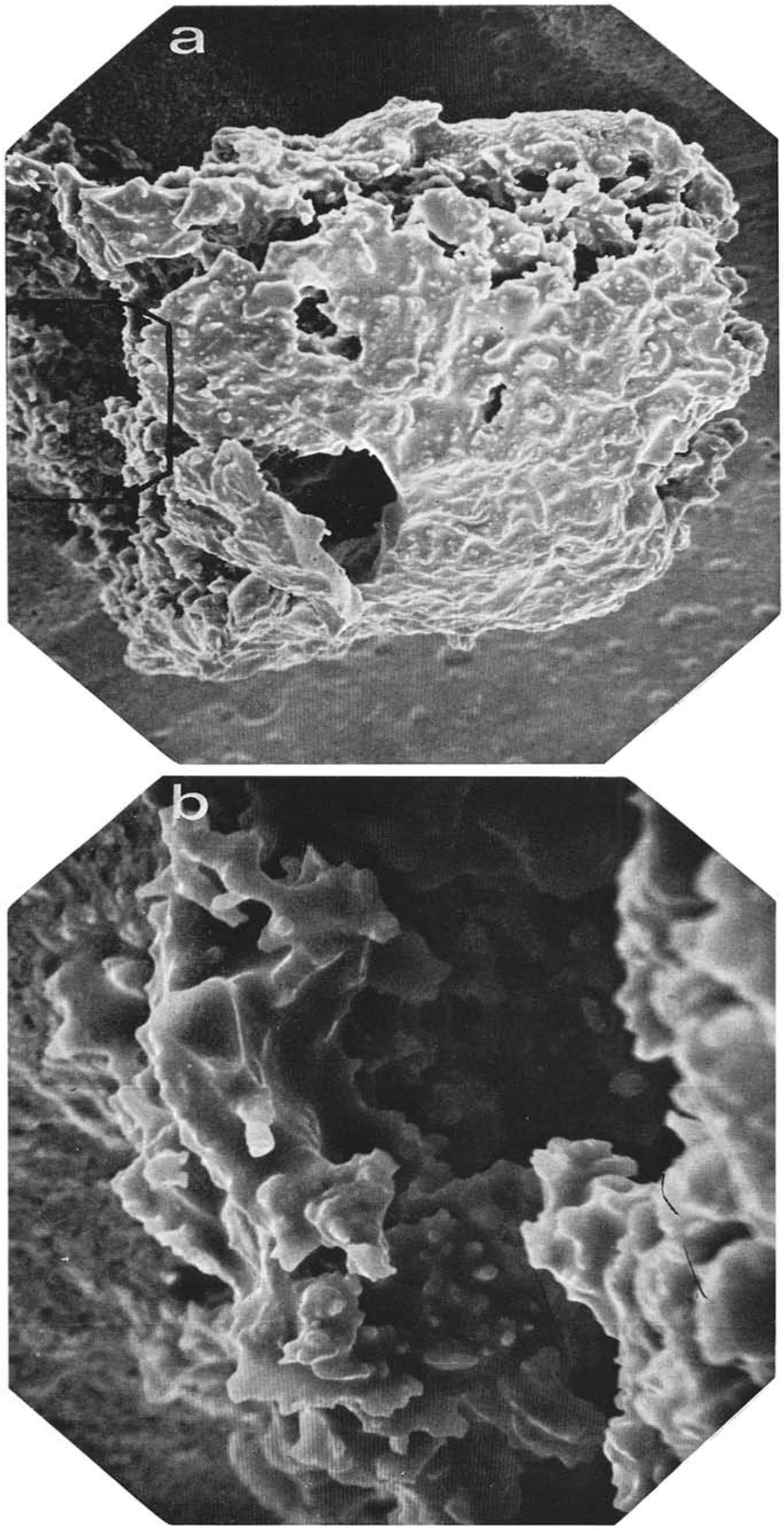
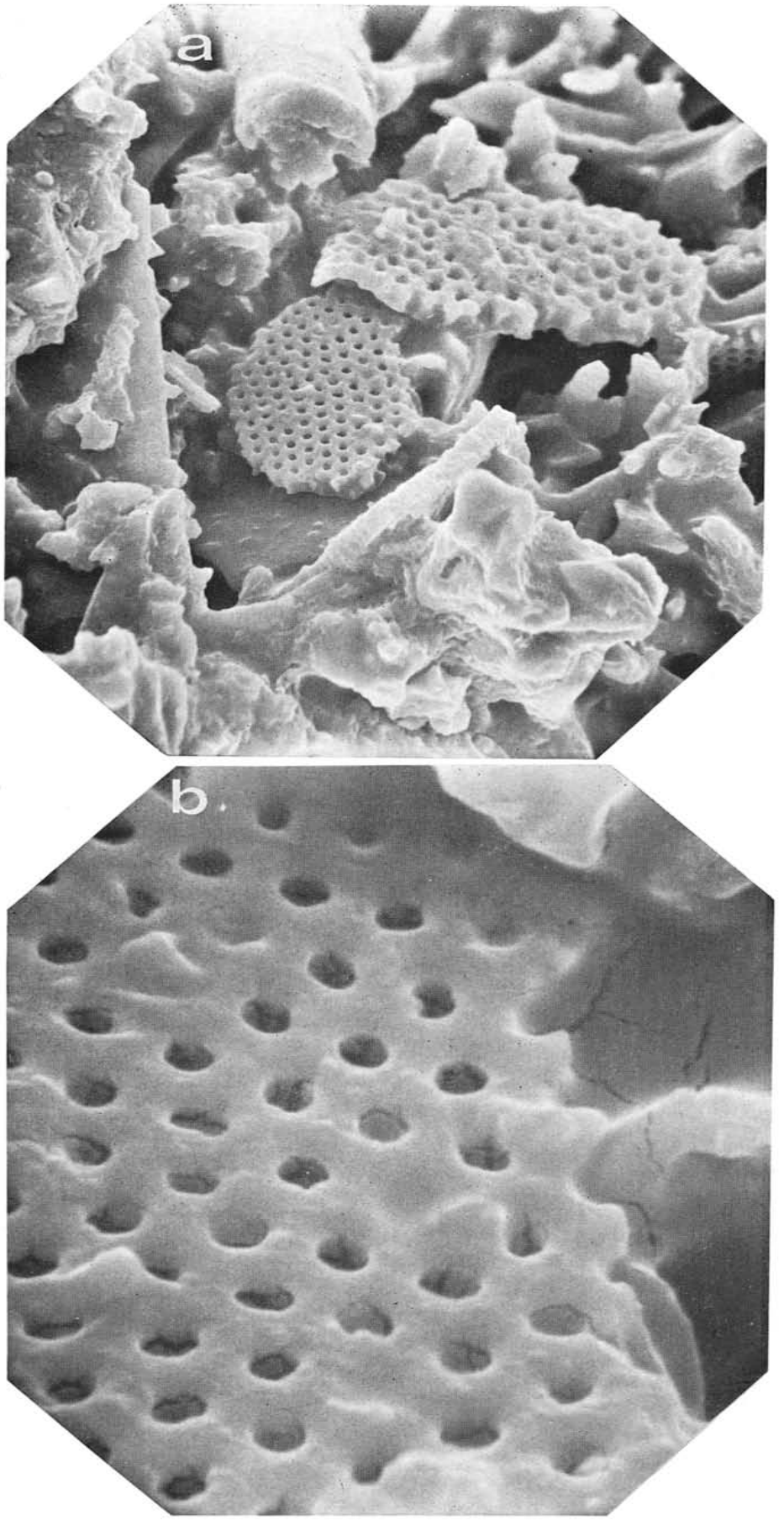


Fig. 5. 25% SE-30 on Chromosorb G, heat-treated. (a) Split particle, 375 × ; (b) Fracture region, detail, 1500 × .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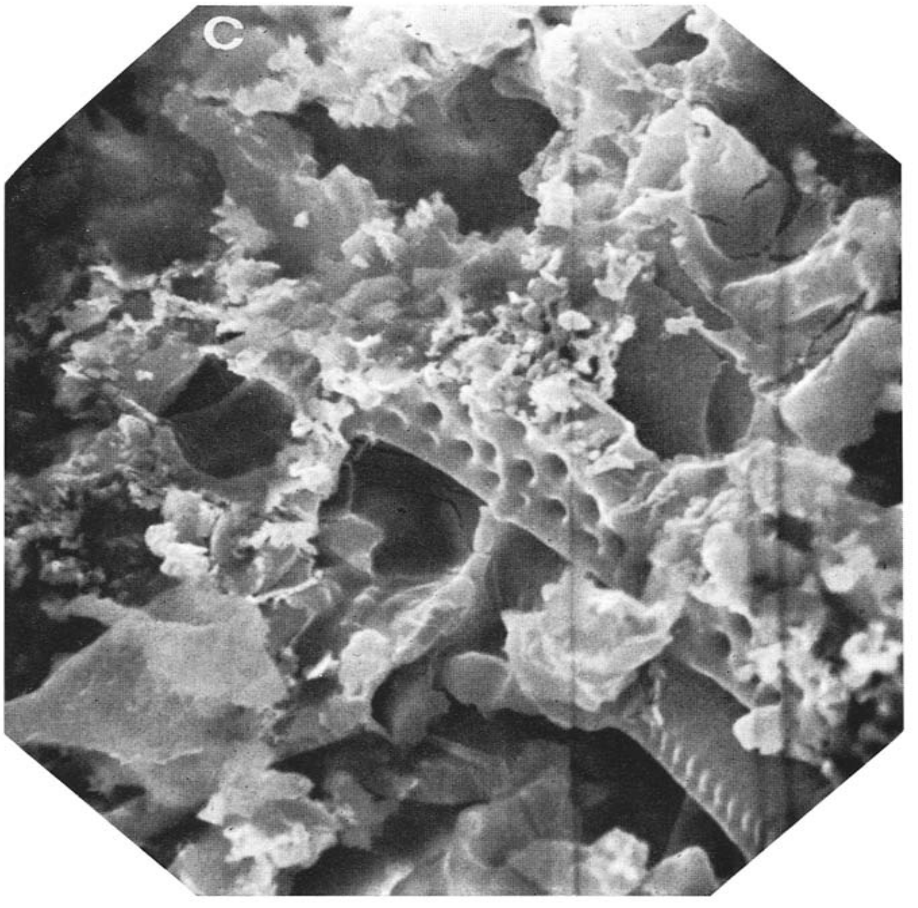


Fig. 6. 40% $[C_{18}H_{37}SiO_{3/2}]_n$ on Chromosorb W, heat-treated, not extracted. (a) Outside, 1400 ×; (b) Outside, detail, 7000 ×; (c) Inside, 3500 ×.

complete absence of polymer on internal surfaces. Rather, one may assume with some physicochemical backing that one or more molecular layers cover the interior. These layers, however, could not be seen by scanning electron microscopy.

Fig. 6c is the only micrograph, in fact, in which we found clear evidence of polymer present inside the particle. This evidence is provided by the experience that in support-bonded silicones at unusually high load, cracks show up in places likely to develop tension. This effect is exhibited most clearly in the "outside detail" shown in Fig. 6b, but it can be observed in several other micrographs. The mentioned inside shot then, Fig. 6c, shows several of these cracks together with typical protrusions and perforations which appear less rugged and jagged than they do in the blanks (Fig. 7).

The predominance of polymer present on the outside of the particles has been found with both octadecyl and dimethyl polysiloxanes coated in different loads on both Chromosorbs G and W (Figs. 1, 3, 4, 6, 8). Heat-treatment did not cause significant visible effects (Figs. 3 and 6 *vs.* 1, 4 and 8).

No such statement can be made about the non-support-bonded, "regular" E-301 and SE-30 phases. The polymers could be clearly recognized in most cases in both inside and outside regions. There seemed to be a slight preference for the exterior, but the necessity to use relatively heavy loads of polymer, and the fact that only two silicones were examined, does not permit a reliable inference on such phases

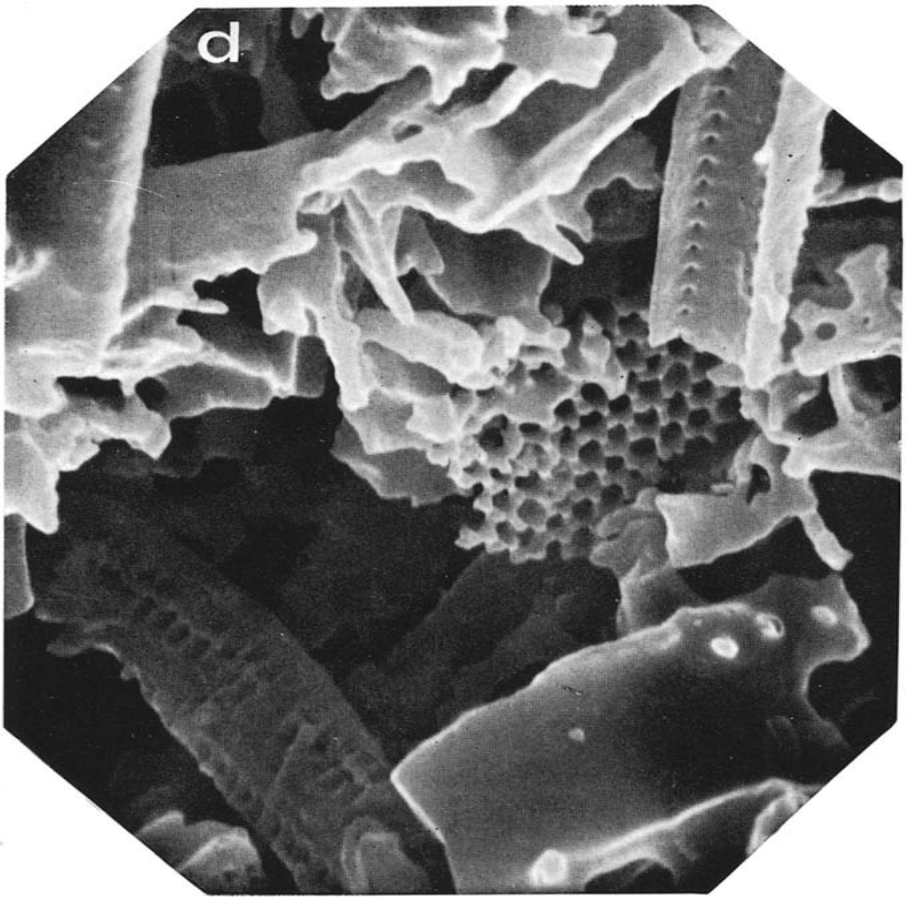


Fig. 7. Chromosorb W, acid washed. Outside, 3750 ×.

in general. One representing the heaviest load of SE-30 which we ever used, is shown in Fig. 5.

It may be interesting to estimate the thickness of the peripheral film assuming an interior devoid of silicone. The phase 5.5% $(C_{18}H_{37}SiO_{3/2})_n$ on Chromosorb G, 60/80 mesh, may serve as an example. The support material, according to the manufacturer, has a "packed density" of 0.58 g/cc and a BET surface area of 0.5 m^2/g. Were the particles spheres with a diameter of 200 μ, their total outer surface would be on the order of approximately 250 cm^2/g of Chromosorb. If we double this figure arbitrarily to pay some tribute to the puckering of the surface, the average thickness of the layer would be approximately 1 μ. It would be difficult if not impossible to arrive at a reasonably accurate value of average film thickness from such images as portrayed by Figs. 1b and 4a; but the layers appear at least to be of the right order of magnitude.

The estimated 500 cm^2 of peripheral surface per gram of Chromosorb G represent 1/10 of the support's BET surface. Consequently, a film covering the entire BET surface would have approximately 1/10 of the thickness of a layer submerging only exterior structures. Such a film would be spread too thin—approximately 100 Å on the average—to be within easy reach of the scanning electron microscope.

It is also interesting to speculate on the effect of mesh size on equal loads of

support-bonded polymers. If the polymer were present exclusively on the outer surface of the particle, a reduction in particle diameter by 1/2 would result in a doubling of the outer surface available for polymer coverage. In such a case, say we compare the same amount of polymer coated on a 120 mesh instead of a 60 mesh support*, the thickness of the peripheral layer on the finer material would be half of that on the coarse material. In a Van Deemter plot, consequently, the two materials would be expected to differ not only in the magnitude of Eddy diffusion, but also in the contribution to peak broadening of solute disequilibrium caused by the stationary phase.

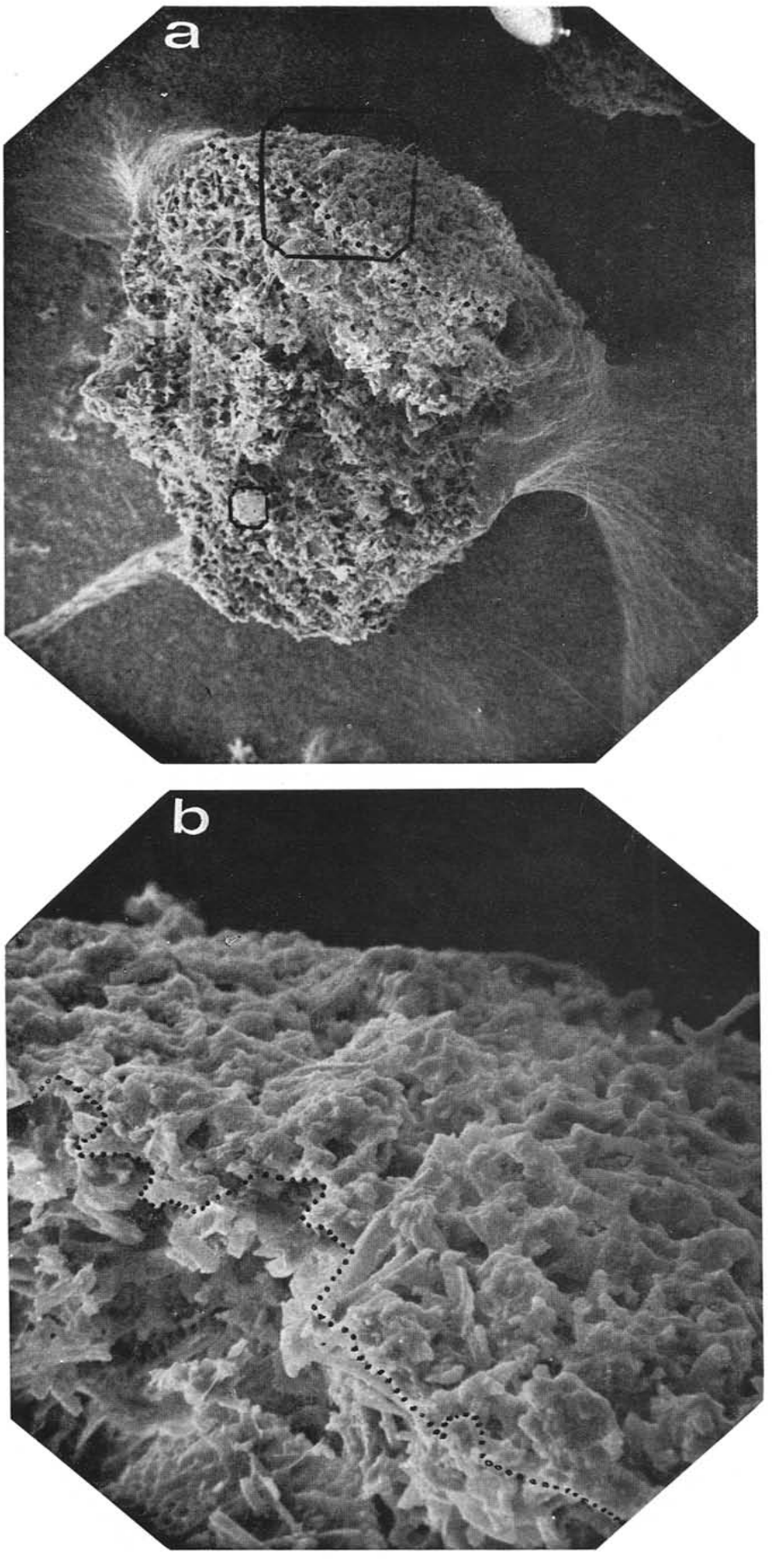
Another obvious avenue of speculation originates from the suitability of these support-bonded phases for the GLC of highly polar compounds including amines, phenols, carboxylic acids, chlorinated hydrocarbons and others[4,5]. Fig. 4b, for instance, shows the outside of a particle where the polymer closes off almost totally the inner regions. What happens if a solute molecule diffuses through the film and reaches the particles' interior which is filled with (more or less) stagnant gas? One should expect serious peak broadening or substance decomposition or both. Neither, however, is the case. Support-bonded silicones give rise to HETP values and gas chromatographic separations which are comparable to the performance shown by the best commercial silicones. One is therefore tempted to assume that the chromatographic process takes place on or close to the gas–liquid interface. Certainly one cannot attribute the high efficiency of these materials to the large internal surface area of the original support, as is the common interpretation for regular phases coated on diatomaceous earths. Taking their SEM-projected appearance, they may rather be comparable to solid-core particles whose rugged, highly structured surface is submerged under a thick polymer coat.

In our experience, support-bonded silicone phases give decidedly better chromatographic performance for highly polar compounds when they are heavily loaded. This effect is common with regular GLC phases; however, these phases are not supposed to exhibit significant differences in average film thickness between internal and external regions (although no one knows for sure). Consequently, the liquid should be much less deep than its support-bonded counterpart and the effective masking of active sites may be expected to require higher loads. Support-bonded films, in contrast, are an order of magnitude thicker and one may speculate that their competitive GLC performance is achieved not by a heavy polymer cover over active sites, but rather by a complete enclosure of the particles which prevents the gas stream with its solute molecules from contact with the complex interior framework.

It is also open to speculation why support-bonded phases, at least the ones which we examined, should predominantly cover the peripheral regions of the particles. One possible explanation may lie in the fluidized bed polymerization used to synthesize these materials. The external as well as the internal surfaces of the particle may well be coated by the monomer when it enters the fluidized bed. There it is carried by a turbulent stream of hot air which contains small amounts of water vapor. Thus, the fast reaction between the monomer and water molecules will occur preferentially on the particle exterior.

As layers of polymer develop, this preference will become more pronounced. There will be a very low concentration of HCl on the outside, but a high one on the

* Meshsize is of course not a linear function of particle diameter.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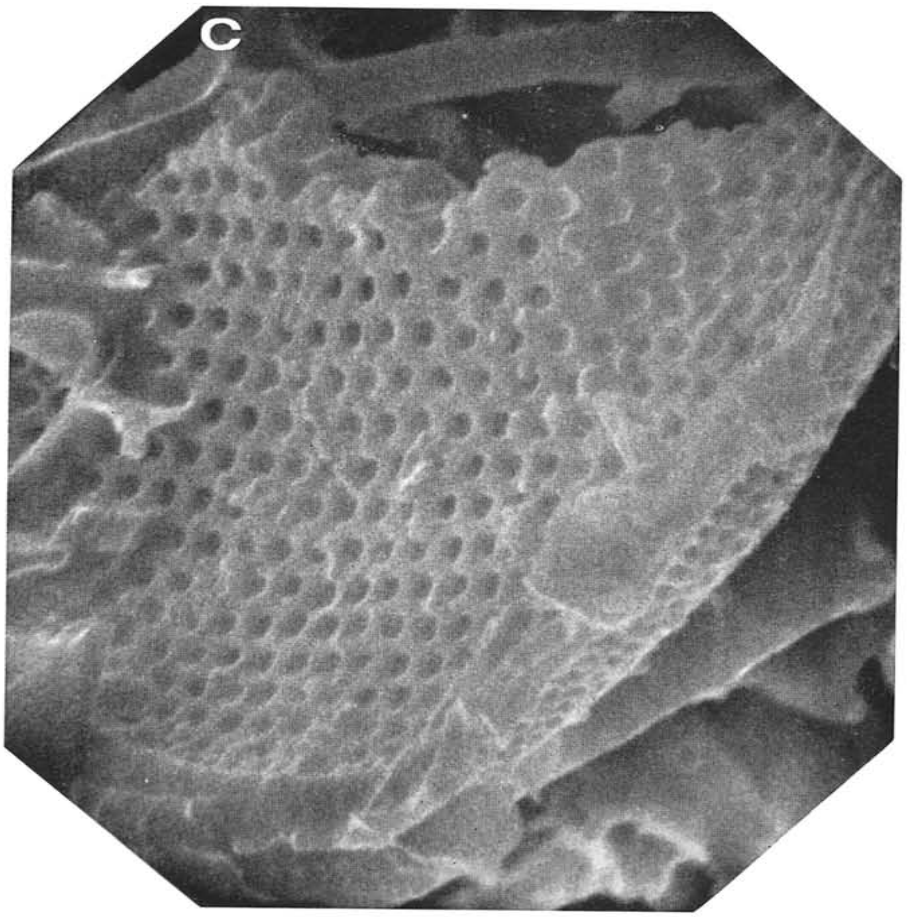

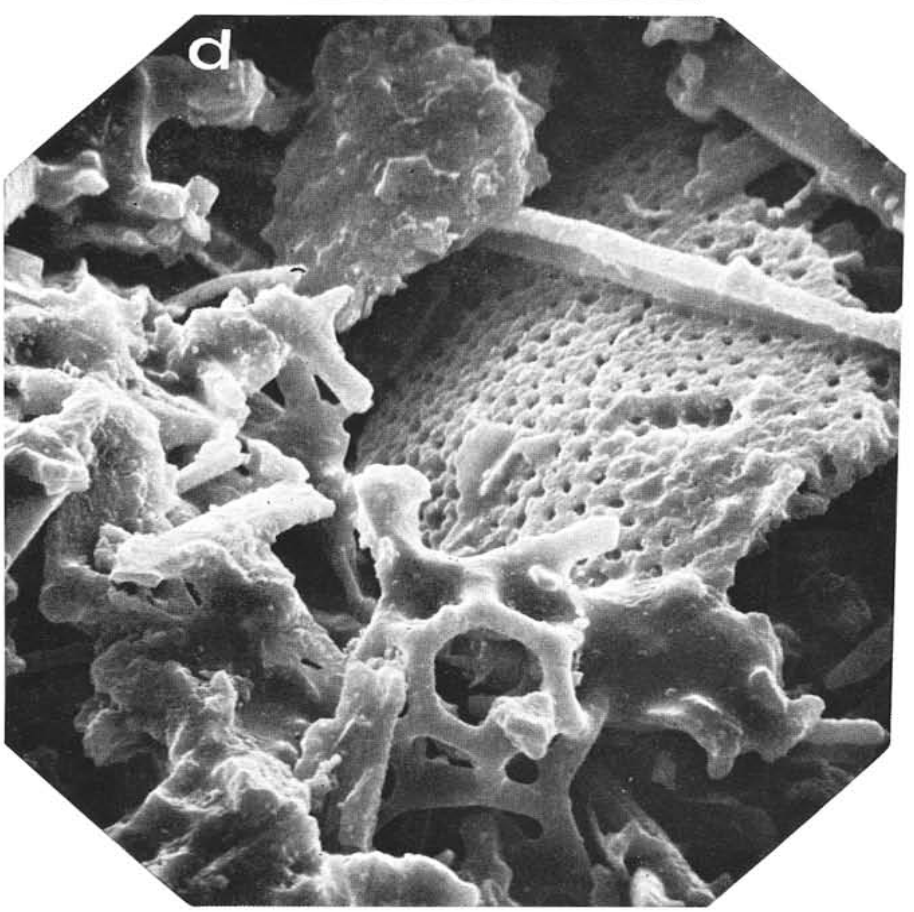

Fig. 8. 18% $[C_{18}H_{37}SiO_{3/2}]_n$ on Chromosorb W, after exhaustive extraction. (a) Split particle in DUCO Cement, 150 ×; (b) Line of fracture, detail, 750 ×; (c) Inside detail, 3750 ×; (d) Outside, 1500 ×.

inside of the particle. Monomer molecules will tend to diffuse out from the internal regions and into the air stream, a process enhanced by the elevated temperatures of the fluidized bed. (In fact, other experiments with some of the more volatile monomers have shown that serious losses of monomer to the carrier air can result if the conditions of the fluidized bed polymerization are not carefully controlled.)

As the polymerization progresses, as holes on the periphery of the particle are being progressively closed off, and as the polymer film grows in thickness, it should become increasingly difficult for water molecules to diffuse through the silicone layer and react with monomer or partially hydrolized monomer in the internal regions of the particle under a high concentration of HCl. For this interplay of transport phenomena and local mass equilibria, as we have rationalized the process, there is certainly no proof. However, it relies on logical premises and could be worth considering as a working hypothesis.

It is obvious that more work, both with support-bonded and regular GLC phases, would be needed to clarify some of the points which have been touched upon in this paper. Besides our particular interest related to support-bonded materials, however, we concur with DEMETS AND LAGASSE that "it should be interesting for all gas chromatography people to have a look at the magnificent materials they are working with daily"[2].

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