BRIT. J. APPL. PHYS., 1964, VOL. 15

Investigations of the disturbed layer of ground quartz

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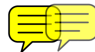
MS. received 10*th October* 1963, *in revised form* 20*th December* 1963

Abstract. It is shown electron microscopically that in 3 μm diameter wet ground quartz powders less than 1% of the mass consists of sub-microscopical 'adhering' particles. The observed decrease in the peak intensities of the x-ray diffraction lines of these 3 μm powders must be attributed to disturbed outer layers of the powder particles. It is shown that the outer layers recover to a considerable extent by a heat treatment at 1200°c and the x-ray and electron diffraction diagrams reveal that the disturbance is rather slight. From the profiles of the x-ray powder lines it can be derived that the thickness of the disturbed layer in these powders is greater than or equal to 0·4 μm.



1. Introduction

The peak intensities of the Debye–Scherrer lines of finely ground quartz powders decrease when the particles become smaller than about 5 μm. When such a powder is etched with hydrofluoric acid, the residue again produces a larger peak intensity.

Nagelschmidt *et al.* (1952), who discovered these effects, attributed them to an amorphous outer layer around the particles of about 0·03 μm thickness.

Gordon and Harris (1955) confirmed this reduction in peak intensity, but also detected some line broadening. These authors suggested that the outer shell was not entirely amorphous but of a gradually decreasing crystallinity towards the surface of the particle.

Brindley and Udagawa (1959) observed a reduction in integrated intensity, of about 20%, in quartz powders that had been ground dry for sixteen hours. No line broadening could be detected and the authors assumed a layer of 'disturbed material' of unknown thickness, "not contributing to the reflected x-ray intensity".

Talbot and Kempis (1960) investigated quartz powders electron microscopically and by electron diffraction. They considered it more likely that all the effects, usually ascribed to the amorphous or disturbed layer, had to be explained by very small sub-microscopical particles, always present in finely ground quartz powders and adhering to the larger ones.

Stöber and Arnold (1961) investigated the enhanced initial solubility of ground quartz powders in water. In contradiction to other authors (Bergman 1963) they attributed this effect exclusively to small adhered particles, although they did not deny the existence of a disturbed outer structure. Hofmann, reviewing Stöber's and Arnold's work, attributed the above-mentioned x-ray results exclusively to small adhering particles without testing this experimentally (Hofmann 1962).

Bergman, Cartwright and Casswell, however, accepted the concept of a disturbed layer around the ground quartz particles (Bergman and Casswell 1962, Bergman *et al.* 1963). They explained the lowered peak intensities completely in terms of line broadening, which, according to these authors, indicates either an increased strain in the crystals or a larger number of very small crystallites, or both. The increased strain might be described in terms of a large dislocation density, whereas the small crystallite effect might be due to multiple twinning in the layer.

In order to test which of the concepts of the several above-mentioned authors is the right one, wet ground quartz powders with a particle size of about 3 μm have been investigated by electron microscopy, and x-ray and electron diffraction, before and after a

heat treatment of the powders. The results indicate that in these powders disturbed layers are present for which it was possible to give a lower limit for the thickness.

2. Experimental

2.1. *Preparation of the quartz powders*

The starting material (obtained from Merck) consisted of fragments of natural quartz of the size of 2 mm; it was ground in an iron ball mill in a slurry with carbon tetrachloride for eight hours. After grinding the quartz powder was washed with hydrochloric acid, followed by a washing with water. From this milled product a powder was prepared (which will be termed unetched quartz in this paper) with particle sizes between about 1 μm and 5 μm. The great majority of the particles already had sizes between these limits but for the sake of accuracy all particles with a smaller or larger size were removed. The particles smaller than 1 μm were removed by centrifugal sedimentation in 0·05 N hydrochloric acid solution (in order to prevent the formation of a colloidal solution of SiO_2) while the particles larger than 5 μm were removed by column sedimentation in methyl alcohol. Suspensions of 0·5% by volume were used and the quartz particles were suspended with the aid of an energetically vibrating stirrer. In an analogous manner a second powder was prepared (which will be called etched quartz). The only difference with regard to the foregoing sample is that the milled and washed powder was etched with hydrofluoric acid in order to dissolve the outer layer of the particles. The etching was carried out with 10% acid for 15 minutes, as described by Brindley and Udagawa (1959), who observed that the intensities of the diffraction lines did not increase any more when the etching was repeated. The excess of acid was removed by sodium hydroxide and after a washing with water the powder was sized in the manner described above.

The particle sizes were determined microscopically in the way described by Cartwright (1956. A suspension of the quartz powders in ethyl alcohol was made and a drop of this suspension (still in motion) was transferred on to a microscope slide. About a thousand particles were measured along two diameters of the practically circular preparation, intersecting at right angles. The mean diameter $d = \Sigma nd^4/\Sigma nd^3$ was 2·82 μm for the unetched and 2·88 μm for the etched quartz powder. In both cases the limits were 1 and 5 μm and the distribution of the sizes was about the same.

2.2. *Electron microscopical and electron diffraction techniques*

For preparing the electron micrographs a drop of the suspension of quartz in ethyl alcohol (taken from the suspension when this was in stirring motion) was transferred on to a microscope covering slide. After drying, platinum shadowed carbon replicas were prepared and examined with a Philips electron microscope E.M.75. (The slide and quartz particles were removed with hydrofluoric acid.) For the electron diffraction powder diagrams, also made with this microscope, the dry quartz powder was transferred on to the specimen grid.

2.3. *X-ray diffraction technique*

All x-ray diffraction measurements were carried out on a Philips diffractometer. Some line profiles were measured by means of point counting, others by chart-recording technique (goniometer scanning speed $\frac{1}{8}$ degree per minute). The specimens were prepared by packing the quartz powder into a rectangular sample holder (20 mm × 10 mm × 1 mm). Ni-filtered CuKα radiation and V-filtered CrKα radiation were used and the intensities were measured with a scintillation or a proportional counter. No internal standard was added to the quartz samples and for this reason great attention was paid to the reproducibility of the measurements.

3. Results

3.1. *Electron micrographs*

The electron micrographs of the unetched and etched powders were practically identical.

The circumferences of the etched particles were somewhat smoother and the particles gave the impression of having slightly fewer of what may be adhering particles or 'protruding parts' of sizes of 0·1–0·01 μm than the unetched ones (figures 1 and 2†). The total mass of these 'adhering particles' was small, in both cases not more than about 1% of the mass of the powder. The electron micrograph of the unetched quartz that had been annealed for 7½ hours at 1200°c (in an oxygen atmosphere) did not show any changes with respect to those mentioned just now (figure 3). In particular it was noticed that the number of very small adhering particles did not change by this heat treatment.

3.2. *X-ray diffraction results*

The broadening of the Debye–Scherrer lines of unetched quartz and the corresponding changes in their line profiles could be observed most clearly in the back-reflection region (the effects were very small in the front-reflection region for powders of the 3 μm size). The x-ray intensity areas and approximated values of the integral breadths are shown in the table. As the measurements of all diffraction lines were carried out in the same way, only one, that of 234, will be given as an example.

X-ray diffraction results

(1)	(2)	(3)	(4)	(5)
234	87·7	0·20	0·40	2
312	95·3	0·08	0·35	2
112	97·1	0·06	0·28	2
114, 310	90·7	0·22	0·40	1
302	89·8	0·15	0·32	1

(1) Debye–Scherrer line; (2) integrated intensities of the lines of unetched quartz expressed in per cent of the intensity of the same line of etched quartz; (3) 'true' integral breadth of the Debye–Scherrer lines of unetched quartz in degrees (approximated value); (4) layer thickness, as derived by the subtracting of line profiles in μm; (5) number of determinations of (4).

The line 234 was measured point by point between $2\theta = 152 \cdot 00°$ and $155 \cdot 50°$ (for CuKα_1, the peak occurs at $153 \cdot 51°$). For estimating the background intensity the diagram had to be measured over a larger range. This was done by the chart-recording method and measurements were carried out between $2\theta = 142 \cdot 00°$ and $157 \cdot 00°$. The lowest background intensity was found at $2\theta = 148 \cdot 65°$. This intensity enabled the value of the background level of 234 to be estimated as follows. The α_1 component of 234, constructed by Rachinger's method (1948), was found to lie between $2\theta = 151 \cdot 95°$ and $155 \cdot 10°$. As the very weak α_2 component of 241 interfered with 234 at $2\theta = 152 \cdot 30°$ it was necessary to extrapolate the low-angle side of the latter. The constructed profile turned out to be an acceptable one as it virtually covered the function $y = c/(1 + k^2x^2)$. Knowing approximately the breadth of the foot of the 234 line, small corrections could be calculated for the background level at $148 \cdot 65°$ by applying this breadth to the lines on either side of $2\theta = 148 \cdot 65°$. These corrections turned out to be 1·5% for the etched and 3% for the unetched quartz, and the resulting background level was taken as the final one. It must be pointed out, however, that this final value may still contain a systematic error. The integral breadth, including the instrumental broadening, of the 234 lines of etched and unetched quartz proved to be 0·42° and 0·62° respectively. From these values a true breadth of the 234 line of unetched quartz of 0·20° could be derived without applying corrections which were applied for the lines at lower diffraction angles (Jones 1938).

The ratio of the area of the diffraction line of unetched quartz to that of etched quartz was 0·88. In a similar way the remaining results were obtained.

All measurements of intensity and breadth were carried out with quartz powders without an internal standard as the object was to measure different diffraction lines under the same circumstances and therefore coincidence of any line with a line of a standard had to be avoided. For the lines 234, 312 and 112, which were measured point by point with

† Figures 1. 2 and 3 printed as a plate at end of issue.

CuKα radiation, the coefficient of variation of a single intensity measurement was 2·5% (derived from 234 and 312; each line was measured three times and for every measurement a new diffractometer specimen was prepared). The coefficient of variation of the integral breadth (instrumental broadening included) was 1·6%. The corresponding values for the other lines, which were measured by chart-recording using CrKα radiation, were 3·7% and 3·5 %respectively.

In all x-ray diagrams of the unetched quartz the background level was found to be higher than that of the etched sample. This fact, which was found at all diffraction angles, had already been observed by other authors (Bergman and Casswell 1962, Talbot *et al.* 1963). In the far back-reflection region the increase was about 17½%; at $2\theta = 52 \cdot 50°$ about 8%; and at $2\theta = 13 \cdot 00°$ about 4%. In the latter case no overlapping could occur as the largest spacing for quartz is at $2\theta = 20 \cdot 84°$.

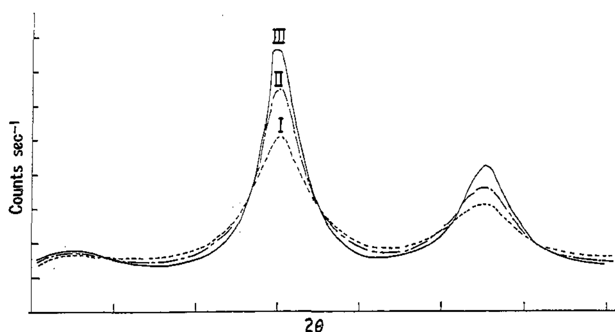


Figure 4. Profiles of the Debye–Scherrer line 234; - - - - - - - - (I) unetched quartz; ·—·—·—·—· (II) annealed quartz; ———— (III) etched quartz.

3.3. *Recovery by heat*

The peak intensities of all x-ray diffraction lines of unetched quartz, annealed at 1200°c for 7½ hours, rose considerably with respect to those of the unheated (and unetched) sample (figure 4). The ratio of the peak intensity of heated unetched quartz to that of etched quartz was 0·81, whereas this value was 0·59 for the unheated powder. The same heat treatment produced no changes in the peak intensities of the x-ray lines of the etched powder. In this case, however, a small decrease could be observed in the peak intensities of the diffraction lines 100 and 101 presumably caused by extinction effects.

In both powders some cristobalite was present after the heat treatment, somewhat more in the etched sample than in the unetched one. This difference can be explained by the fact that after the etching the hydrofluoric acid was neutralized with sodium hydroxide.

3.4. *Electron diffraction results*

The electron diffraction patterns of the etched and unetched quartz samples, obtained with 75 kv electrons, showed only slight differences. This had already been noticed by Gibb *et al.* (1953). The lines of the unetched quartz were rather diffuse and continuous, with spots, while those of the etched quartz were less continuous, with sharper spots. A similar observation was interpreted by Gibb *et al.* as some evidence for a reduction in the size of crystallites towards the surface of the unetched quartz grains. However, contrary to the observations of these authors, who found an appreciable difference between the two samples when using 20 and 25 kv electrons, in the present investigation no noticeable differences were found with respect to the 75 kv diffraction patterns, when using 25 and 30 kv electrons.

4. Calculation of the lower limit of the thickness of the layer

It was assumed that the powder particle consisted of an undisturbed crystalline core with

a disturbed crystalline outer layer. Such a layer, as distinct from an amorphous one, contributes to the intensity of the Debye–Scherrer lines. It is not possible to split the experimental line profile in a simple way into a 'disturbed' and an 'undisturbed' part and to calculate the thickness of the layer from their integrated intensities. One can, however, calculate the lower limit of the latter in the following way (figure 5). From the Debye–Scherrer line of the unetched quartz, fractions of the same line of the etched quartz were subtracted. As the line profile that originates from the disturbed outer layer can have only one maximum, a remaining profile with two maxima points to too high a value of the fraction of the sharp profile. Consequently, that value of the fraction at which the one maximum tends to change into two constitutes its limit.

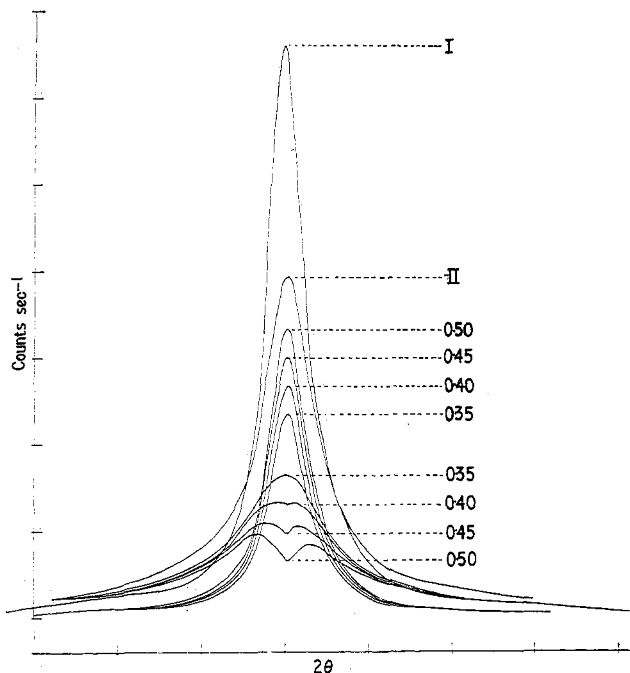


Figure 5. The splitting up of the profile of the Debye–Scherrer line 234.

It must be emphasized that it cannot be claimed that this fraction represents the true size of the undisturbed core of the particle. The latter may be smaller but not larger. For calculating this maximum size of the core it was assumed that the powder consisted of spherical particles all with the same radius of 1·4 μm. For 234, for example, the largest fraction of the sharp profile was 0·35, the radius of the core is therefore less than or equal to 1·00 μm and the thickness of the outer layer is greater than or equal to 0·40 μm.

The table shows the lower limit of the layer as obtained with the different diffraction lines. In deriving these quantities the absorption of x rays was neglected (in a layer of SiO_2 of 0·4 μm the absorption is about 0·4% for CuKα radiation). The average difference between the values that were established twice (using different diffractometer specimens) was about 0·03 μm.

5. Discussion

The electron microscopical investigation revealed that all 3 μm quartz powders that were examined hardly contained sub-microscopical particles or 'protruding parts' between 0·1 μm and 0·01 μm. In principle they will cause line-broadening but by reason of their

small total mass this will hardly or not at all be observable in the experimental line profiles; a slight difference in the number of 'adhered particles' in the etched and unetched powders will certainly not be detectable. Therefore 'adhering particles' cannot cause the established difference in the X-ray line profiles, and it is obvious that the line-broadening must be caused by a 'disturbed' structure that occurs in the outer layers of the particles (as is evident from the etching with hydrofluoric acid).

This conclusion was supported by the sharpening of the X-ray diffraction lines in the diagram of unetched quartz that had been annealed at 1200°c. This fact indicated that the deformation brought about by grinding recovered by this treatment.

It is difficult to decide on the basis of these experiments (the measured line-breadths) whether the line-broadening is due to strain or to a more or less breaking up of the outer layer into small crystallites, e.g. by multiple twinning (Bergman and Casswell 1962).

The observed X-ray line-broadenings were rather small (as compared, for example, with those of metal filings) and therefore indicated that the disturbances in these wet ground 3 μm powders were rather slight. This was in agreement with the slight differences that were observed in the electron diffraction diagrams.

Calculations of the thickness of outer layers were carried out by Nagelschmidt *et al.* (1952) and Gibb *et al.* (1953), who all assumed amorphous layers. Nagelschmidt *et al.*, who discovered the decrease in the peak intensities of the X-ray powder lines, were, with their techniques, unable to show a line-broadening (only the finest powders gave very slight line-broadening in the back reflection region). Therefore, they assumed that amorphous material had been formed during grinding. Taking the peak intensities of the Debye–Scherrer lines at about $2\theta = 95°$ as a measure of integrated intensity, the thickness of the amorphous layer was calculated at 0·03 μm. As, however, line-broadening has turned out to be distinctly present in such powders, calculations with peak intensities are meaningless. In principle the thickness of this layer, if it were amorphous, could be derived by means of the calculation of Nagelschmidt *et al.* but in their formula

$$y = r\left\{1 - \left(\frac{\text{intensity of unetched quartz}}{\text{intensity of etched quartz}}\right)^{1/3}\right\}$$

integrated intensities must be used (y is the thickness to be found and r the radius of the particles, which are considered to be spheres). Using the ratios of the integrated intensities shown in the table, the following thicknesses for an amorphous layer would be found with the different diffraction lines (in the order of the table): 0·067, 0·022, 0·014, 0·046 and 0·048 μm. These values fall considerably with decreasing diffraction angles. This is probably due to the systematic errors in the background levels, especially in those of the unetched quartz. They are caused by the overlapping of the diffraction lines and they are largest in the back reflection region. Therefore, in practice, no amorphous layer can be calculated in this way (see also Talbot *et al.* 1963). A similar decrease in integrated intensities was observed by Bergman and Casswell (1962). When the above-mentioned increase in the background intensity was added to the integrated intensity of the Debye–Scherrer lines of the unetched quartz, the total intensity was about the same as the integrated intensity of the etched quartz, indicating that the integrated intensities hardly change with etching.

Gibb *et al.* based their calculations on the varying penetration depths of electrons of different kv and especially on the fact that an amorphous electron diffraction pattern was found with unetched quartz samples when using 20 and 25 kv electrons (the particle size range of their powders was between 0·25 and 10·0 μm). The electron diagrams of the unetched quartz (of mean particle size 3 μm) of this investigation show a crystalline pattern, both with 25 and 30 kv electrons. Hence, the findings of Gibb *et al.* are not confirmed.

The present method of determining the lower limit of the thickness of the disturbed layer by subtracting two line profiles is not affected by systematic errors in the background level (they can only shift the remaining profile over small vertical distances, and do not affect its form). It is emphasized that this subtracting does not yield the true layer thickness, but a value equal to or smaller than the true one. These values of the lower limit

decrease with decreasing diffraction angle. This is necessary since the line-broadening decreases in the same way. The sharp profiles at small diffraction angles automatically give a lower minimum for the disturbed layer. This variation is detrimental neither to the concept of a disturbed layer nor to the method of subtraction of the profiles as it does not concern the thickness itself but the lower limit. Extrapolation to zero diffraction angle would give the smallest possible value of this lower limit. If no particle size line-broadening is present this smallest value is zero. It is clear that the layer is better described by the lower limit derived from back reflection lines. As a matter of fact, extrapolation to 90° diffraction angle would give the true thickness since the diffraction line of the accepted (idealized) model at this angle would consist of a sharp profile (corresponding with the undisturbed core) superposed on the diffraction effect of the disturbed layer, which is completely flattened out at this angle. With the techniques of the present authors, measurements could not be performed beyond $2\theta = 160°$.

The layer here discussed should be distinguished from a much thinner outer shell of about 0·001 to 0·005 μm which, according to Bergman *et al.* (1963), is responsible for the enhanced initial solubility of quartz in water. Such a layer, which can be removed by etching with 0·1 M sodium hydroxide, plays no important role in the rather coarse samples studied here, as is also evident from the measurements of X-ray intensities by Bergman *et al.* (1963). Some relation may exist between this layer and the increase in the background level of 4% at $2\theta = 13°$.

The results are to be conceived as a rough picture of the disturbed outer layer, which only holds for these wet ground 3 μm quartz powders with size limits of 1·0 and 5·0 μm (as the peak intensities of the X-ray lines vary within the particle size range of the samples used in this investigation). For more detailed results it would be necessary to examine powders with narrower size ranges. Finally it is emphasized that the model of the particle assumed in this paper is an ideal one. Actually the layer will show a gradual increasing change in crystallinity from the surface of the particle towards the interior.

6. Conclusion

In wet ground quartz powders with a mean size of about 3 μm (limits 1 and 5 μm), the particles are surrounded by (on an average only slightly) disturbed outer layers of thickness greater than or equal to 0·4 μm.

Acknowledgments

The authors are indebted to Ir. J. G. R. Rockland for preparing the electron micrographs and electron diffraction diagrams and to Mr. J. A. van Beek for his assistance in preparing the quartz powders.

References

Bergman, I., 1963, *J. Appl. Chem. Lond.*, **13**, 356.
Bergman, I., and Casswell, C., 1962, *Brit. J. Appl. Phys.*, **13**, 621.
Bergman, I., Cartwright, J., and Casswell, C., 1963, *Brit. J. Appl. Phys.*, **14**, 399.
Brindley, G. W., and Udagawa, S., 1959, *J. Amer. Ceram. Soc.*, **42**, 643.
Cartwright, J., 1956, *S.M.R.E. Research report* No. 128 (London: H.M. Stationery Office).
Gibb, J. G., Ritchie, P. D., and Sharpe, J. W.,1953, *J. Appl. Chem. Lond.*, **3**, 213.
Gordon, R. L., and Harris, G. W., 1955, *Nature, Lond.*, **175**, 1135.
Hofmann, M., 1962, *Ber. Dtsch. Keram. Ges.*, **39**, 272.
Jones, F. W., 1938, *Proc. Roy. Soc.* A, **166**, 16.
Nagelschmidt, G., Gordon, R. L., and Griffin, O. G., 1952, *Nature, Lond.*, **169**, 540.
Rachinger, W. A., 1948, *J. Sci. Instrum.*, **25**, 254.
Stöber, W., and Arnold, M., 1961, *Kolloidzschr.*, **174**, 20.
Talbot, J. H., Bradley, A. A., and Kempis, E. B., 1963, *Brit. J. Appl. Phys.*, **14**, 399.
Talbot, J. H., and Kempis, E. B., 1960, *Nature, Lond.*, **188**, 927.

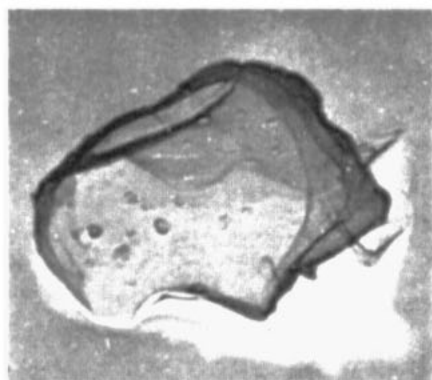


Figure 1 Electron micrograph of an unetched quartz particle.

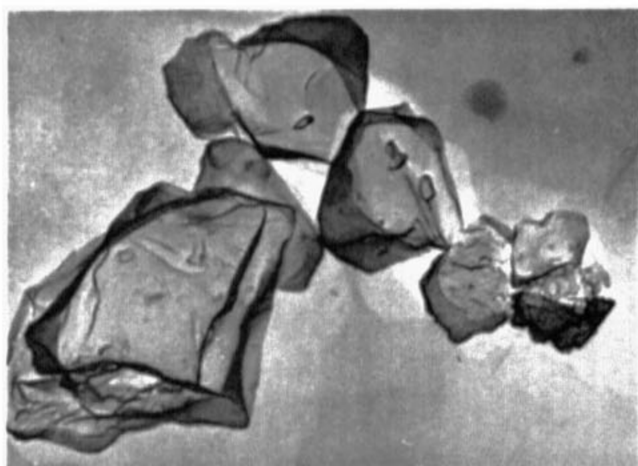


Figure 2. Electron micrograph of some etched quartz particles.

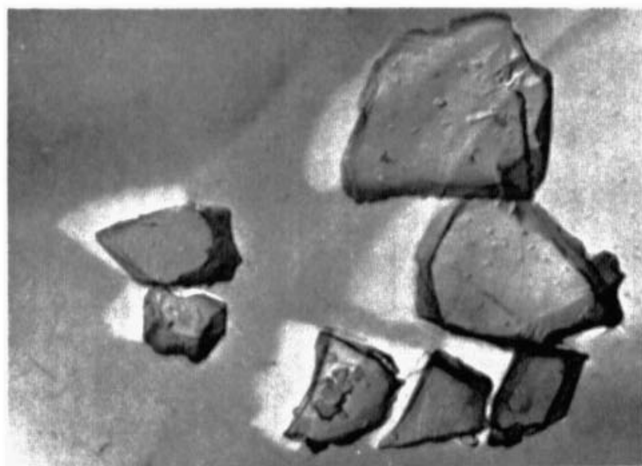


Figure 3. Electron micrograph of some annealed unetched quartz particles.