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INTERGRANULAR PRESSURE SOLUTION IN THE
TUSCARORA ORTHOQUARTZITITE.

The University of Oklahoma, Ph.D., 1975
Geology

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THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

INTERGRANULAR PRESSURE SOLUTION IN THE

TUSCARORA ORTHOQUARTZITITE

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

DUNCAN F. SIBLEY

Norman, Oklahoma

1975

INTERGRANULAR PRESSURE SOLUTION IN THE TUSCARORA
ORTHOQUARTZITE

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Acknowledgements

My sincere thanks to Dr. Harvey Blatt for directing this dissertation and to Dr. Charles Mankin for his generous effort in getting this project off the ground. I appreciate the comments and criticisms of Dr. Howard Day, Ric Jones, Dr. Leon Reiter and Dr. Thomas Vogel. Dr. Robert L. Folk graciously provided many samples for this study.

This work was made possible by the generous aid of Dr. Robert Sippel and Mobil Oil Corporation who provided use of the luminoscope, Union Oil of California Foundation which provided financial support for this project, and Mr. Bowles of Marathon Oil who prepared many of the thin sections.

Most of all I thank my wife, Claire, for her unique personal sacrifice.

ABSTRACT

Intergranular pressure solution is believed by many sandstone petrologists to be the major source of silica for the cementation of orthoquartzites, although there is no quantitative supporting evidence from thin-section petrology. The white Tuscarora orthoquartzite, often cited as a good example of cementation by pressure solution, has been studied using luminescence petrology to evaluate this hypothesis.

Point counts were made to determine the volumetric abundances of pressure solution phenomena and authigenic silica in 185 thin-sections from Pennsylvania, Virginia, and West Virginia. Luminoscope measurements show large amounts of pressure solution to be an uncommon phenomenon in the Tuscarora throughout the study area. It can account for only 30-35 percent of the pore-filling quartz cement.

Proximity to folding, grain size, sorting and caly content are factors that have been suggested as controls on the amount of pressure solution in orthoquartzites. Of these, only clay appears related to the occurrence of pressure solution in the Tuscarora. Furthermore, the well-cemented samples show less pressure solution than more friable samples, but contain more pore-filling cement.

It is concluded that the cementation by silica during diagenesis has prevented widespread development of intergranular pressure solution by equalizing the distribution of stress along grain boundaries. Of the many possible sources of silica other than pressure solution, stylolitization, clay mineral diagenesis and transport of H_4SiO_4 in ground water seem the most likely sources of the majority of the cement found in the Tuscarora.

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Introduction

In orthoquartzites, cementation is a major porosity-reducing process, filling up to forty percent of the rock volume. This quartz cement occurs as optically continuous overgrowths, and therefore, differentiation of authigenic versus detrital components using normal petrographic techniques is difficult and often impossible. This is the major problem in applying petrographic techniques to the study of mechanisms of porosity reduction in orthoquartzites. Because authigenic and detrital quartz have different luminescence characteristics, cathodo-luminescence petrography allows detailed and precise differentiation of these components (Smith and Stenstrom, 1965; Sippel, 1968) and, thus, the processes which result in porosity reduction can be studied in detail.

Many investigators (see Blatt et al., 1972, pp. 359-360 and Pettijohn et al., 1972, pp. 424-426, for recent reviews) have considered intergranular pressure solution to be a major mechanism of porosity reduction in quartz arenites. Consequently, a major target of this investigation has been a quantitative evaluation of the importance of this process. The results of this investigation indicate that intergranular pressure solution is not the major source of authigenic silica in the rocks studied and, therefore, other possible sources of silica are discussed. Other sources of authigenic silica which may be viable are the diagenetic alteration of smectite - illite + quartz, stylolitization and the precipitation of quartz overgrowths from ground water.

The Tuscarora orthoquartzite (Silurian) was chosen for this study because it has many characteristics which make it amenable to the study of porosity reduction in orthoquartzites and especially the role

pressure solution may play in this process. Outcrops of the Tuscarora are easily accessible for detailed sampling over a large area and because the outcrops occur in a folded region, samples may be collected from structurally different positions. The stratigraphy of the Tuscarora has been worked out in considerable detail (Butts, 1940; Woodward, 1941) and an excellent description of the petrography is provided by Folk (1960). Most important in the choice of the Tuscarora was the fact that Tuscarora has been cited as showing extensive evidence of pressure solution (Folk, 1960) as well as some of the other mechanisms that are thought to be significant in changing porosity in ortho-quartzites.

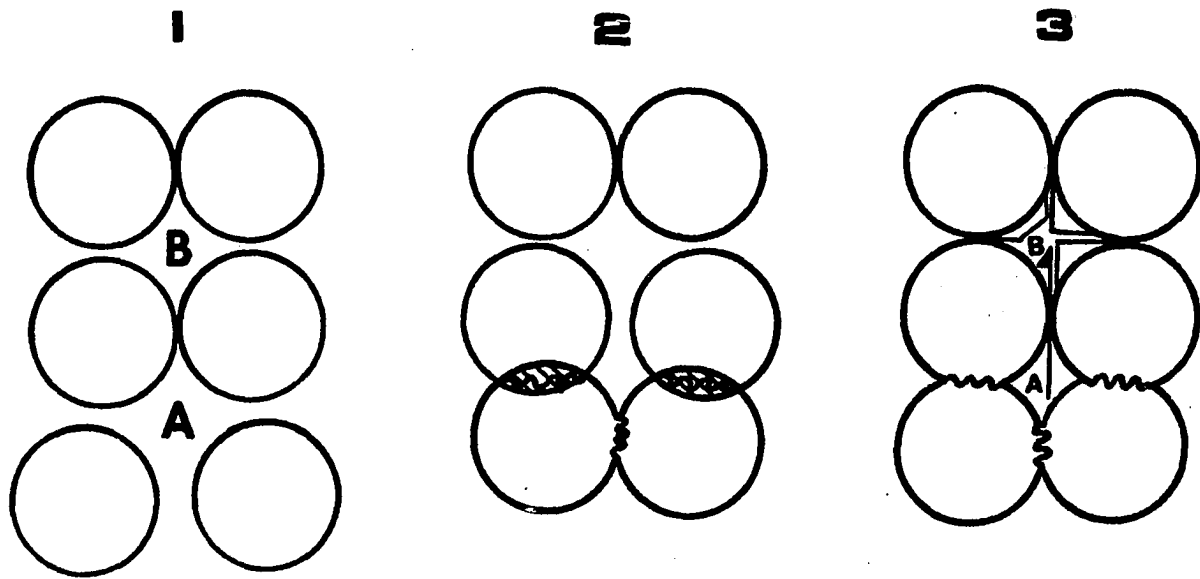
Methods

Samples of the Tuscarora were collected from twenty outcrops in the Valley and Ridge Province of the Appalachians in Pennsylvania, Virginia and W. Virginia. Four samples were taken from cores of the Tuscarora in the Plateau province of West Virginia. The sample locations and the number of samples collected at each location are shown in Figure 1. Four locations were chosen for detailed sampling to allow comparisons between outcrops. At two locations, Baker, West Virginia and North Fork Gap, West Virginia, samples from both limbs of anticlines were collected so that comparison between samples from different structural positions could be made. Most of the thirty-five samples from Mills Gap, West Virginia were collected by R.L. Folk. At the other three locations where more than thirty samples were collected, sampling was at evenly spaced intervals along a line normal to bedding. Twenty-eight additional samples of twenty other orthoquartzites were collected either from the author's own collections or other university collections. In total, two hundred and ninety-six samples were collected and examined petrographically.

The samples were examined with a luminoscope described by Sippel (1965, 1968). Luminescence petrography permits one to see many features which are otherwise invisible in many orthoquartzites (see Figures 5-12). It also permits quantitative determination of the amount of pressure solution in a thin section. Intergranular pressure solution is identified petrographically as an area of interpenetrating detrital cores, therefore, "pressure solution" can be considered a component for modal analysis and treated in the

same fashion as any other component (See Figure 2). The method has some limitation in that it demands a subjective reconstruction of original grain shapes in order that a point be ascribed to an area of interpenetrating detrital cores. However, most detrital grains in orthoquartzites are well rounded and therefore, reconstruction of original grain shapes is relatively straightforward. The modal analysis was performed by counting two hundred points on a thin section. Because some of the specimens examined showed several alternating bands of intense and minimal pressure solution, precautions were taken to avoid unacceptable bias in the data due to the banding. The banding always appeared parallel to bedding; therefore, thin sections were cut normal to bedding to insure that the slide was representative of the rock specimen. Also, since the areas of most intense pressure solution showed maximum grain shortening parallel to bedding, sections cut normal to bedding should expose the true amount of pressure solution. The point counts were made along an orthogonal grid laid at 25° to bedding. The angle of inclination was dictated by the construction of the luminescope stage. As shown by Chayes (1956, Figure 8, p. 26), as long as the angle of inclination between the banding and the grid is greater than 20° , there can be, at most, approximately 2 percent analytical error associated with the measurement. For a large number of samples this error should be averaged out and thus, the fact that there is some banding in the rocks sampled should not cause the data from the point counts to be biased.

Each point encountered on the grid was recorded as detrital quartz, authigenic quartz, an area of pressure solution (see Figure 2), clay, pore space or other. Points falling on fracture zones were not counted. The primary reason for making the point counts was to determine the



Sequence of stages in the development of sand grains cemented by pressure solution. In stage 1 the sand has not yet been compacted. In stage 2 pressure solution has begun, decreasing the volume of pore space A. In stage 3 some fluid from A escapes to B, reduces pressure and precipitates quartz. The shaded area in 2 shows areas which would be considered pressure solution points in a modal analysis. (Modified from Siever, 1962.)

Figure 2

relative proportions of pressure solution and authigenic silica, for if local pressure solution is the major source of authigenic silica the relative proportions of the two should be about equal in the modal analysis. Grain size of the samples was determined by measuring the long diameter of thirty grains for each sample and sorting was determined by visual comparison with Figure 12-1 in Compton (1962).

Initial Porosity

Before the processes of porosity reduction can be properly evaluated, it is necessary to make some assumptions about the initial porosity of the Tuscarora. Gratton and Fraser (1935) examined the possible geometric packing arrays for spheres and found that the porosity could range from 26 percent for rhombohedral packing to 48 percent for cubic. There is no evidence that natural sands are packed in geometric arrays (Kahn, 1956) and, therefore, most work on packing has been through the less direct approach of measuring porosity. There are a large amount of data which suggest that prior to lithification a well sorted, slightly compacted, medium sand size sediment such as the Tuscarora will have a porosity of 40 ± 3 percent (King, 1898, Tickel and Hiatt, 1938, Gratton and Fraser, 1935; Gaither, 1953 and Beard and Weyl, 1973).

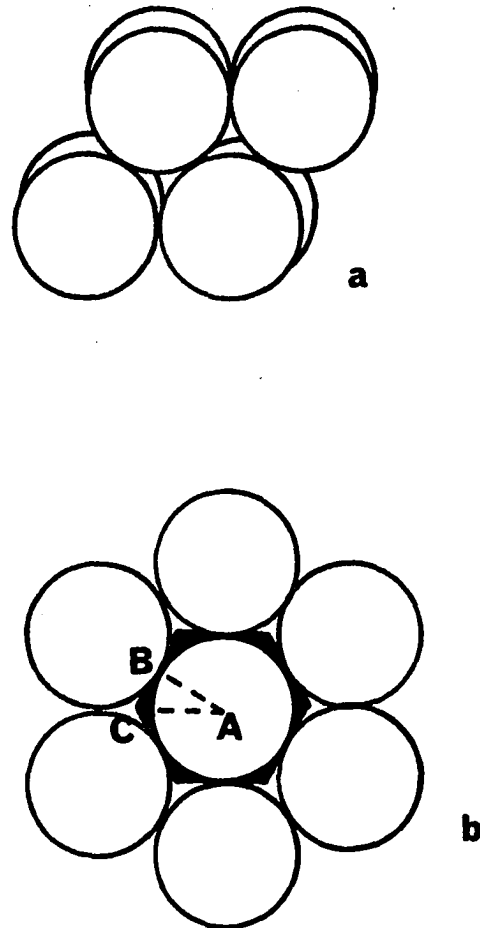
Mechanisms of Porosity Reduction

There are four major processes, not necessarily mutually exclusive, which may alter the depositional porosity of a pure quartz sand; 1) compaction, 2) fracturing which may allow grains to rotate to a closer packing, 3) solution and 4) cementation. Intergranular pressure solution involves both a reduction in porosity due to solution and repacking and a reduction in porosity due to precipitation of the silica derived from the dissolved grains. Therefore, pressure solution is just a special case of dissolution and precipitation but it is given particular attention here due to its suspected importance.

The most extensive tests on the compaction and fracturing of unconsolidated quartz sand (Borg, et al., 1960) showed that in

simple compression tests, porosity may be reduced from 38.3 to 33.6 percent with a maximum confining pressure of 500 bars on a dry sediment with a grain size of .2 to 3 millimeters. Only 23 percent of the sand grains remained unbroken after the test. A similar sediment underwent triaxial compression with a confining pressure of 1,000 bars and a strain of 9.9 percent which resulted in a porosity change from 37.4 percent to 24.2 percent with only 8 percent of the grains remaining unbroken. Maxwell (1960) performed compaction tests on sands under conditions simulating burial between 16,000 and 35,000 feet and compaction of the sediment occurred primarily by fracturing. Maxwell (1964) presented data showing linear decreases in porosity with depth for a large number of quartz sands and implied that much of the porosity reduction was due to fracturing.

Because intergranular pressure solution is a process which involves both dissolution and cementation, pressure solution reduces porosity in two ways. As grains dissolve, points of contacts become planes of contact and the grains become more closely packed. This causes a "mechanical" reduction in porosity. The effects of mechanical reduction in porosity due to pressure solution have received very little attention, with the notable exception of Rittenhouse (1971) and Manus and Coogan (1974). They determined the effects of pressure solution on porosity by reference to simple geometric models. The use of geometric models to represent porosity and permeability in sands has been treated in great detail by Gratton and Fraser (1935). They considered four basic packing schemes which may be derived from the stable arrangement of four spheres in square and rhombic layers. An orthorhombic array of spheres may be constructed by vertically

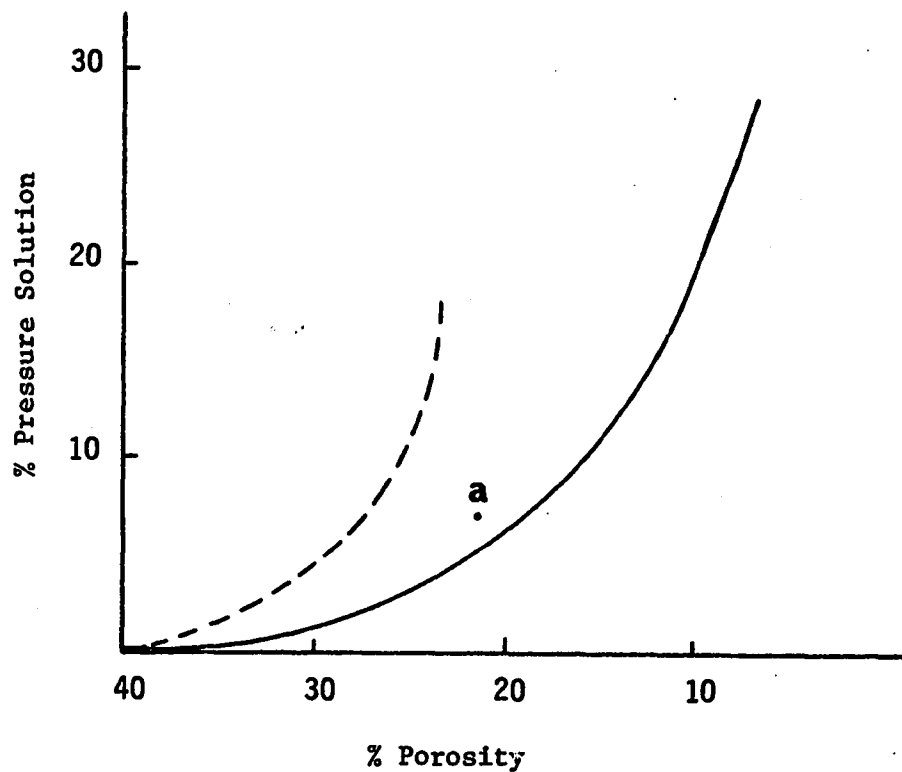


Spheres in orthorhombic packing (a) and associate pore space (b) where each sphere is in contact with eight other spheres. The triangle ABC is referred to in the appendix.

Figure 3

stacking rhombic layers or by stacking square layers off set 60 degrees (see Figure 3a). In such an arrangement each sphere will be in contact with eight others (see Figure 3b) and the array will have a porosity of 39.5 percent. There are no data which show packing of natural sands is non-random and therefore models based on a regular arrangement of particles must be viewed with caution. However, for lack of a better approach the author will follow the lead of Rittenhouse (1971) and Manus and Coogan (1974) who felt an orthorhombic packing best represents the natural situation. There are two reasons for favoring this scheme. First, it results in a porosity of 39.5 percent which is within the 40 ± 3 percent range expected for slightly compacted, well sorted, well rounded, medium sand size sediment. Secondly, a study of randomly packed lead spheres showed that at atmospheric pressure there were approximately 7.5 contacts per sphere (Marvin, 1939). The orthorhombic packing causes eight contacts per sphere. Rittenhouse investigated shapes other than perfect spheres and with various degrees of sorting and found that no type of packing and no variations in grain sphericity, roundness, or sorting lead to higher pressure solution-to-porosity loss ratios than found for equal sized spheres in orthorhombic packing. Therefore, the orthorhombic packing model is a good approximation for maximum pressure solution-to-porosity ratios.

Figure 4 shows two curves illustrating the relationship between porosity and volume percent of the grains dissolved, assuming none of the dissolved material precipitates as cement. The dashed curve in Figure 4 is from Rittenhouse (1971) and represents his approximation of the maximum percent pressure solution for a given remaining porosity



Curves show the relationship between maximum percent pressure solution and porosity for orthorhombic packed spheres. The curve represented by a dashed line is from Rittenhouse (1971) and is based on the assumption of all strain being in the verticle plane. The solid curve is based on the assumption that strain is equal in all directions. Point (a) is the mean pressure solution and porosity for all Tuscarora samples.

Figure 4

based on an initial orthorhombic packing and assuming all strain is verticle. The solid curve is based on the same assumptions as Rittenhouses curve except strain is assumed to be equal in all directions. [The method for calculating this curve is shown in Appendix 1 and is essentially the same as that used by Rittenhouse.] Neither all verticle nor homogeous strain is valid for natural sands and so a better estimate might be a curve falling somewhere between the two shown in Figure 4. Also, because true sands are not composed of uniformly sized perfect spheres the curve for a true sand should lie to the right of the curves in Figure 4. That is, the pressure solution to porosity ratio should be somewhat less than depicted in the diagram.

The curves shown in Figure 4 may be used as follows. If one determines that a sandstone is composed of 75 percent detrital grains and 25 percent authigenic cement then the "minus-cement-porosity" is 25 percent. By reference to my curve one can determine the maximum amount of dissolution at grain contacts which might have occurred. In this instance a "minus-cement-porosity" of 25 percent indicates a maximum of 3.2 percent by volume of the grains has been dissolved. If we assume that all of the material dissolved reprecipitated as cement then $\frac{3.2}{25}$ or approximately 13 percent of the cement found in the rock may have been derived from pressure solution at grain to grain contacts.

Precipitation of quartz cement without prior intergranular pressure solution may also be an important process in porosity reduction in orthoquartzites. The problem with understanding this mechanism has been finding the source of the authigenic silica. Diagenesis of clay minerals, dissolution of biogenic silica and desilication of volcanic debris are some of the more commonly proposed sources.

Petrographic Observations

Overgrowths - One of the major advantages of luminescence petrography is that it often allows reliable distinction between detrital grains and overgrowths in orthoquartzites. In almost every thin section of the Tuscarora some overgrowths are distinguishable by careful searching for the dust ring or cloudy center-clear rim criterion. Dust rings are most commonly formed from gas or fluid inclusions and they mark the boundary between the authigenic and detrital parts of a grain. Fluid inclusions may be abundant within detrital grains either due to fracturing or prevailing conditions at the time of crystallization where as authigenic overgrowths will generally have fewer inclusions. This results from the fact that they have not been subjected to postdepositional fracturing and because crystals which form at lower temperatures have fewer inclusions than the same mineral formed at higher temperatures because the latter grow slower (Chernov and Khadzi, 1968). Thus, in a grain with an inclusion-ridden (cloudy) center and a clear rim the cloudy center is inferred to be detrital and the clear rim is authigenic. Figures 5A & B show two photomicrographs of quartz grains from the Tuscarora. In 5A a quartz grain with a dust ring and cloudy center is shown. Figure 5B illustrates that within the dust ring the quartz luminesces but outside of the dust ring the quartz is non-luminescing. In all of the instances where the dust ring or cloudy center-clear rim criterion can be applied to Tuscarora samples, the authigenic quartz luminesces dull red or is non-luminescing and the detrital quartz luminesces either red or blue. In the Tuscarora, the contrast between the luminescence of the detrital grains and authigenic overgrowths is sufficient to allow the distinction

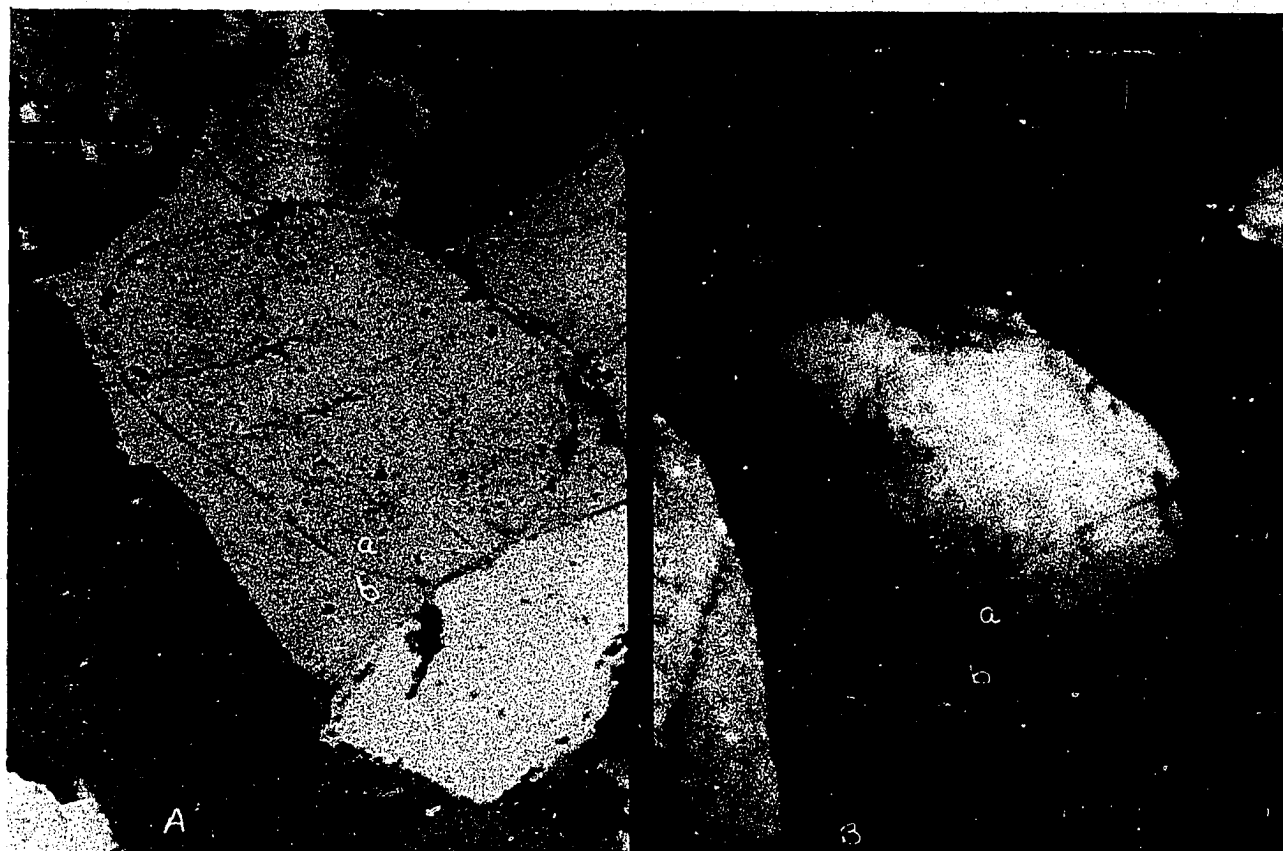


Figure 5 (A) Photomicrograph in plane polarized light with the grain in the center showing an obvious "dust ring" which allows one to distinguish the detrital core (a) from the authigenic overgrowth (b). (B) The same field of view using the luminoscope. With the luminoscope the detrital grains luminesce red (dark) or blue (light) (a) while authigenic overgrowths (b) and fracture fillings do not luminesce at all (black areas). Scale bar = .1 mm.

between authigenic and detrital quartz. The degree of difference in luminescence between detrital and authigenic quartz is variable and this variation is greatest between outcrops. For instance, overgrowths in samples from Baker, W. Virginia tend to be almost totally non-luminescing on initial irradiation but become almost as red as the red luminescing detrital grains after approximately ten minutes of irradiation. Overgrowths on samples from North Fork Gap, W. Virginia (approximately 90 miles to the east) luminesce a very dull red on initial irradiation but do not increase in luminosity with prolonged exposure.

Multicycle overgrowth - the presence of detrital secondary quartz (non-luminescing) could conceivably represent a major source of error in this study since this would invalidate the luminescence criterion for distinguishing authigenic from detrital quartz. There are several lines of evidence indicating that the amount of detrital non-luminescing quartz is insignificant.

The most direct evidence was obtained by point counting five samples of the lower Tuscarora in which the predominant cement is relatively impermeable clay and/or iron oxide. In these samples less than 2 percent of the quartz is non-luminescing and all of this non-luminescing quartz is attached to luminescing grains. Therefore, this quartz may be in situ cement or cement which has not been abraded off grains from a previous cycle. Since this quartz is not necessarily from a previous cycle it represents a maximum percentage of detrital, non-luminescing quartz.

A less direct line of evidence stems from inspection of the data for all samples. If we assume that the total of the percent non-luminescing quartz plus present pore space equals the initial porosity then we find that none of the samples have an initial

porosity greater than about 40 percent, a reasonable figure for the Tuscarora. If there was a large amount of detrital, non-luminescing quartz, then it would be likely that some samples would show anomalously high minus-cement porosities. The fact that none of the samples have anomalously high values argues against significant amounts of detrital non-luminescing quartz.

Pressure Solution - In the early 1860's, Sorby noted the interpenetration of detrital polycrystalline grains in clastic carbonate rocks and inferred that the interpenetration was the result of solution of those grains at points of contact. Unfortunately, in quartz sandstones, cement forms optically continuous overgrowths because nearly all grains are monocrystalline. This makes it very difficult to distinguish cement from detrital grains and, therefore, it is very difficult if not impossible to reliably determine whether or not detrital grains are interpenetrating. In view of the inability to distinguish detrital grains, many investigators have looked for sutured boundaries as evidence of pressure solution. However, Sipple (1968) showed that this criterion may not always be reliable.

With the luminescope, unambiguous recognition of intergranular pressure solution can be based on interpenetrating detrital grains because, as pointed out above, the detrital and authigenic quartz can be differentiated on the basis of their luminescence. Figure 6 illustrates the advantage of the luminescope for recognizing pressure solution. Figure 6A is a photomicrograph of a thin section of the Tuscarora in plane polarized light. The grain in the center

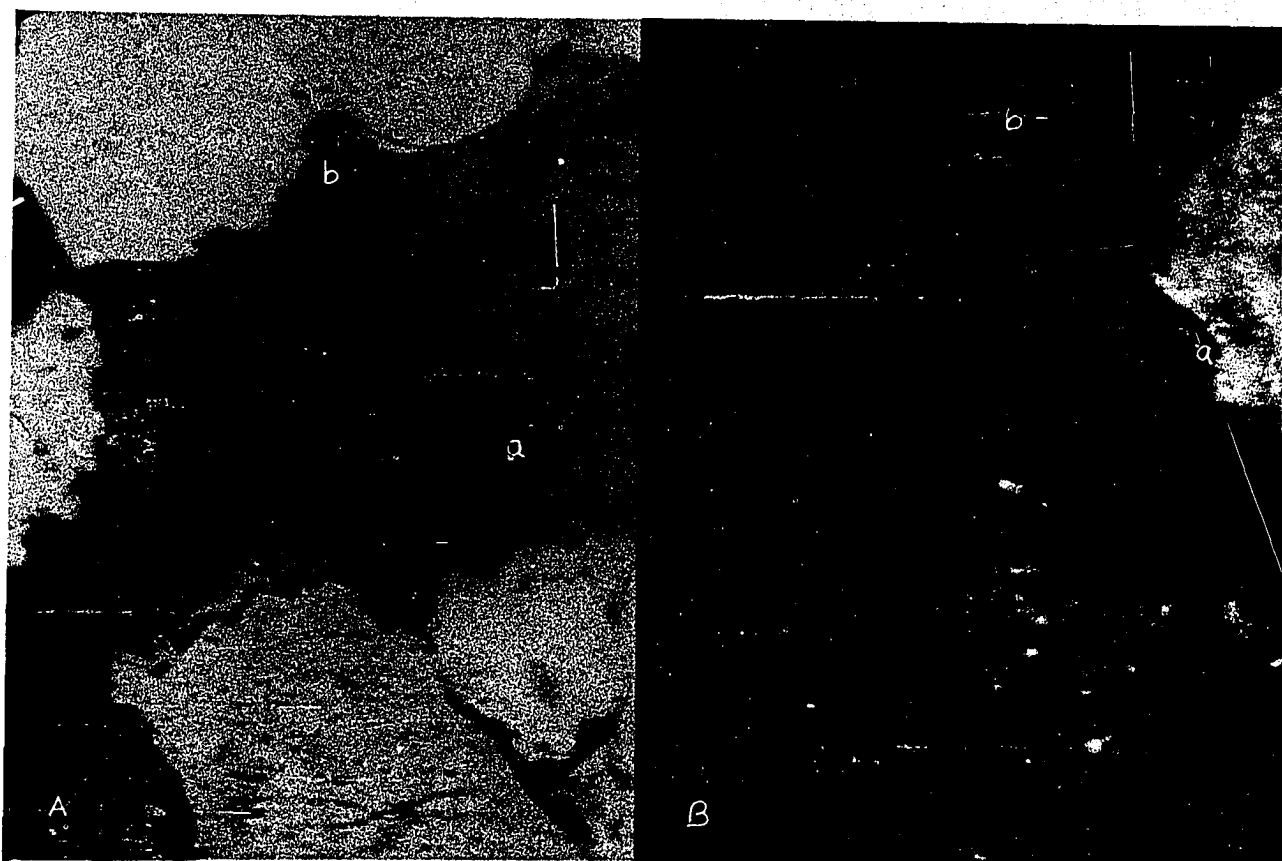


Figure 6 (A) Photomicrograph taken in plane polarized light with the grain in the center having both smooth (a) and irregular (b) contacts with the surrounding grains. (B) With the luminoscope, it can be seen that the smooth boundary between the central grain and that in the upper right portion of the photomicrograph is an area of probable interpenetration of detrital cores. Scale bar = .1 mm.

joins most of the surrounding grains with a sutured contact which might be assumed to have resulted from intergranular pressure solution. The boundary between the central grain and the grain in the upper right of the photograph is smooth. Figure 6B is the same area viewed with the lumnoscope. Because of the differential luminescence of the detrital and authigenic quartz, it is clear that the only area of interpenetrating detrital quartz is that marked by the smooth boundary. The sutured contacts appear to be the result of intergrown quartz overgrowths. Figure 7 shows an area of a photomicrograph which is typical of most samples of the Tuscarora. Without the lumnoscope, it is impossible to determine how much, if any, pressure solution has occurred. With the lumnoscope, it is obvious that most grains are "floating" in cement and therefore, very little pressure solution has occurred. Figure 8A is very similar in appearance to Figure 7A. Therefore, when viewed in plane polarized light (8A), one might conclude that there has not been any pressure solution in this area. When the same area is viewed with the lumnoscope (8B), however, it is apparent that the smooth boundaries are interpenetrating and therefore, there has been pressure solution in this area. Figure 9 shows a portion of a thin section with several important features. The grain in the center of Figure 9A has a sutured boundary and the grain in the upper left appears to be a polycrystalline quartz grain. These relationships are clarified by viewing the same area with the lumnoscope (9B). The sutured contact is shown to be another overgrowth phenomenon and the polycrystalline quartz grain



Figure 7 (A) Photomicrograph taken in plane polarized light and representing an area which is indicative of the Tuscarora. With the luminoscope (B) it is obvious that most of the grains are "floating" in cement and thus, this is not an area of pressure solution. Also, notice the fractures which are filled with non-luminescing quartz. These fractures are obvious only when the section is viewed with the luminoscope. Scale bar = .2 mm.

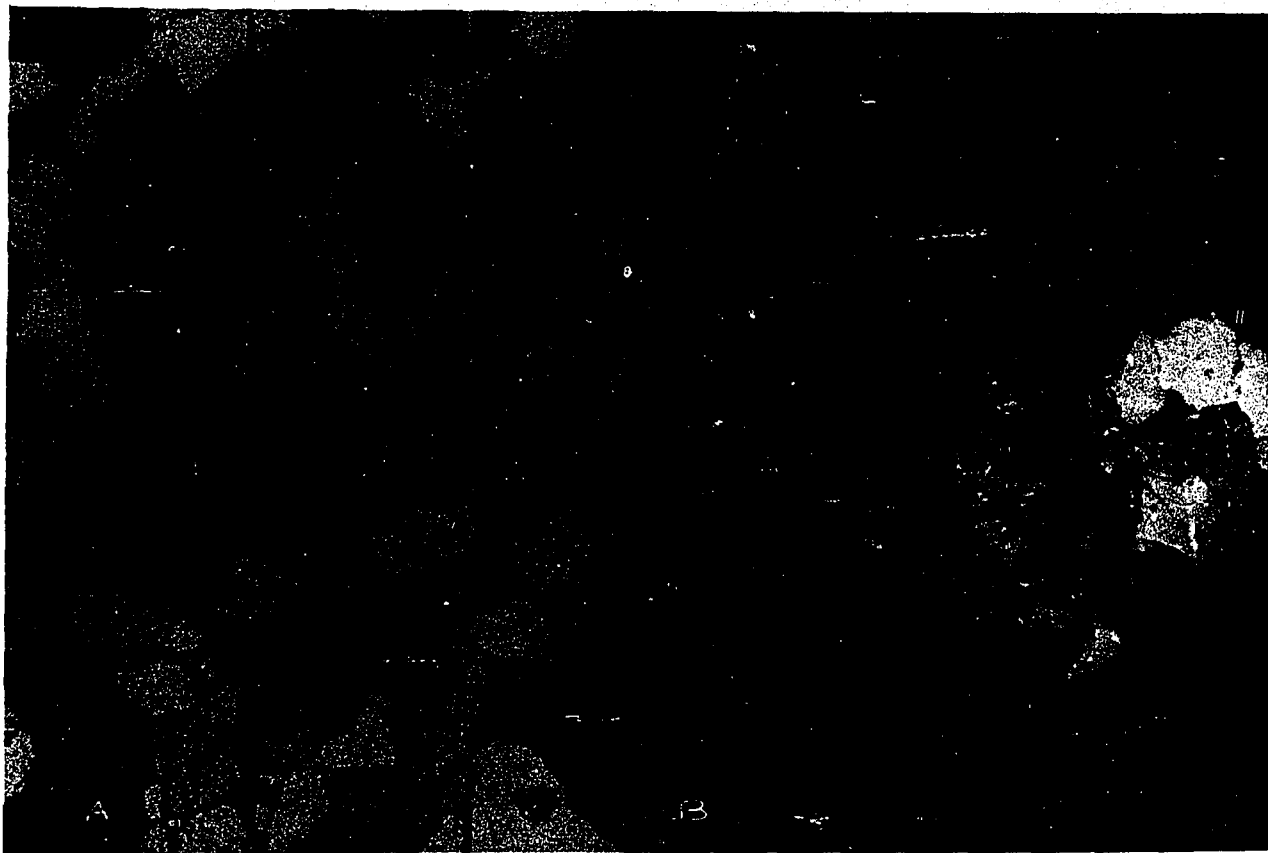


Figure 8 (A) In the plane polarized light this area looks similar to Figure 7 (A). (B) With the luminoscope it is obvious, however, that this is an area of intense pressure solution. Scale bar = .2 mm.

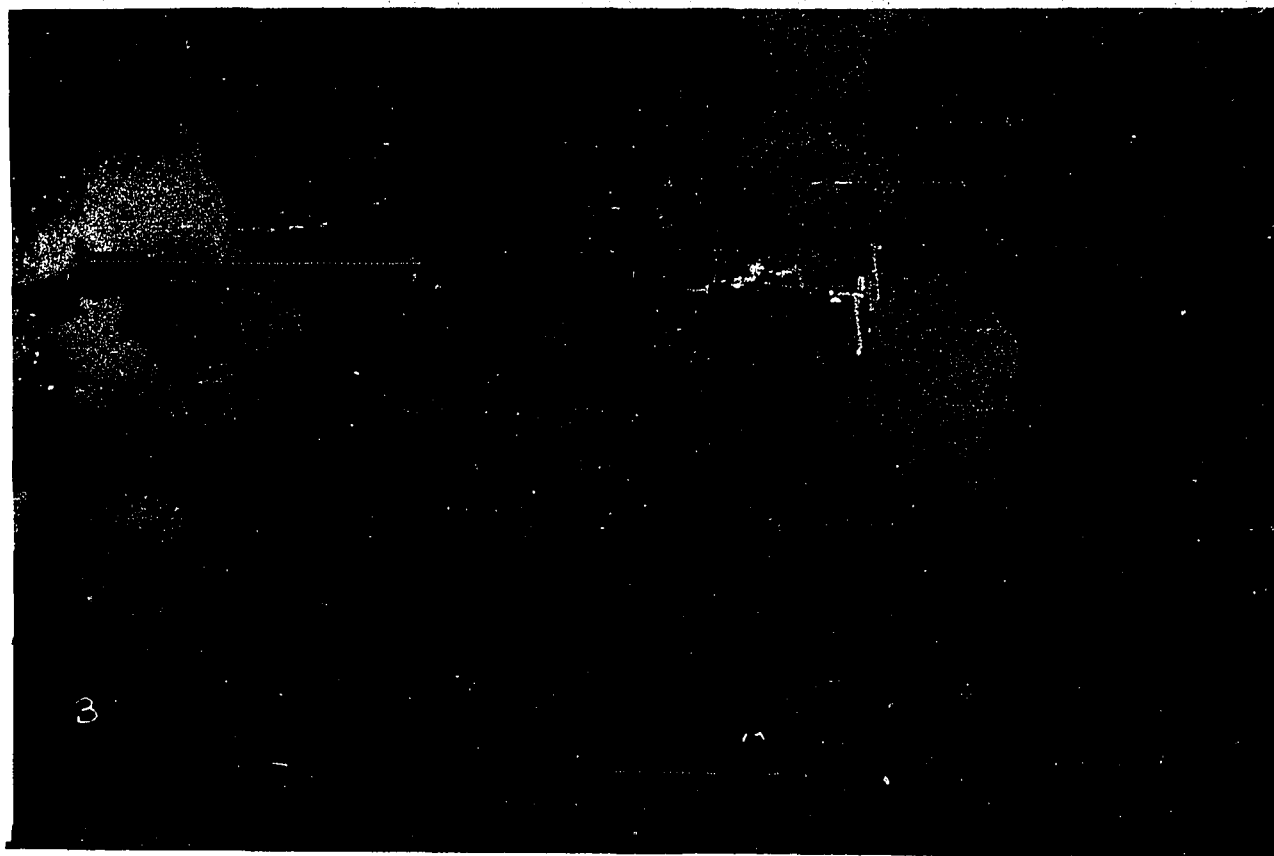


Figure 9 (A) Plane polarized light view showing a number of unusual features. In the center is what appears to be a sutured contact and in the upper left is a polycrystalline quartz grain. The same area viewed with the luminoscope (B) indicates that the sutured boundary is the result of cementation not pressure solution and the polycrystalline quartz grain appears to be one grain which has been subjected to considerable fracturing. Scale bar = .2 mm.

is the result of fracturing of a single monocrystalline grain and subsequent healing with authigenic quartz. Finally, Figure 10 shows a plane polarized light view and a lumnoscope view of the same area of a thin section in which sutured boundaries do indicate an area of intense pressure solution. The lumnoscope view demonstrates that the grains along the sutured boundaries are detrital and therefore, this is an example of interpenetrating detrital cores.

The preceding observations demonstrate that pressure solution boundaries may be either smooth or sutured. Smooth pressure solution boundaries are commonly observed between some grains in all samples and these grains appear to be scattered throughout the specimen with no apparent pattern. Reconstruction of the probable original grain shapes indicates that only one of the two grains in contact has been dissolved. Sutured pressure solution boundaries between grains usually occur concentrated in zones. These zones are quite distinct in some samples, particularly those from Susquehanna Gap where there are zones of intense pressure solution one to four millimeters wide and parallel to bedding. The top of the zone may be marked by a stylolitic-like surface while the bottom of the zone grades into a region of minimal pressure solution. This zonation is particularly obvious in uncrossed nichols because the zone of high pressure solution frequently contain a few percent clay and no authigenic overgrowths while the adjacent zones are well cemented by authigenic silica and contain very little clay. This zonation of pressure solution is shown in Figure 11, a sample from Susquehanna Gap. In 11B the area of minimal pressure solution is easily recognized due to the fact most of the luminescing grains appear to be floating in authigenic silica.

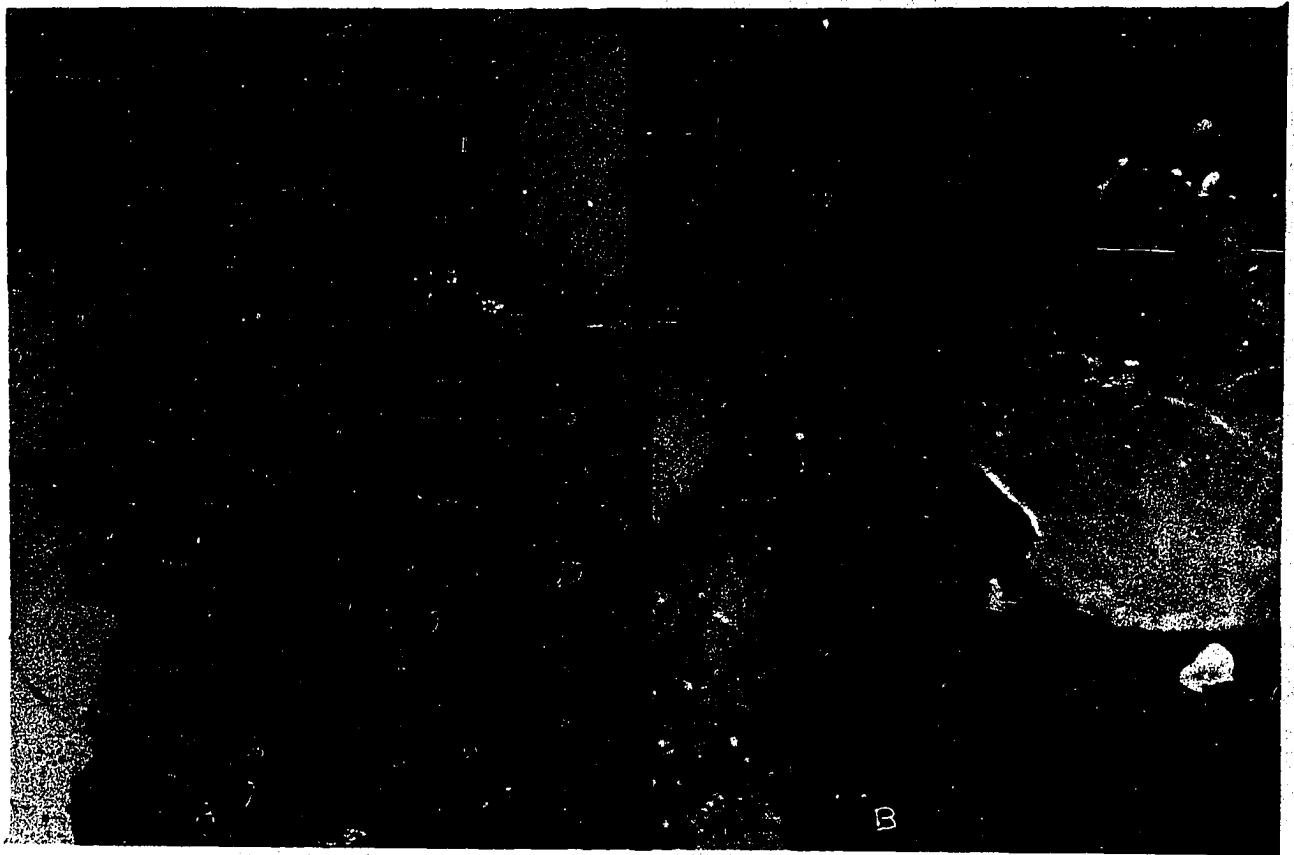


Figure 10 (A) and (B) Plane polarized light and luminescence view of an area where intense pressure solution has resulted in strikingly sutured boundaries. Scale bar = .1 mm.

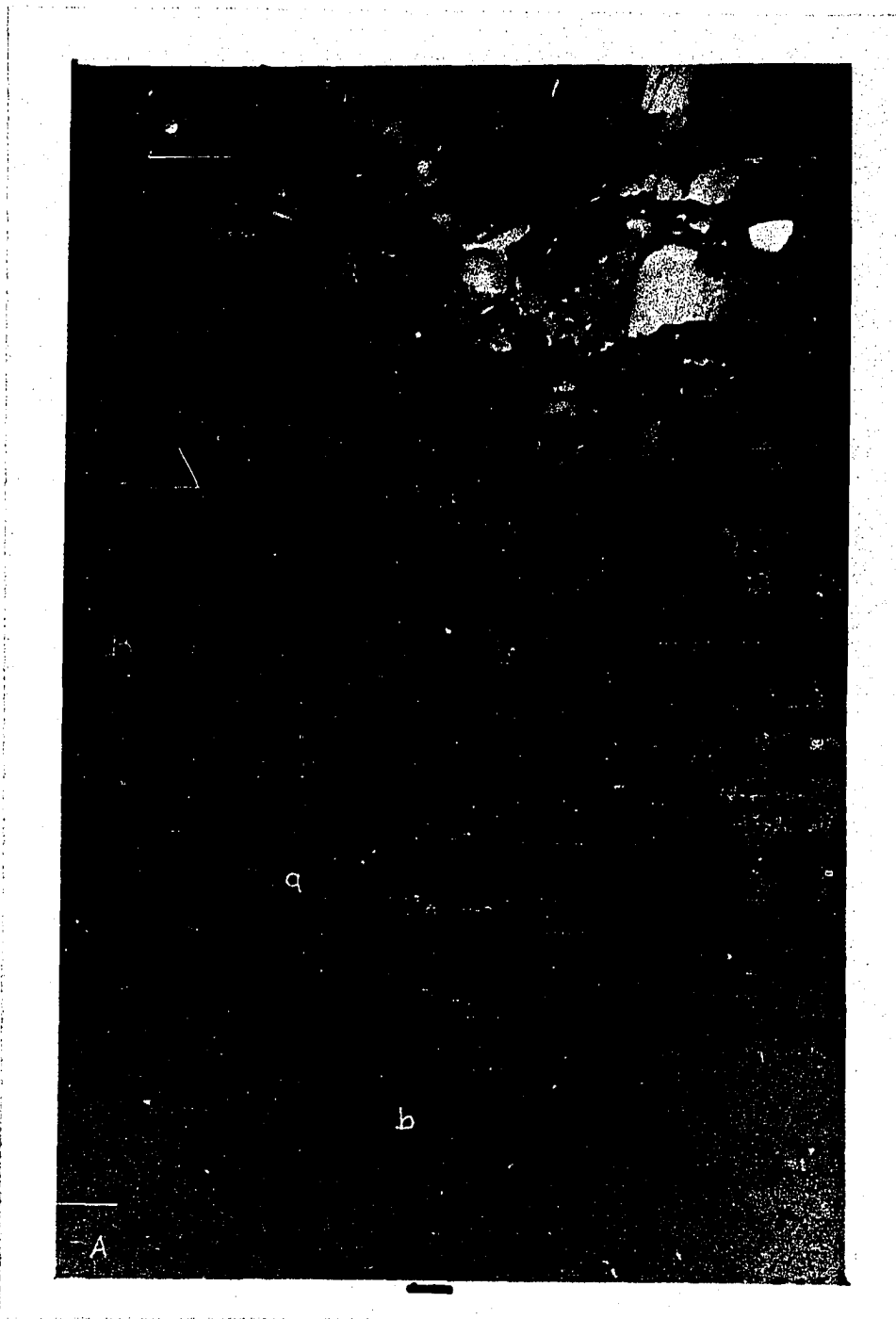


Figure 11 (A) Plane light view of an area showing the effects of differential cementation. (B) With the luminoscope, the area with little cement and intense pressure solution (a) is easily distinguished from those areas above and below it which show grains surrounded by cement (b). Notice also, the extension fractures (dark lines) which are very obvious with the luminoscope. Scale bar = .2 mm.

In the area of intense pressure solution, luminescing grains are more tightly packed and the dark material separating the grains is predominantly illite.

Approximately thirteen percent of the samples show a zonation between areas of high pressure solution but the zonation usually is not as distinct as that shown in some of the samples from Susquehanna Gap. It is more common to find vaguely defined zones in which there is very little authigenic silica and considerable amounts (>10%) of intergranular pressure solution. These zones may be anywhere between a few millimeters to more than 2.5 cm (the width of a thin section) in width. Frequently, there are clay flakes between grains having undergone pressure solution. There are also striking examples of intense pressure solution with no associated clay. Pressure solution boundaries may be smooth or sutured in these zones with one of the two types being the dominant for any given zone. The one common feature to all zones of intense pressure solution is the distinct lack of authigenic silica, even though there frequently is a remaining intergranular porosity within the zones.

Fracturing - Most in situ fractures in quartz sandstones are healed and can sometimes be recognized by the presence of bubble trains which are fluid inclusions trapped in the fractures when they are healed by secondary quartz. However, in many instances bubble trains do not form and in these cases there is no petrographic evidence of the fracturing. These fractures may be made visible with the luminoscope because the authigenic silica which fills the fracture does not luminesce although the detrital fractured grains luminesce red or blue.

Both pre- and post-cementation fractures are apparent when thin sections are viewed with the luminoscope. Pre-cementation fracturing is evidenced by fractures in single grains that are filled with non-luminescing quartz. These fractures were formed in situ as demonstrated by the fact that the fractures often nucleate at points of contact. The fracturing is not common and they apparently healed rapidly because the fractured grains are always in tact. Therefore, it is doubtful that the fracturing significantly effected the porosity of the sand. The fracturing indicates the cementation process was not completed until the sediment was deeply buried and/or subjected to tectonic overpressures. Post-cementation fractures cross cut many grains and may be filled with non-luminescing quartz (Figure 11b) or may be marked by areas of intense granulation and polygonization with little or no non-luminescing quartz.

Point Count Data

Of two hundred and sixty-four samples of Tuscarora collected, one hundred and eighty-five were chosen for point counting. These include one hundred and forty-nine samples from four outcrops and thirty-six spot samples from sixteen outcrops. The spot samples were a part of an initial sample group which was used to determine what type of regional variation might be present. Samples which are not included in the point count data are those from either (a) the four outcrops which were later sampled systematically; (b) from highly fractured zones; (c) from rocks too fine grained to allow reproducible analysis with the luminoscope; or (d) matrix cemented. The results of the point count are summarized in Table 1. The most important information in the table is the percent authigenic quartz and pressure solution. The percent pressure solution is simply the volume percent of luminescing quartz that appears to be interpenetrating with other luminescing quartz. The mean percent of pressure solution for all samples is 7 percent. The amount of authigenic silica which may have been derived from pressure solution is equal to the percent pressure solution. Therefore, of the 21 percent authigenic quartz, only 7 percent or one-third might have been derived from intergranular pressure solution and two-thirds must have been derived from some other source.

Table 2 gives the correlation coefficients between the amount of pressure solution and the other variables counted. The strongest correlation is a negative correlation between pressure solution and authigenic quartz. The correlation coefficients between clay, size, and sorting for all samples are .19, .12, and .20 respectively.

	Detrital Quartz	Authigenic Quartz	Clay	Pore	Other	Size (mm)	Sorting	Pressure Solution	
All Samples	74	21	2	2	1	.3	2	7	n = 185
Susquehanna Gap	74	20	4	1	1	.4	2	8	n = 25
Mills Gap	75	20	2	2	1	.4	2	8	n = 26
North Fork Gap	75	21	1	3	0	.3	1	7	n = 36
Baker	74	23	1	2	0	.3	2	6	n = 62

Table 1

Mean values from point count data for 185 Tuscarora Samples

Sorting was calculated by 1 = very well sorted, 2 = well sorted, 3 = moderately

	Detrital Quartz	Authigenic Quartz	Clay	Size	Sorting
All Samples	.48	-.69	.19	.12	.20
Susquehanna Gap	.73	-.79	.05	-.14	.21
Mills Gap	.46	-.82	.25	.22	.14
North Fork Gap	.38	-.60	.18	.21	.38
Baker	.49	-.66	.20	.02	.19

Table 2

Simple correlation coefficients between variables in Table 1 and pressure solution.

These data do not suggest any relationship between these three variables and pressure solution.

In a number of studies on pressure solution, it has been suggested that a small amount of clay along grain boundaries may tend to enhance pressure solution (Thomson, 1959; Weyl, 1959; Heald, 1965; Elliott, 1973). Therefore, I felt that a more definitive test of the relationship between clay and pressure solution was necessary. The point count data for the samples are based on two hundred points per sample and thus, are not sensitive enough to detect a small variation in a minor component. Therefore, to better test the relationship between clay and pressure solution, forty samples, twenty with at least ten percent pressure solution and twenty with four percent or less pressure solution, were recounted by counting one thousand points. The group of samples with high percentages of pressure solution were chosen at random from all samples having at least ten percent pressure solution. For each of these samples a counterpart showing a small percentage of pressure solution was chosen by finding the stratigraphically closest sample with four percent or less pressure solution. The limits of four and ten percent were chosen arbitrarily. The clay content of the group with a high percentage of pressure solution varies from 16.7 to .2 percent with a mean of 4.2 percent and the range for the group with minimal pressure solution is 7.2 to 0 percent with a mean of 1.7 percent (see Table 3). By t-test, these means are significantly different at the .05 probability level.

The point count data fail to demonstrate any relationship between pressure solution and structural position. Many of the anticlines sampled are asymmetric and samples were collected from

Sample	A	
	% Pressure Solution	% Clay
5B	3	.2
30B	0	1.2
42B	2	0
44B	2	0
67B	2	1.0
3SG	2	3.5
11SG	4	3.5
13SG	4	6.5
21SG	2	3.6
27SG	3	.5
4NG	4	.4
6NG	2	.7
20NG	2	0
34NG	1	0
43NG	0	0
45NG	3	0
48NG	2	0
20MG	3	4.8
27MG	4	7.2
32MG	2	1.1

$$\bar{X} = 2.4 \quad \bar{X} = 1.7$$

Sample	B	
	% Pressure Solution	% Clay
6B	10	1.4
31B	15	5.2
40B	22	3.6
46B	12	3.5
65B	21	.2
2SG	13	10.2
15SG	16	15.4
17SG	22	2.0
26SG	13	.2
28SG	12	4.8
1NG	20	6.1
2NG	12	.9
9NG	14	1.0
21NG	21	6.0
24NG	12	.8
46NG	29	.3
47NG	20	.3
22MG	12	2.7
28MG	30	2.2
33MG	18	16.7

$$\bar{X} = 17.2 \quad \bar{X} = 4.2$$

Table 3

Percent clay for groups of samples with $< 4\%$ pressure solution (A) and $> 10\%$ pressure solution (B).

both limbs of the anticlines. There is no difference between the amounts of pressure solution in samples from the near-vertical limbs of the anticlines and those from the more gently dipping limbs (25-40°).

Table 4 shows the results of point counts of orthoquartzites other than the Tuscarora and means from the Tuscarora. It is significant that the data are consistent with that for the Tuscarora and do not indicate the Tuscarora contains unusually low amounts of pressure solution.

Some samples have distinctive zones of intense pressure solution. This observation raises the question of whether or not the samples examined can be considered to be a random sample of the outcrops from which they were collected. That is, did the sampling scheme used result in an over or under representation of the amount of pressure solution in the parent population. An over representation would occur if the distance between successive zones of intense pressure solution coincided with the sampling interval and the first sample collected was taken from a zone of intense pressure solution. In fact any regular interval between zones of intense pressure solution could result in bias in the data by causing either an over or under representation of samples with large amounts of pressure solution. A test for this possibility is the Runs test for randomness. This test does not demand any prior knowledge of the distribution of a variable in the parent population. It simply examines the order of occurrence of events and asks, what is the probability of a given order being the result of chance. Twenty-five samples were collected at Susquehanna Gap. If the samples, one

through twelve had high amounts pressure solution and samples thirteen through twenty-five had low amounts of pressure solution, one would immediately suspect a non-random sample. Also, if every other sample had high percentages of pressure solution, the chances are that the sample is non-random. The Runs test enables one to quantify the probability of a given distribution being due to chance.

To use the Runs test, the observations must be in two classes. A sample which consists of measurements or percentile data can be divided into two classes by splitting the measurements into those above and below the median. Having the observations in two classes and knowing the order in which the samples were collected, one can test for the amount of clustering of observations of a similar kind (i.e., the percent pressure solution above the median). These data may then be represented as less than or equal to the median (-) or greater than the median (+). Each group of pluses or minuses is called a run. Thus for ten samples one might get a series as follows:

(++) (-) (+) (- - -) (+) (- -)

This series has six runs.

Runs tests were performed on each of the groups of samples collected at Baker, Mills Gap, North Fork Gap, and Susquehanna Gap. In each case the series failed to show non-randomness at the 5 percent level. For instance, at North Fork Gap, thirty-six samples were collected. The number of runs for this group of samples was 16. Non-randomness at the 5 percent level would have been indicated by r (number of runs) equal to or greater than twenty-four or equal to or less than eleven. The Runs test indicates that we may assume that the samples with large amounts of pressure solution are randomly distributed. Therefore,

the fact that there are some zones of intense pressure solution has probably not introduced bias into the data.

An operational difficulty associated with zones of intense pressure solution is the reconstruction of original grain shapes. When this problem arose, benefit of the doubt was always given to pressure solution with the feeling that it would be better to over estimate rather than underestimate the amount of pressure solution. However, the possibility remains that some of the original grains within these zones have been completely dissolved and as a result more silica may have been lost than has been accounted for by the point counting technique.

	Detrital Quartz	Authigenic Quartz	Clay	Pore	Other	Pressure Solution
Age Unk Alberta, Can.	75	23	0	2	0	3
Abe Ss, Pm, N.M.	73	22	2	3	0	0
Haymond Boulder Bed, C? TX	79	18	3	0	0	10
Ecca Ss Pm, S. Africa	87	5	0	8	0	21
Eureka Ss Ord; VT	78	20	2	0	0	6
Roubidoux Ss. Ord., MD	67	31	2	0	0	2
Keefer Ss. Sil., W. VA	80	16	3	0	1	10
Lyons Ss Pm., CO	69	25	3	3	0	8
Homewood Ss. Penn., W. VA	75	22	0	1	2	Aver. of 2 5
Price River Fm. Creta., VT	71	28	1	0	0	3
Juniata Fm. Ord., PA	76	24	0	0	0	4
Unk. Fm. Ord., MO	76	11	2	11	0	4
Oriskany Ss. Dev. W. VA	68	23	1	7	1	Aver. of 5 4
All Tuscarora Samples	74	21	2	2	1	7

Table 4

Mean values from modal analysis of selected orthoquartzites

Interpretation

The point count data presented in Table 1 demonstrate that pressure solution is an important but not the major source of cement in the Tuscarora. Assuming that all the silica dissolved during pressure solution was reprecipitated as cement then approximately one third of the cement may have been derived from this source. The other two thirds of the silica (14% of the rock volume) must be derived from other sources and these are discussed in the next section.

The data and observations also allow some important inferences to be drawn concerning some of the variables which effect pressure solution. The two most meaningful variables seem to be the amount of cement and the presence of clay between grains. The correlation coefficient between percent pressure solution and the percent authigenic silica for all samples is $- .69$ indicating an increase in pressure solution with decreasing cement. One might argue that the correlation is an artifact of decreasing available pore space with increasing pressure solution. To some extent this must be true. However, if this were the only reason for the negative correlation coefficient between pressure solution and authigenic quartz, there should be an equally strong coefficient between detrital quartz and pressure solution because as the pore space decreases the detrital fraction must increase. The fact that the r value for detrital quartz is much less than that for authigenic quartz and the fact that the two r values are significantly different at $P = .01$ indicates that the two correlation coefficients are not from a common correlation population. Furthermore, there are qualitative observations which

support the relationship between cement and pressure solution.

In many samples with intense pressure solution, there is a remaining porosity and a few authigenic quartz often terminate within these pores, indicating a lack of available silica. Thomson (1959) noted a similar lack of cement in zones of intense pressure solution in the Green Pond Conglomerate. He presumed the lack of cement was the result of increased solubility of the quartz in solution due to interstitial clay. An alternative explanation is that the most intense pressure solution occurs in zones of the rock which were not lithified during earlier diagenesis. Those areas which were cemented earlier in the diagenetic history would undergo less pressure solution because as cementation occurs stresses become more homogeneously distributed throughout the rock rather than being concentrated at grain boundaries.

The point count data from the two groups of sample shown in Table 3 demonstrates that samples with intense pressure solution (>10%) tend to contain more clay than samples with minor pressure solution (<4%). The fact that the relationship is not apparent from the correlation coefficient is probably due to the high variance associated with that data. By excluding samples with intermediate amounts of pressure solution (5 - 10 percent) and increasing the number of points counted per sample, the variation within the populations was minimized.

Various explanations have been proposed to explain the association of clay with zones of intense pressure solution. Thomson (1959) proposed that intergranular illite may enhance pressure solution by altering the pH of the pore fluids adjacent to the quartz crystals.

He suggested that exchange of Ca^{++} for K^+ in the illite releases potassium to the pore fluid which forms potassium carbonate, a strong base. The presence of the base increases the pH, increasing the solubility of the quartz. The clay in the Tuscarora is illite, however, it is well crystallized and therefore, would have limited exchange capacity. Also, less than one percent of the total dissolved potassium is likely to be present as potassium carbonate.

Weyl (1959) suggested that clay along grain boundaries promotes pressure solution by enhancing diffusion of the dissolved silica from the grain boundaries to the pore fluids. The data from the Tuscarora is consistent with this hypothesis.

Clay coatings on grains may also promote pressure solution by impeding overgrowth formation. Pittman and Lumsden (1968) showed that chlorite coatings inhibit overgrowth formation in the Spiro Sand. Heald and Larese (1974) have suggested that the illite in the Tuscarora may inhibit overgrowth formation. This is consistent with the correlation found between pressure solution and cementation.

It has been suggested that there should be an inverse relationship between pressure solution and grain size (Renton, et al., 1969; Wely, 1960 and many others). The relationship could be due to either an increase in solubility with size or a decrease in the length of the diffusion path along grain boundaries with decreasing size. The former explanation can not be true since quartz solubility does not change appreciably with size until the size is reduced to approximately 0.1μ (Blatt, Middleton and Murray, 1972, pp. 532). The latter explanation is reasonable but my data does not support it. Perhaps the variation in grain shape is more important than grain size in

the sand size fraction such that there may not be a strong correlation between grain size and length of the diffusion path.

There were no apparent differences in the amount of pressure solution among the four outcrops which were sampled in detail and there was no apparent difference between the amount of pressure solution in samples collected from steep versus gentle limbs of the anticlines. Where there were distinct zones of pressure solution, these zones parallel bedding. These observations indicate that pressure solution probably occurred independently of folding. However, it must be remembered that the samples are biased in that they came only from limbs of anticlines.

There is no apparent correlation between fracturing and the amount of pressure solution. The samples from Susquehanna Gap have been subjected for far more fracturing than any of the other suites of samples yet they have not undergone any more pressure solution. Furthermore, there are many examples of zones of intense pressure solution and no associated fracturing. In one instance, a fracture which intersected a zone of intense pressure solution at about 60° was observed. The fracture was not displaced across the zone as it would have been had the fracturing preceded or been contemporaneous with the pressure solution. Thus, the fracturing occurred after pressure solution. Some individual grains were fractured and in a few cases these grains have also been partially dissolved by pressure solution. In these instances fracturing may inhibit further pressure solution by releasing the stress on the grains. However, the number of instances in which the association between fracturing and pressure solution exists is too small to consider the stress release by intergranular fracturing important.

There is one obvious difference between samples taken from different outcrops. At North Fork Gap and Susquehanna Gap there is a tendency for zones of intense pressure solution to be a few millimeters thick and parallel to bedding. At Baker, West Virginia and Mills Gap the zonation is much less marked and the zones of intense pressure solution tend to be greater than the width of a thin section. The reason for the apparent difference in zonation is not known.

The value for the means of pressure solution versus porosity (authigenic quartz plus pore space) is plotted on Figure 4. As predicted, the point falls between the curve calculated with the assumption that there are equal amounts of pressure solution in all directions and Rittenhouse's curve which assume that all pressure solution occurs normal to the direction of maximum pressure. The data for the Tuscarora plot closer to the curve which assumes homogeneous strain. This is quite important because the two curves imply major differences the role pressure solution may play in the mechanical porosity reduction of sands. Rittenhouse's curve implies that it would be very unlikely for intergranular pressure solution to mechanically decrease porosity to less than 20 percent. My curve predicts that only about 6 percent pressure solution is necessary to reduce the porosity to half its original value. If my curve is a reasonable approximation to porosity - pressure solution trends in real sands, then it is consistent with the contention that intergranular pressure solution can account for most of the mechanical porosity reduction which has occurred in the Tuscarora.

Other Sources of Silica

Since intergranular pressure solution can not account for the majority of the authigenic silica in the Tuscarora, other sources must have contributed. The sources most commonly suggested are stylolitization, clay mineral diagenesis, dissolution of biogenic silica, desilication of volcanic debris, and normal subsurface water. In the following, each of these is evaluated as a source of silica for the Tuscarora within the limits of the presently available data. Unfortunately, none of these proposed sources can be tested in a straightforward manner as was possible with intergranular pressure solution.

Stylolites - Stylolites are best known in carbonate rocks where they frequently form columns tens of centimeters high. They probably form by pressure solution along planes of increased permeability, frequently clay seams, which follow bedding planes. They occur most commonly in nearly monomineralic rocks and they are usually quite obvious due to the clay and "insoluble" residue which mark their surfaces. Most stylolites parallel bedding, even in folded strata and, therefore, they formed prior to folding. There are examples, however, of stylolites at a high angle to bedding.

Stylolites are common in quartz arenites although they are less spectacular than those forming in carbonate rocks. Presumably, the lower solubility of quartz prevents the development of tall columns. Thus, in sandstones they usually have only a few millimeters of relief and are relatively inconspicuous. Heald (1959) noted that stylolites form in sandstones with up to 26 percent remaining porosity

and, therefore, they may be a significant source of authigenic silica.

Approximately eight percent of the samples from the Tuscarora had possible stylolites. Many of these stylolites are of doubtful origin because they have only a few tenths of a millimeter of relief and cut individual quartz grains. Even the most obvious stylolites have relief less than a millimeter and lateral extent parallel to bedding of a few centimeters. At Baker, W. Virginia there are surfaces which parallel bedding along which the rock has separated. These surfaces may extend for several feet then die into massive, coherent rocks. The surfaces have a hummocky topography with up to a few centimeters of relief. These are not marked by an insoluble residue or clay seam and are not seen in thin section leading me to believe they are probably not stylolites. It seems likely that they are joints along which there has been solution unaided by pressure and may have formed very recently.

The stylolites in the Tuscarora formed after cementation had begun because they truncate authigenic silica: however, whether or not the sediment was completely lithified is impossible to determine. Similarly, one can only roughly estimate the amount of material which may have been dissolved by stylolitization. Heald (1955) estimates fifteen percent loss of original volume in the Tuscarora due to stylolitization. The estimate is based on the length of the columns and concentration of heavy minerals along the seams. If this is correct the stylolitization along with intergranular pressure solution could account for the authigenic silica in the Tuscarora.

Silica cement derived from dissolution of biogenic debris and desilication of volcanic materials may be locally important as sources of authigenic silica. Desilication of volcanic debris has been proposed as an important source of opal cement in the Ogallala Formation (Swineford and Franks, 1959) and for quartz cement in Dushesne River Formation (Warner, 1965). Dissolution of biogenic silica has often been cited as a source of silica for the formation of chert and may be important in local cementation of some sands. The Kirkwood Formation (Miocene) is locally cemented by opal and chalcedony (Friedman, 1954) which may have been derived from the dissolution of biogenic silica. However, it is unusual to find thick, areally extensive deposits of either biogenic silica or volcanic debris associated with orthoquartzites and there is no evidence of such an association in the Tuscarora. Therefore, dissolution of biogenic and volcanic sediment are unlikely as major sources of authigenic silica in the Tuscarora.

The idea that clay mineral diagenesis might be an important source of authigenic silica was suggested by Siever (1962) and Towe (1962). The transformation of smectite to illite may be written such that for every two grams of illite formed, one gram of quartz is formed (Siever, 1962). Confirmation that the smectite to illite transformation occurs is given by Keller (1963), Dunoyer De Segonzac, et al., (1968), Burst (1969), Perry and Hower (1970) and Schmidt (1973). Hower and Eslinger (1973) found that in the 0.1 μ size fraction of Gulf Coast sediments taken from 4,000 - 19,000 feet the changes in the atomic proportions of K_2O, Al_2O_3 and SiO_2 "closely approximate the reactions: $smectite + Al^{+3} + K^+ \rightarrow illite + Si^{+4}$ ".

Yeh and Savin (1973) found isotopic fractionations between fine-grained quartz and illite/smectite consistent with the same reaction. Petrographic evidence that this process may be effective in quartz cementation is given by Fuchtbauer (1967) who found that quartz cementation in the Dogger sandstone increases toward the shaley margin of the bed.

To apply this model to the Tuscarora, it is necessary for it to be associated with a shaley sequence. The Tuscarora is overlain by approximately five hundred feet of shales and siltstones which make up the Rose Hill Shale (Folk, 1960). Underlying the Tuscarora is either the Juniata Formation or an unconformity, both of which are, in turn, underlain by the Martinsburg Shale (approximately 3,000 feet thick). The predominant clay mineral in both of the Martinsburg and the Rose Hill is illite (McBride, 1962 and Folk, 1960). This represents a potentially massive source of silica.

A gross calculation of the maximum amount of quartz which may be derived from a montmorillonite to illite transformation may be made as follows. Assuming the Martinsburg to be 60 percent clay [the average shale is 60 percent clay (Shaw and Weaver, 1965)], then the total clay thickness is $.60 \times 3,000$ ft. or 1,800 feet. Assuming thirty percent of the original clay in the Martinsburg was montmorillonite [the average abundance of clays for the world ocean basins is 38 percent montmorillonite and 37 percent illite (Blatt, Middleton and Murray, 1973, p. 318)], then $.30 \times 1,800$ feet equals 540 feet, which is the thickness of illite which was originally montmorillonite. According to Siever (1962) for every two grams of illite, one gram of silica is produced, so that assuming the density of illite and quartz are

about equal, 540 feet of illite should yield half that thickness or approximately 270 feet of quartz. Since we need sufficient silica to account for fourteen percent of the twenty-one percent authigenic silica in the Tuscarora, a thickness of approximately forty-two feet of silica is necessary. Applying the same arguments to the Rose Hill shale as we applied to the Martinsburg, 62 feet of quartz can be derived. Clearly, this type of clay mineral diagenesis is capable of supplying a massive amount of silica.

Unfortunately, a number of problems still remain in the above model. First, Siever (1962) assumed that the alteration of montmorillonite to illite involves a dissolution of montmorillonite and a precipitation of illite and the mass balance of materials appears to have been based on an assumption of constant aluminum in the clays (a slight arithmetic error in the equations makes it difficult to be sure). Towe (1962 and 1974 personal communication) assumed that the montmorillonite to illite transformation occurs by Mg and Fe addition to the octahedral layer where they substitute for aluminum which then displaces Si to produce SiO_2 . This model presupposes that the structural state of the starting material is conserved and Towe (1962) estimates 3 grams of silicon (6.5 grams of silica) derived per hundred grams of illite formed. This is only twelve percent of the amount proposed by Siever and indicates a maximum of approximately 34 feet (12% of 270 feet) of silica which might be derived from a montmorillonite - illite transformation in the Martinsburg.

A second problem with the model involves the migration of the silica after any smectite to illite conversion has occurred. The

isotopic data of Yeh and Savin (1973) show fine grained quartz in isotopic equilibrium with deeply buried Gulf coast clays. This can be interpreted as indicating that at least some of the silica from the smectite to illite transformation remains within the mudstones as authigenic quartz or chert and therefore, can not be a source of silica for cementation in adjacent sandstones.

The stratigraphic associations of orthoquartzites and shales also pose a problem. If shales are the major source of authigenic silica in orthoquartzites, one would expect a close association between shales and silica-cemented sandstones. A literature reconnaissance of the stratigraphic position of a number of well known orthoquartzite sequences does not reveal such an association. For example, the Baraboo quartzite (P₁C) and Drake (P₁C) quartzites are overlain by slate but the thickness of the slate overlying the Baraboo is much less than the thickness of the Baraboo and therefore, could not be a major source of authigenic silica. The Berea Sandstone (Mississippian) is overlain by a thick shale sequence but the Berea contains very little authigenic silica and is only locally an orthoquartzite. The Dakota sandstone is locally an orthoquartzite and overlain by thick marine shales which may be a major source of silica. In contrast, the Mesnard Quartzite (P₁C), Lamotte Sandstone (P₁C-₂), Antietam Formation (P₁C-₂), Potsdam Formation (P₁C-₂), Penrith Sandstone (Permian), Darwin Sandstone (Permian), the Ordovician quartzites in the Cordilleran miogeosyncline, and the Precambrian quartzites associated with the Road Antelope ore bodies of Zambia are not associated with thick shales. The most common association is with shallow water carbonate-evaporite sequences.

There are also tectonic questions to be raised in considering the possibility of the Martinsburg Formation being the major source of authigenic silica for cementation of the Tuscarora. If significant dewatering and diagenesis occurred in the Martinsburg during the Taconic orogeny then it is unlikely that it could represent a major source of silica for cementation of the Tuscarora. Alternatively, if the major diagenesis and dewatering occurred during the Appalachian Orogeny, then the Martinsburg may have supplied large quantities of silica and compaction during deformation may have caused expulsion of silica-rich pore fluids from the Martinsburg into the Tuscarora. Unfortunately, the evidence for the Taconic orogeny becomes increasingly equivocal toward the southern part of the Appalachians. The major arguments of twenty-six investigators are summarized by Epstein and Epstein (1969) who conclude that the Taconic orogeny in east central Pennsylvania was of only minor importance and that the major deformation of the Martinsburg Formation occurred during the Appalachian orogeny. Therefore, although the smectite-illite transformation potentially represents a major source of authigenic silica, we can't assume with any degree of certainty that it is the source of the authigenic silica in the Tuscarora.

Subsurface water - Analyses of subsurface waters show that 90 percent of ground waters are supersaturated with respect to quartz (Davis, 1964). Whatever the source of this silica, common ground waters can play a significant role in cementation if enough water can be moved through the rock.

To calculate the amount of water which must flow through a sandstone in order to cement it, it is only necessary to know the

concentration of silica in solution and the amount precipitated. In the case of the Tuscarora only the latter is known. The amount of silica in solution may be estimated from the data of Davis (1964). For arithmetic convenience, we assume an initial concentration of 32.5 ppm SiO_2 in solution from which 26.5 ppm is precipitated. The volume of quartz precipitated per pore volume of water will be the grams of quartz per cubic centimeter of water divided by the density of quartz or:

$$\frac{26.5 \times 10^{-6} \text{ gm SiO}_2}{\text{cm}^3 \text{ H}_2\text{O}} \div \frac{2.65 \text{ gm SiO}_2}{\text{cm}^3 \text{ SiO}_2} = \frac{10^{-5} \text{ cm}^3 \text{ SiO}_2}{\text{cm}^3 \text{ H}_2\text{O}}$$

Assuming the rock is always water saturated, this becomes equal to 10^{-5} pore volumes of quartz per pore volume of water. This is equivalent to saying the porosity of the rock will decrease by one 10^{-5} th for each pore volume of water which passes through the rock. Then the number of pore volumes of water necessary to reduce the porosity to half its original volume will be expressed by:

$$V_{\frac{1}{2}} = \frac{1}{K} \ln 2 = \frac{.693}{10^{-5}} \approx 7 \times 10^4 \text{ pore volumes of water.}$$

In the Tuscarora, there is approximately 21% authigenic quartz, 7% of which may have been derived from intergranular pressure solution. If the other 14% was derived from subsurface waters with an initial concentration of 32.5 ppm and a final concentration of 6 ppm, the number of pore volumes necessary to reduce the porosity from 14% to 1.85% would be three half volumes or approximately 2×10^5 pore volumes of water. This value demonstrates the vast number of times a fluid must circulate through a sand body in order to cement it.

An increase in the amount of silica precipitated to 265 ppm (the solubility of amorphous silica is only about 120 ppm at 25° C) causes only a small reduction in the number of pore volumes of water required, to 2×10^4 .

To determine how long it will take to move a given volume of water through a rock will depend on the flow velocity and distance. The velocity will, of course be a function of the permeability of the rock and the hydraulic gradient. The distance traveled will be determined by the relationship of bed to flow geometry. The thickness of the Tuscarora is approximately 100 meters while its width from east to west is approximately 5×10^5 meters. Therefore, a unit volume of water must travel three and a half orders of magnitude further if flow is parallel to the deposit than if it is normal to the deposit. The average flow rate of ground waters in aquifers is about 10 meters per year (Blatt, Middleton, and Murray, 1972, p. 353), while diffusion rates in stagnant basins may be as low as about 10^{-5} m/yr (Orcharenko, 1974). Therefore, flow rates may vary by about six orders of magnitude and the flow distance may vary within about three orders of magnitude but the concentration of silica in solution is not likely to vary by more than one or two orders of magnitude. In a system where the silica is derived from outside of the volume of rock being lithified, the key to cementation will be the flow velocity and direction. The concentration of silica only needs to be high enough to initiate precipitation.

Assuming the cementing waters entered the Tuscarora in its eastern reaches and flowed to its western extent at a rate of 10 meters per year, one pore volume of water would pass through the

formation every fifty thousand years (5×10^5 m/10 m/yr) and 2×10^5 pore volumes would pass through in 10^{10} years. Since no effects of reduced permeability are accounted for in this calculation, the ten billion years should be regarded as a minimum estimate for cementation. Vertical flow at a rate as low as 10 cm/yr is temporally realistic as a mode of cementation. The distance in this case is only 100 meters, allowing one pore volume of water to pass through the formation every thousand years (100 m/.1 m/yr). Therefore, 2×10^5 pore volumes would pass through the Tuscarora in two hundred million years. If cementation occurred soon after deposition it could have been completed by the end of the Paleozoic.

Summary and Conclusions

Petrographic investigation of the Tuscarora Orthoquartzite has shown it to contain an average of twenty one percent cement and two percent pore space. Assuming an initial porosity of 40 percent, this indicates a seventeen percent mechanical decrease in porosity and a twenty one percent chemical decrease in porosity. The investigation has also shown an average of seven percent pressure solution. Comparison with a simple geometric model indicates that seven percent pressure solution could cause more than a twenty percent decrease in pressure solution. Therefore, the data and observations are consistent with the conclusion that pressure solution is the cause of most of the mechanical porosity reduction which probably occurred in the Tuscarora. The data also shown that pressure solution is a significant source of authigenic silica; accounting for nearly one third of the authigenic quartz found in the Tuscarora.

The amount of authigenic quartz and the amount of clay are the only variables which were found to show any statistically significant relationship to the amount of pressure solution observed in a given specimen. The relationship between authigenic quartz and pressure solution is an inverse one possibly because cement equalizes stress throughout the rock volume and thus reduces stress concentration at the grain boundaries. The effect of clay may be to enhance diffusion rates or to impede cementation. Grain size, sorting or position relative to fold axes show no apparent relationship to the amount of pressure solution.

Sources of silica other than intergranular pressure solution must have provided the majority of the authigenic silica found in

the Tuscarora. The sources most commonly suggested are stylolitization, clay mineral diagenesis, dissolution of biogenic silica, desilication of volcanic debris and normal subsurface water.

According to Heald (1955) stylolitization may be a major source of silica. Clay mineral diagenesis may represent a vast potential source of silica depending upon nature of the smectite to illite transformation. However, even assuming the maximum amount of silica that might be generated during this transformation, problems still exist in determining the amount of silica which will leave a shale and the rate at which it may enter a sandstone. Dissolution of biogenic silica or volcanic debris may be important sources of silica in special circumstances but there is no evidence that they were important in the cementation of the Tuscarora. Many analyses of normal subsurface waters contain sufficient silica to cement a sandstone if sufficient volumes of that water can be moved through the rock. Flow rates and geometry are likely to have a much greater effect on the efficiency of cementation than the concentration of silica in solution. Therefore, clay minerals diagenesis and/or normal ground water are likely sources of silica in the Tuscarora, but we do not have any means of rigorously testing the efficiency of either possibility.

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Appendix

Sample Calculation of Pore-Space Reduction, Orthorhombic Packing

I. Calculation of original porosity (this is the same as shown by Rittenhouse (1971) p. 90). Each sphere in Figure 3a may be considered to be the solid part of a unit cell that has the hexagonal cross section shown by shaded area and a length equal to the diameter. The pore space is the difference between the volume of this hexagonal prism and the volume of the sphere. Then,

$$\text{Original porosity (\%)} = \frac{\text{vol. of hexagonal prims} - \text{vol. of sphere}}{\text{vol. of hexagonal prism}} \times 100$$

$$\text{The volume of the sphere} = \frac{4}{3} \pi r^3$$

$$\text{If the radius (r) is 1, the volume of the sphere} = \frac{4}{3} (3.1416) (1)^3 = 4.1888$$

$$\text{The volume of the hexagonal prism} = \text{area of the hexagon} \times 2 r$$

$$\text{The hexagon area} = 12 \times \text{area of triangle ABC}$$

$$\text{The area of triangle ABC} = \frac{BC \times AC}{2}$$

$$AC = r = 1$$

$$BC = AC \tan 30^\circ$$

$$BC = 1 (0.57735)$$

$$\text{Area of triangle ABC} = \frac{0.57735 \times 1}{2} = 0.288675$$

$$\text{Area of hexagon} = 12 \times 0.288675 = 3.4641$$

$$\text{Vol. of hexagonal prism} = 2 \times 3.4641 = 6.9282$$

$$\text{Original porosity (\%)} = \frac{6.9382 - 4.1888}{6.9282} \times 100 = 39.54$$

II. Calculation of porosity after solution at grain contacts.

After solution has reduced the spheres by 1/10 of the sphere radius in Figure A1 then $AE = 0.9 r$. Each unit cell will be a regular polygon and if the dissolved material is not redeposited.

$$a. \text{ Porosity (\%)} = \frac{\text{vol. of hexagonal prism} - \text{vol. of solid}}{\text{vol. of hexagonal prism}} \times 100$$

$$b. \text{ Vol. dissolved} = \text{Vol of 8 spherical segments}$$

$$c. \text{ Vol. of solid} = \text{Vol. of original sphere minus vol. of eight spherical segments.}$$

1. volume of hexagonal prism

$$= \text{area of hexagon} \times 2 r$$

$$\text{area} = 12 \times \text{area of triangle ABC}$$

$$\text{area of ABC} = \frac{BC \times AC}{2}$$

$$AC = r = .9$$

$$BC = AC \tan 30^\circ$$

$$= .9 (0.5774)$$

$$ABC = \frac{.5197 \times .9}{2}$$

$$= .2338$$

$$\text{area of hexagon} = 12 \times .2338 = 2.8062$$

$$\text{Vol. hexagon} = 2.8062 \times 2 (.9) = 5.0512$$

2. Vol. dissolved = vol. spherical seg. x 8

$$= \frac{1}{3} \pi h^2 (3r-h) \times 8 \text{ where } h \text{ is height}$$

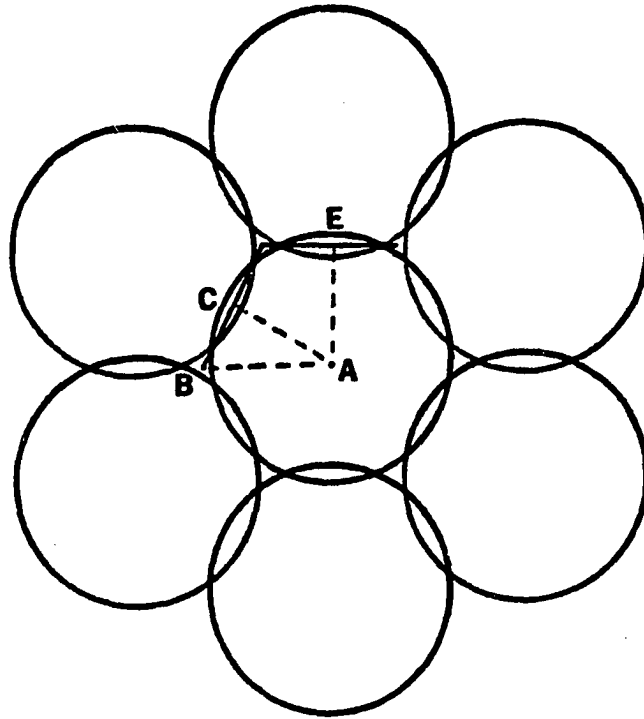
$$= .33 (3.1416) (.1)^2 (3 - .1) \times 8$$

$$= .2405$$

$$\begin{aligned} 3. \text{ Vol. solid} &= 4.1888 - .2405 \\ &= 3.9483 \end{aligned}$$

$$\begin{aligned} 4. \text{ Vol. porosity (\%)} &= \frac{5.0512 - 3.9483}{5.0512} \times 100 \\ &= 21.8 \end{aligned}$$

$$\begin{aligned} 5. \text{ Vol. dissolved (\%)} &= \frac{.2405}{5.0512} \times 100 \\ &= 4.8\% \end{aligned}$$



Spheres and associated pore space in orthorhombic packing after equal amounts of solution at all points of contact

Figure A1