

MINERALOGY OF CHERTS AS A FACTOR IN THE
USE OF SILICEOUS AGGREGATES FOR CONCRETE

by

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B. S., Kansas State College
of Agriculture and Applied Science, 1950

A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Geology and Geography

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1953

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INTRODUCTION

Chert has, for many years, been considered undesirable as a concrete aggregate. Service records of concretes in which chert has been used have shown many different types of failure.

Not all cherts, however, cause failure when used in concrete. The chert obtained from crushing lead and zinc ores, in the Tri-State (Mo., Kans., Okla.) mining district, has been used extensively as a concrete aggregate and has shown an excellent, over all, service record.

Other areas have produced suitable concretes using chert as an aggregate, but this production is not consistent. The purpose of this investigation was to determine the reason, or reasons, why one chert is good and another is bad when used as a concrete aggregate. It was also desired to devise or discover, if possible, an economically feasible method of determining whether or not a particular chert will make a suitable aggregate.

Although it was beyond the scope of this paper to attempt the solution of the problem of the origin of cherts, certain facts came to light during the course of the study which pertained to the origin. From these facts certain interpretations were made and conclusions reached. These were included because the origin relates to the petrographic nature which in turn relates to their use as an aggregate.

DEFINITIONS

The term chert has been used for a wide variety of rocks. It was defined by Tarr (1938) as a dense crypto-crystalline rock, composed mineralogically of chalcedony and crypto-crystalline quartz. It has also been defined as "those cryptocrystalline varieties of quartz which are opaque, save on thin edges and are white, pink, green, grey or blue grey in color" by Tarr (1926); "almost any rock composed of micro-crystalline or cryptocrystalline silica" by Walker (1939); "any opaque natural micro-crystalline or micro-aphanitic silica whose structure and environment does not permit it to be otherwise classified" by Sosman (1927).

Tarr's (1938) definition, although more concise, does not fit the common usage as well as the other definitions which are more inclusive. If Tarr's definition is accepted then many of the beds commonly referred to as chert are not chert because they are composed largely of opal.

In describing the California cherts of the Monterey formation, Bramlette (1946) stated:

The name chert is applied to the relatively pure silica rocks of the Monterey formation that are dense and vitreous, regardless of whether they consist mainly of opal or mainly of chalcedony and regardless of their color which varies greatly.

The term flint has been widely used as a synonym for chert. Tarr (1926) stated that flint was a dark colored

chert but recommended in a later paper (Tarr, 1938) that the term be dropped or reserved for artifacts.

The term jasperoid is widely used in the Tri-State district for a very dark, siliceous rock, which commonly contains sphalerite. Pettijohn (1949), p. 320, states that "jasperoid is the term applied to the siliceous rocks formed by metasomatic replacement of limestones of the Tri-State mining district". This investigation has shown part of this jasperoid to be the result of cavity filling.

In this paper the term flint has not been used.

Since the exact mineralogy of the cherts is in doubt the definition as given by Sosman (1927) seemed to be the most usable.

The term jasperoid was used meaning the very dark siliceous rock of the Tri-State district.

"Cotton Rock" was used to refer to the white periphery so common near the outer edge of chert nodules and to the white border near the contact of other beds in the bedded cherts.

REVIEW OF THE IMPORTANT LITERATURE

Chert as an Aggregate

An early observation of the greater desirability of Tri-State chert as an aggregate was made by F. V. Reagel (1924) who stated:

No action is apparent in connection with the flint obtained from crushing lead and zinc ore, but very serious effects are found in connection with the crushed chert found in crushed limestone formations thus far investigated.

Some effects from chert were described by Sweet (1940) as popouts, lower flexural strength than calcareous aggregate, map cracking and excessive expansion of concrete. He stated that:

The first indication of a popout is a circular crack that forms the base of a conical piece of concrete. At the apex of the cone will be found a fragment of chert with another portion of the chert imbedded in the main body of the concrete. The chert piece has split with such force as to break and lift out the concrete.

He further stated that "map cracking was caused by a marked reduction in strength after freezing and thawing occurred."

T. E. Stanton (1940), from studies on California cherts, concluded that a reaction between opal aggregates and the alkali hydroxides, released by the portland cement minerals during hydration, was the cause of the expansion and cracking of some concrete structure in California. A jelly-like substance was always found to be present in such expanded concretes and analyses showed it to contain appreciable amounts of alkali silicates.

Stanton's (1940) publications opened a new line of investigation. They were followed by numerous discussions of his publications as well as many new, original research

papers. Stanton had shown opaline silica to be reactive. Tests were begun at that time to determine whether or not other minerals were reactive.

A table showing rocks and minerals known to be reactive with high alkali cements was given by Mielenz (1946) as follows:

TABLE I. Rocks and Minerals Which are Deleteriously Reactive with High Alkali Cements

Reactive Minerals: Chemical		: Physical Character
: Composition		:
Opal	$\text{SiO}_2 \cdot n\text{H}_2\text{O}$	Amorphous
Chalcedony	SiO_2	Cryptocrystalline fibrous
Tridymite	SiO_2	Crystalline
Reactive Rocks		Reactive component
Siliceous Rocks		
Opaline Cherts		Opal
Chalcedonic Cherts		Chalcedony
Siliceous Limestone		Chalcedony and/or opal
Volcanic Rocks		
Rhyolites & rhyolite tuffs		Volcanic glass, devitrified glass and tridymite
Dacites & dacite tuffs		
Andesite & andesite tuffs		
Metamorphic Rocks		
Phyllites		Hydromica (?)
Miscellaneous Rocks		
Any rocks containing veinlets, inclusions or grains of the reactive rocks or minerals listed above		

Carlson (1944) stated that four conditions are required for expansion due to cement-aggregate reaction to take place:

As is well known now, the large expansion seems to occur only (1) after months or years, (2) when the aggregate is reactive, (3) when a high-alkali cement is used, and (4) when the concrete is maintained neither fully wet or dry.

Writers frequently refer to high-alkali or low-alkali cement but they rarely define either of them. Carlson (1944) made tests on a mildly reactive aggregate with cements which had alkali contents (Na_2O plus K_2O) of 0.36, 0.46, 0.75, and 1.15 percent. He reported that after two years of observation "only the two highest alkali contents produced appreciable expansion". A cement containing more than 0.50 percent alkali is commonly regarded as a high alkali cement.

Studies by Hansen (1944) indicated that over a period of time, reactive aggregates would cause expansion, even though a low alkali cement had been used. Tremper (1944), in a discussion of Hansen's paper, stated that such expansion could probably be avoided altogether by use of a low alkali cement.

Parsons and Insley (1944) made etching tests with sodium and potassium hydroxides. Their results were included in part here because of applicability to this investigation.

Opal. A green, waxy-looking opal from Nevada was placed in all the etchants. In NaOH and KOH the surface was distinctly etched in 20 minutes and the polish completely removed in 1 hour at 50°C . In a week at room temperature the surface became thickly coated with gel formed at the expense of the opal.

Chalcedony. Chalcedony was not visibly etched in any of the solutions at room temperature, but in NaOH

and KOH at 90° C. for 3 hours the surface was strongly etched and deeply pitted.

Quartz and Chert. Specimens of quartz and of chert composed of microcrystalline quartz were not etched by any etchants at any temperature or in any time periods so far tried.

Glass Bearing Rocks. Specimens of obsidian, pitchstone glassy rhyolite, and the glass bearing Parker Dam andesite were treated with the various etchants. A slight etch of the surfaces of the glassy constituents was apparent in as little as 1 hour at 90° C. in NaOH and KOH, but the etching progressed slowly with longer time intervals.

Chert in General

The origin of chert has been a topic of discussion for many years. Numerous theories have been advanced and very little agreement reached.

Very early observers believed the nodular cherts to be the result of coagulation of a gel on the sea floor and the bedded cherts to be the result of the collection of these gel masses into continuous strata.

Other early investigators considered the cherts to be metamorphic. Ransome (1894) discovered radiolarians in the Franciscan cherts and concluded that they were sedimentary and were siliceous because of the contained siliceous organisms.

In subsequent years evidence was gathered which indicated that chert was the result of replacement of limestone and dolomite beds. The older idea of gel precipitation was largely dropped for a time.

Tarr's (1917) publication describing features of the chert in the Burlington limestone in Missouri and presenting his views concerning origin of this chert revived the idea of gel precipitation or syngenetic formation. He implied that the replacement theory was not capable of explaining most chert occurrences. He did admit, however, that more work was necessary before his syngenetic theory could be applied to all chert occurrences.

Van Tuyl (1918) discussed Tarr's paper and cited evidence which supported a replacement theory. He stated that most chert could be explained by replacement.

A relationship was noticed between volcanism and chert formation. Bramlette (1946) described pyroclastic material in the Monteeey cherts. We also described associated extrusive and intrusive igneous rocks.

Ruby (1929) concluded that the siliceous Mowry shale was related to altered volcanic ash. He stated that the Mowry consisted of "volcanic ash, clay, silt, sand, and organic matter and a large amount of chemically precipitated silica." He also reviewed the literature pertaining to chert and associated volcanism.

The theories concerning the origin of chert are outlined by Pettijohn (1949), p. 329, as follows:

I. Syngenetic silica

1. Clastic quartz

- 2. Chemical silica
 - a. Biochemical silica
 - b. Chemical precipitate
 - c. Magmatic precipitate
- II. Penecontemporaneous silica
- III. Epigenetic silica
 - 1. Precipitation in zone of cementation
 - 2. Precipitation in zone of weathering

There was existed and still exists, a diversity of opinion as to the source of silica. Tarr (1917) supposed that ordinary sedimentation processes were sufficient to provide the necessary silica. He pointed out that the present day streams carry abundant silica but that silica is nearly nonexistent in sea water. He interpreted this as meaning silica has been precipitated by sea water.

Other writers do not believe that normal processes are adequate. They argue that the silica is of magmatic origin and is contributed by contact with submarine lavas, by submarine springs of magmatic water, or by ash falls.

MATERIAL AND METHODS

Collection of Samples

In preparation for the study of the cherts it was decided to collect only a few samples and study them intensively rather than to collect many samples and not be able to study them so carefully. Tri-State samples were collected from three beds in the Blue Goose mine of the Eagle Picher Mining Co., located at Picher, Oklahoma. Those beds were the M bed, the R bed, and the OPQ bed, of the Boone

formation. O bed, P bed and Q bed are undifferentiated in this particular mine.

The samples collected in the Manhattan area were from Schroyer and Threemile limestone members of the Wreford formation and from the Florence limestone member of the Barnston formation. These formations are in the Chase group of the Wolfcamp series and are of Lower Permian age. These samples have been referred to as "local cherts" throughout this paper.

The Threemile sample was collected in a roadcut for highway K-13 in sec. 21, T11S, R8E, Riley Co., Kansas. The Schroyer and Florence samples were taken from sections 28 and 32 respectively, T11S, R8E, Geary Co., Kansas. The Schroyer sample was taken from a K-13 road cut and the Florence sample from a rock quarry in the southeast corner of the section.

An attempt was made to collect samples of local chert which showed a contact with the surrounding limestone. It was believed that this contact zone would best show evidence pertaining to origin and to weathering.

Polished Section Study

A sample from each bed was polished for study with a reflecting microscope. This was done on a grinding wheel, the final polish being made with 3-F abrasive. The sections

were then studied by means of an ore microscope.

Although this study resulted in some valuable information, it was seriously handicapped by the inability to identify the non-opaque minerals. The greatest contribution was in identification of the sulfides which were present in the Tri-State cherts.

Thin Section Study

A thin section was made from each of the beds being studied. In all cases the thin section was taken from as near the area which had been studied in polished section as possible. Standard petrographic microscope techniques were applied in the study of these sections.

Differential Thermal Analysis

Differential thermal analysis has proven valuable in clay studies. It was believed that some of the finer particles in the chert could be identified as a clay mineral by this method. It was also believed that a rough quantitative relationship between quartz and opal could be obtained.

Samples were taken from as near as possible to the sections studied. They were ground to less than 120 sieve size and run in the standard manner.

Bromoform Separation

Samples of the local cherts were ground to less than 250 sieve size. A solution of bromoform and alcohol was adjusted to a specific gravity of 2.45. It was believed that quartz and chalcedony could be separated from opal in this solution in spite of the very fine grain of the cherts.

The Threemile sample was run in this 2.45 specific gravity solution. Subsequent separations were made in a solution which was not so carefully adjusted. It was decided that it would be sufficient to adjust the bromoform to float opal and sink quartz. Therefore, in the Schroyer and Florence separations, the specific gravity of the bromoform was between 1.95 and 2.65.

Crushed Fragment Study

The final study was to examine fragments, less than 250 sieve size, in index of refraction oils. Due to the extremely fine grain of the cherts this proved to be more effective in mineral identification than had been the thin section study. It is believed by the author that any study of chert should include a crushed fragment study.

By this method it was possible to distinguish between microcrystalline quartz and chalcedony, in grain sizes

ranging downward to about .004 mm. Index of refraction was measured which proved to be a significant difference between Tri-State and local cherts.

INFORMATION GAINED BY THIS INVESTIGATION

Tri-State Chert

The Tri-State cherts were seen to represent three stages of chert deposition and two stages of brecciation. One slide taken from OPQ bed showed a fragment, containing silicified marine fossils and minute carbonate grains, which had been cemented with microcrystalline quartz. The contact between the fragment and the cement was very sharp, which was interpreted as evidence that the fragment had been chert at the time the cement had been deposited. Displacement could be measured along a cemented crack in the fragment. The surrounding cement showed lineation which followed the sharp corners of the fragment. This lineation could be seen to become less angular at points further from the edge of the fragment. This dying out, indicated that the quartz represented the filling of a cavity.

The fossils and the minor calcite indicated that the fragment had been a limestone at one time but had been replaced by silica. The sharp contact indicated that it was chert at the time of brecciation. It seemed unlikely that replacement could have taken place after brecciation without

destroying or changing the outline.

Another slide, taken from R bed, showed fragments which seemed to represent fragments of the chert of the second stage. The fragments showed the lineation of the included material which had been seen in the slide from the OPQ bed. There were no fossils observed. The grain size was about the same as that of the cementing chert of the OPQ bed. In the R bed slide the cementing chert was seen to contain considerable sphalerite and some pyrite. In the hand specimen this sphalerite bearing chert was seen to be the dark jasperoid. It was determined microscopically that this jasperoid was dominately a mixture of sphalerite and microcrystalline quartz. It was concluded that the jasperoid owes its dark color to very fine sphalerite, scattered throughout the quartz.

A slide cut from a sample of M bed chert, showed fossil bearing fragments which were cemented by sphalerite bearing chert. Some of the fragments showed very sharp contact between the fragment and the cement. Other fragments, when viewed in transmitted light, graded imperceptibly into the cement. These same fragments, however, when viewed in reflected light showed a distinct line where the color changed from the grey of the fragment to the brown of the jasperoid. It was concluded that the fragments showing sharp outline represented rock which had been converted

to chert before brecciation but the less distinct outline represented alteration at the time of deposition of the jasperoid.

The paragenesis was, therefore; (1) deposition of a limestone, (2) partial replacement of this limestone by chert, (3) brecciation, (4) cavity filling and cementation by chert, (5) further brecciation, (6) cavity filling and replacement by hydrothermal solutions which also carried sulfides which were deposited with the jasperoid.

No criterion was observed which would indicate replacement of limestone at the time of the first cavity filling and cementation but it seems quite likely that this could have occurred. It also seems probable that this first cavity filling was accomplished by hydrothermal solutions.

The fossils were very much altered and in most cases contained no calcite. The largest and most complete fossil seen in the Tri-State chert was a brachiopod which was in the OPQ bed slide. This fossil was partly calcareous. The same slide contained numerous spines or apicules, probably sponge spicules, which showed up only as lighter areas in the chert. The M bed fragments contained vague outlines of brachiopods as well as completely silicified spicules.

Mineralogically the Tri-State cherts were seen to be predominately microcrystalline quartz. The fragment areas rarely showed grain size over .018 mm. and grain size graded

down to cryptocrystalline in size. In the hydrothermal areas the grains were larger, being dominately about .02 mm. across and still larger crystals were present as drusy coatings in the cavities. Many of the grains in the hydrothermal areas were large enough to obtain an interference figure which identified them as quartz. The finer grains of the fragment areas appeared, in many cases, to have a wavy extinction. After a study of crushed fragments, it was concluded that the apparent wavy extinction had been due to grains going to extinction above and below the grain under observation. In the crushed fragments the smaller grains could be seen to have very definite extinction positions.

The index of refraction proved to be quite uniform in all samples of Tri-State chert. It was greater than 1.54 and less than 1.55. Relief was extremely low in 1.55 oil, indicating that the index was very close to 1.55. Fast and slow direction indices could be measured only in the fragments having relatively large grains. These indicated no greater than 1.55 and no lower than 1.55. These larger grains, however, were already known to be quartz.

The quartz grains of the chert contained very fine particles of less than .003 mm. diameter which defied identification. The particles reflected white light, and heterogeneous distribution of them caused the mottled appearance of the chert when viewed in reflected light.

This mottling and the occurrence of the fine particles has been noted by many writers in their descriptions of various cherts. Tarr (1917) stated that opal occurred in this manner in the Burlington cherts. Twenhofel (1919) described limonite having this occurrence in the Wreford of southern Kansas. Fowler and Lyden (1935) stated that it was organic matter in the Boone chert of the Tri-State district. Bramlette (1946) believed them to be included clay particles in cherts of the Monterey formation.

Of these authors only Bramlette presented any evidence to support his statements concerning the fine particles. He presented chemical analyses of cherts showing aluminum which could be attributed to clay inclusions.

In attempting to identify this extremely fine substance, differential thermal analyses were made but the curves would not be interpreted as any known clay mineral. Neither did they seem to represent limonite, organic matter, or opal.

A small sample was treated with hydrogen peroxide for two weeks but the inclusions remained. This should not be interpreted as meaning that it was not organic matter, since the particles could have been so tightly encased in silica as to prevent the peroxide's reaching them.

Clay staining techniques were tried but did not produce results. This may have failed due to the reason stated

above; the particles not being reached by the solutions.

Local Chert

It was not the purpose of this investigation to describe field relationships of the cherts but since cherts are commonly classified as either bedded or nodular, a brief description was included to provide this classification. The Schroyer and the Threemile follow definite bedding planes but are still best classified as nodular. The Schroyer nodules are very irregularly shaped. The Threemile nodules tend to be flat shaped and unite to form almost a continuous bed in places.

The Florence chert is distributed throughout the thickness of the limestone. It tends to have thin beds of chert with nodular chert dispersed between these beds. The nodular chert appears to be largely interconnected and is irregular in shape. The rocks used in this study were from the nodular zone.

A study of a thin section of the Florence showed it to be composed of quartz, calcite, chalcedony, and isotropic silica. This section showed that the Florence contained more quartz than the other local cherts studied. It occurred mostly as a replacement of calcite in the larger fossils.

The slide showed a cross section of a large brachiopod shell. It was about 2 mm. thick. Evidence of replacement

of calcite by quartz and by chalcedony was very good in this cross section. Subhedral crystals of quartz with inclusions of calcite could be seen. There was lineation of included particles in the unaltered calcite. This lineation could be seen to continue through the crystals of quartz. All stages between unreplaced calcite and complete replacement by quartz were seen.

While quartz occurs as a replacement mineral throughout the calcite band, chalcedony was the dominate replacement material near the contact with the chert. The chalcedony is obviously not a forerunner of the quartz, since the quartz commonly contained included calcite while in no case was the chalcedony seen to have calcite inclusions.

It was also apparent that chalcedony was a replacement of calcite. Under crossed nicols, the fibers of chalcedony were seen to be continuous with the lineation in the calcite.

The bulk of the slide was made up of chert which appeared dark grey and light grey mottled in reflected light. The areas which appeared to be darker in reflected light could be seen to be clearer in transmitted light. The light grey color was due to reflection of white light by very fine inclusions which could not be identified.

A minor amount of opal was present. It occurred in rhomb shaped grains about .03 mm. across. In a few cases the rhomb was seen to be composed partially of carbonate

and partially of opal. It was concluded that these were pseudomorphs after dolomite, since dolomite tends to form rhombs when present in a limestone.

Marine fossils were abundant in the siliceous areas. Most of them were composed of calcite which had been more or less replaced by fibrous chalcedony. Many were completely replaced by chalcedony. Brachiopods were the most common form. Pelecypods, fusulines, sponge spicules, and bryozoans could be identified.

Imperfect spherulites and siliceous oolites were common but not abundant.

Large grains of fibrous chalcedony formed island-mainland relationships with the finer grained silica. Since no additions or subtractions of material were indicated, this was interpreted as a recrystallization process.

Well rounded to subrounded grains of quartz showing secondary growth indicated that these were detrital grains deposited with the original calcareous sediments. Broken fossils and oolites were indicative of revoking of the sediments, but the presence of a few unbroken fossils showed that the reworking had not been extensive.

In the Threemile slide, a bryozoan was observed which cut across the contact of the chert and limestone. This fossil was calcareous in the limestone area and siliceous in the chert area. A brachiopod in the limestone area was

partially replaced by chalcedony. An optically continuous, subangular carbonate grain in the limestone area was partially replaced by chalcedony. All of these features occurred at, or within 3 mm. of, the chert-limestone contact. These criteria were considered evidence of replacement along the contact.

Non-fossil fragments of calcite were observed in the chert near the contact. These formed an island-mainland structure of sorts, which indicated replacement.

The fibrous nature and the interference color seemed to be positive identification of the chalcedony. The index of refraction of the fibrous material was determined for comparison with Tri-State chert. It was 1.53.

The Threemile thin section showed the contact between chert and limestone. The contact between the siliceous zone and the limestone was sharp. In the siliceous zone, at the contact with the limestone, was the area known as cotton rock. This zone is milky white in reflected light. It grades into the chert, which is a blue grey color in reflected light. The width of this cotton rock zone varies in different specimens from a very thin zone of about .2 mm. to about 25 mm. In the slide studied it was about 1 mm. wide.

This cotton rock area contained a very high percentage of finely divided calcite. The greatest part of this calcite

was in grains of less than .003 mm. When a similar area in a hand specimen was tested with acid it was seen to effervesce. On this basis the cotton rock could be classified as a limestone rather than with the chert in spite of the fact that the sharp line of demarcation is between the limestone and the cotton rock. Apparently cotton rock owes its white color to the fine calcite particles.

A hand specimen of the Threemile showed the cotton rock to be about the same width at the upper and lower contact. The gradation from cotton rock to chert was also similar. This showed that the process, which formed the chert and cotton rock, worked in both directions; either away from or toward the center of the bed or nodule.

The preliminary examination of the local cherts in thin sections, led to the conclusion that they contained considerable opal and very little quartz. Isotropic particles was observed in all slides of local chert which were studied. It was assumed that this was opal. The index of refraction seemed too high for opal but this was attributed to an aggregate effect with the chalcedony, since the two were so intimately intermixed.

It was thought that a strong opal curve would show up on a differential thermal analysis and support the assumption that opal was present. This was not the case.

In the Schroyer thin section, small, irregular, yellow,

isotropic bits of silica were observed. They had an index of refraction slightly less than balsam and a peculiar, bumpy surface texture. They averaged about .020 mm. in size and had very angular outlines. It was realized that these could be glass shards, but it was believed that they were opal.

The same sort of small, yellow, shard shaped particles were observed in the Threemile and the Florence. They were less abundant in the Threemile than in the Schroyer and were rare in the Florence.

When the opal failed to show up on the D.T.A. curves, it was thought that there was simply not enough opal in the sample to show up. It was then decided that perhaps the opal could be separated in an adjusted bromoform solution.

Bromoform was adjusted with alcohol to a specific gravity of 2.45. All samples to be separated were crushed to less than 250 sieve size.

The first separation made was of the Threemile. In subsequent separations the specific gravity was adjusted with mineral samples to float opal and sink quartz, rather being adjusted with samples having a specific gravity which is known to the second decimal place. Therefore the Schroyer and Florence separations were not so closely controlled as the Threemile but the liquid specific gravity was known to be between 1.95 and 2.65.

After the separation was made the light fraction of the Threemile was examined in 1.53 index oil. This fraction had abundant isotropic particles. Most of them were yellow in color and many had the irregular shape of shards. The index of refraction was lower than 1.53 but the relief was definitely not high enough for opal.

In a study of the heavy fraction, similar shard shaped, yellow, isotropic particles were observed. In the case of the heavy fraction, however, the index of refraction was greater than 1.53.

The indices of refraction were determined by the oil immersion method. The index of the isotropic material in the lighter fraction varied somewhat, but most of it had an index between 1.50 and 1.51. In the heavy fraction the variation of index was even greater. The highest index measured was 1.56, the average being about 1.55.

The shard shaped particles, therefore, varied in index of refraction from 1.50 to 1.56. Roughly 70 to 80 percent had an index very close to 1.50. All isotropic particles of specific gravity greater than 2.45 had an index of refraction greater than 1.53 and less than 1.57. The isotropic particles having a specific gravity lower than 2.45 had an index of refraction lower than 1.53 but greater than 1.50.

Johannsen (1931), p. 1, gives the following table:

Specific Gravities and Refractive Indices of Various Natural Glasses

Name of Rock:	No.:	Sp. Gr.	Sp.Gr.:	Index	Index
		Range	Ave.	Range	Ave.
Obsidian	: 19	: 2.13-2.45	: 2.323	: 1.48-1.51	: 1.492
Pitchstone	: 9	: 2.22-2.51	: 2.335	: 1.492-	: 1.500
	:	:	:	: 1.506	:
Perlite	: 5	: 2.23-2.30	: 2.346	: 1.488-	: 1.497
	:	:	:	: 1.506	:
Pumice	: 2	: - - - -	: - - -	: 1.488-	: 1.497
	:	:	:	: 1.506	:
Dacite	: 4	: 2.45-2.55	: 2.505	: 1.504-	: 1.511
	:	:	:	: 1.529	:
Trachyte	: 4	: 2.25-2.60	: 2.411	: 1.488-	: 1.512
	:	:	:	: 1.527	:
Andesite	: 8	: 2.37-2.65	: 2.489	: 1.504-	: 1.512
	:	:	:	: 1.529	:
Leucite-	: 2	: 2.52-2.59	: 2.562	: 1.525-	: 1.550
tephrite	:	:	:	: 1.580	:
Tachylite,	:	:	:	:	:
diabase, ba-	:	:	:	:	:
salt glass,	: 10	: 2.50-2.99	: 2.757	: 1.506-	: 1.575
palagonite,	:	:	:	: 1.612	:
etc**	:	:	:	:	:

*The numbers of specimens given in this column are those listed by George (William O. George: The Relation of the Physical Properties of Natural Glasses to their Chemical Composition, Jour. Geol. XXXII, 1924, 353-72), p. 356-357. They do not represent the number used in the determination of the average. Stark alone gave 133.

**These values do not include a determination of 3.16 to 3.17 for the specific gravity of a tachylite given by G. A. Stonier: On the Occurrence of Basalt glass (tachylite) at Bulldelah. Rec. Geol. Sur., New South Wales, III, 1893, 118-19

On the basis of shape and size of particles, their isotropism, and interpretations from Johannsen's table, it was concluded that the isotropic material was volcanic glass. The bromoform specific gravity of 2.45 would have caused a definite separation between perlite and dacite. Therefore, the glass contained in the chert was considered to be approximately eighty percent, of obsidian, pitchstone, or

perlite composition. The remaining twenty percent was of a more basic composition.

Examination of fragments from the Schroyer showed that glass made up the bulk of the light fraction. There appeared in the heavy fraction many glass particles with an index of refraction lower than 1.53 as well as many with an index higher than 1.53. The better separation and the greater variation of index in the heavies, indicated a lower specific gravity of the bromoform than had been used in the Threemile separation.

The Florence showed fewer glass particles than the Schroyer or the Threemile.

In fragments from all three cherts studied there were many particles which had the same shape, color, and surface texture as the glass shards. They were different in that they were partially or wholly composed of chalcedony. As more and more of these particles were studied a pattern became apparent, which was interpreted as stages of alteration from glass to chalcedony. As the chalcedony content increased, the yellow color faded, the specific gravity increased, the index of refraction became higher, and minute inclusions appeared within the shard.

Both in the slide and in the crushed fragments much chalcedony was observed which appeared to be cement for the shards. It contained particles which appeared to be organic

matter and which were largely removed when treated with hydrogen peroxide. It was deduced that the chalcedony occurred both as altered glass and as a cement, since it would be difficult to visualize another method of inclusion of organic matter. The possibility exists that the shards were cemented by calcite and subsequently replaced, but no calcite was observed which appeared to have that relationship.

It seemed logical that the chalcedony which acts as cement would have gone through an opaline stage but there was no evidence of this. The only opal observed in any of the rocks studied was that which appeared to be pseudomorphous after dolomite.

After the data on volcanic glass had been evaluated, the slides were re-examined to determine the relation between the shards and the chalcedony which occurred as replacement. The shards were extremely difficult to see in thin section due to their small size and to their being surrounded by chalcedony. No shards were observed in the cotton rock zone. Most of the shards were at least 12 mm. from the contact with the limestone. The shard nearest the contact with limestone was about 7 mm. This was in the Schroyer slide.

In view of the observations made, it was concluded that chalcedony occurred as altered shards, as cement, and as

replacement of limestone.

As in the Tri-State chert there were inclusions of less than .003 mm. in size which could not be identified. Since they appeared to occur as alteration products of a volcanic glass, it seemed logical that they were a clay mineral. Although they have the same general characteristics as the fine particles of the Tri-State chert and may indeed be the same mineral, it is extremely doubtful that they were of similar origin.

DISCUSSION AND CONCLUSIONS

Chert as an Aggregate

Sweet (1940) believed that weathering and consequent porosity were the factors which determined usability of siliceous rocks as an aggregate. There is this possibility in the case of the cherts studied. The local cherts were more weathered than the Tri-State cherts. This study, however, has shown petrographic differences which account for the usefulness of Tri-State chert as an aggregate.

The Tri-State chert is composed predominately of quartz, with minor sulfides and very minor chalcedony. The local cherts are predominately chalcedony, with appreciable amounts of volcanic glass, and with minor quartz and opal. According to Bramlette (1946), the California cherts of the Monterey formation are largely equal.

According to studies by Stanton (1940), Mielenz (1946), Parsons and Insley (1944), and others, quartz is non-reactive while chalcedony, glass, and opal are reactive.

Percentage determinations were extremely difficult in the cherts due to the fine grain. Estimates were made, however, and chalcedony appeared to compose eighty to ninety percent of the local chert. Quartz appeared to compose over ninety percent of the Tri-State chert.

The conclusion was reached, that cherts containing appreciable amounts of opal, chalcedony, or glass would probably cause expansion and failure when used as a concrete aggregate. A chert composed largely of microcrystalline quartz, such as is found in the Tri-State area, would probably cause no such reaction and would make an excellent concrete aggregate.

Origin of Chert

General Discussion. As each individual chert throughout the world, has been studied and evaluated on the basis of evidence found locally, certain conclusions have been reached concerning its origin. In nearly every case the investigator has presented valid field or petrographic evidence in support of his conclusions. Most authors agree that chert can be formed in many different ways. Most studies have been conducted on the basis of evidence found only in the particular

chert being investigated.

A few authors have been guilty of attempting application of their favorite theory to other occurrences of chert, without sufficient study of that chert. This has led to much confusion concerning the origin of cherts and in some cases has tended to discredit some of the earlier work of the author.

It appears that chert has formed in many ways. If this is true then each chert should be approached with an open mind and investigation conducted accordingly. As Twenhoeel (1919) expressed it:

Nature forms the same things in different ways and rare indeed is the occurrence of a geologic result which was produced through the operation of a single factor. History, beginning with the founders of geology, notably Werner, has recorded the errors of these who have thus assumed.

If cherts are polygenetic, then they may, in the future, be classified on the basis of genesis. A petrographic classification would be extremely difficult at the present time but improvement of petrographic methods may allow that sort of classification.

Origin of Tri-State Chert. The results of this study agreed with the work done by Fowler and Lyden (1935). They recognized, however, only two periods of chert formation. They referred to "older" chert and "younger" chert. They also recognized the mineralization period. It was observed

in this investigation that a great deal of chert and jasperoid was formed during this mineralization period.

It should be pointed out that the cherts used in this study were taken from the highly mineralized fault zone of the Blue Goose mine. The work of Fowler and Lyden (1953) was with cherts collected from surface outcrops, which occur many miles from the highly mineralized zone. It is understandable that only minor chert and jasperoid, of the mineralizing period, would occur in the areas they studied. Briefly their evidence is as follows: (1) association of chert bodies with fault and joint planes, (3) a tendency for chert to follow laterally along a stylolite plane, (4) a decrease in thickness of chert, away from a structural weakness, (5) replacement, on one side only, along a stylolite seam. The paper also presented microscopic evidence of replacement.

This study showed evidence of replacement during the first stage of chert formation and indicated both replacement and cavity filling during the second and third stages.

Tarr (1933) stated that the chert of the Boone formation is syngenetic; that it was "deposited chemically on the sea floor at the time of deposition of the enclosing limestone beds". He objected to the epigene theory on the basis of (1) the widespread occurrence of chert and (2) the lack of a satisfactory source of silica.

Fowler and Lyden (1935) admitted that they could not satisfactorily explain the source of silica but pointed out that the evidence of replacement could not be ignored.

The author has postulated an idea which seems to explain satisfactorily the features of the Tri-State chert.

Tarr's (Tarr, 1926) explanation of the source of silica seems well founded. He presents analyses of streams from all over the world which show them to be high in silica. Analyses of sea water, however, indicate a very low silica content. He explains this change of silica content on the basis of precipitation by electrolytes. If, however, the silica separated out as a density current it would fail to show up in an analysis of sea water when sampled at the surface. Also, it would tend to be intimately mixed with the sediments on the sea floor.

Pettijohn (1949), p. 332, suggested that the source of silica for some cherts may have been the underlying or overlying shales, but he failed to elaborate on this idea. If in the process of compaction, the limestones became lithified while the shales were still only partially compacted the shales would contain enormous quantities of silica bearing connate water.

Upon further compaction these connate waters would be forced out. If the silica was still in solution, it could very easily be precipitated by adjoining limestones. The tendency would be to follow planes of weakness, such as

joints and stylolites, if these had formed, or smaller channelways if the larger features were not present. This idea is applicable in explaining the vast quantities of hydrothermal silica. A magmatic source capable of the mineralization which is present could be a source of considerable silica. It could also be capable of extensive alteration of the sedimentary rocks present. If silica bearing connate waters were present in deeper shales they might have been liberated by heat alone. This would cause upward migration of silica bearing fluids, particularly along zones of weakness, and deposition of silica both as a replacement and as a cavity filling. This helps explain the large amount of silica in the Tri-State district.

Although much work is needed before this idea is accepted or rejected, it does explain some features which have been confusing.

Origin of Local Chert. Twenhofel (1919) postulated diagenetic origin for chert of the Wreford formation, which he studied in southern Kansas. It is interesting to note that his theory needed little revision to accomodate the new information concerning volcanic glass, which has been presented in this paper.

His "theory of partial replacement of unconsolidated lime sediments either before or during the process of con-

solidation" is briefly stated;

This theory in its broadest statement maintains that the silica replaced unconsolidated sediments either before or during the process of consolidation, the silica being derived from organic and other silica mingled with the sediments, either in solid form or in solution. The silica in solution in sea water is not excluded from aiding in the formation of the chert.

In describing the growth of a nodule he states:

The process of the growth of a nodule is thought to have been something as follows. As silica in solution was carried through the sediments by diffusion, it is believed to have been precipitated about centers, such as small pieces of silica, fragments or organic matter, and, slightly extending previous conceptions, perhaps a very small "gel mass" of the type postulated by Tarr. The dominating factor in the process of nodule growth was the attraction exercised on the dissolved silica by the growing nodule. As silica was taken from solution, it destroyed the equilibrium of the solute, resulting in more silica being diffused toward the nodule. A relatively sharp boundary was maintained between the limestone and the chert by the pressure which the growing nodule exercised on the associated lime sediments and which favored their going into solution.

Although Twenhofel's Theory is worthy of consideration, it needs some revision to account for all facts observed. Probably the lack of a reasonable process by which great amounts of silica could be accumulated into beds was the principal reason for the development of his diffusion accretion idea, although he described banding in the nodules which could have been accretive. Banding was not observed in the specimens used in this investigation, except that described as cotton rock.

The local cherts show no tendency to thicken at points of structural weakness as has been observed in the Tri-State chert but show a very even areal distribution.

The conclusion was drawn, that the local cherts were originally ash beds which fell in the site of deposition of limestone. Due to the fine size of the glass particles they were easily suspended in the air, and in the water into which they fell. This being the case the period of time for accumulation of the ash, on the ocean floor, was extensive. During this period, normal deposition of lime continued, but was overshadowed by silica deposition. During and after the ash fell, considerable silica was dissolved by sea water and being of slightly greater density than sea water and being of slightly greater density than sea water became mixed with the pyroclastic glass. After cessation of glass deposition the lime continued to be deposited. Although this silica was bedded, it was in a mushy state; perhaps the "gel mass" of Tarr (1926). Replacement of calcareous fragments and fossils within the chert began as soon as sufficient silica had accumulated. As compaction due to further sedimentation continued, there was a tendency for the silica to replace the surrounding lime or limestone, and to fill the interstices.

The glass particles and altered glass particles account for the source of silica, and explain the wide distribution and great continuity of the chert beds. The process described

above accounts for abundant evidence of replacement. The cotton rock zone appears to be a zone of replacement of limestone by silica. Compaction could account for the sharp contacts between chert and limestone. It was concluded that the local cherts were formed in this manner.

It should be pointed out that Twenhofel's diffusion accretion idea could be correlated with Pettijohn's idea of adjoining shales as a silica source, and application made to these cherts. This is especially true if glass shards are considered the nuclei of accretion as described by Twenhofel. If this was the case, the silica source would have been dominately normal sedimentary processes with an undetermined contribution of silica made by volcanic glass. The original amount of glass present would be very difficult to determine.

In view of the identification of volcanic glass and the postulation of the origin described above, the question arose concerning the source of such great quantities of pyroclastic material. Moore (1949), p. 233-4, made the following statement:

No record of Permian folding is found in the western United States, but crustal unrest is indicated by association of fossiliferous Permian strata with volcanic deposits, which in some areas total thousands of feet. Such rocks occur in California, Oregon, and Idaho, and each area includes lava flows, ash beds, and tuff. This evidence of volcanism is noteworthy, inasmuch as Paleozoic rocks older than Permian in the western United States are not associated with volcanic rocks.

The volcanic glass particles were small enough to have

been carried by air currents for great distances. The prevailing westerlies would have tended to carry such particles from west to east. This appears to be the logical answer to the question of source of volcanic glass.

Evaluation of Chert as an Aggregate

Differential Thermal Analysis. The D. T. A. curves consistently showed stronger inversions at or near 580°, the inversion point of quartz, for the Tri-State cherts than for the local cherts. Curves illustrating this may be seen on page 39. These curves should not be interpreted to mean that every chert which shows a strong quartz inversion is a usable aggregate. The Florence shows a quartz inversion but the quartz was observed to be largely subhedral replacement of calcite.

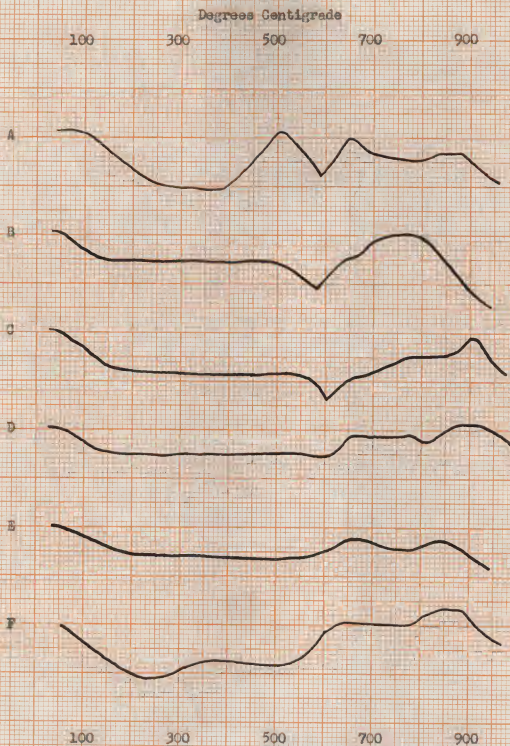
These curves are not a usable criterion at present. They were presented here to illustrate the possibility of use at some future date.

Petrographic Examination. When viewed in thin section the finer grains of Tri-State chert appeared to have wavy extinction. A high percent of each slide could be seen to be quartz, even in thin section, but it appeared that the finer material was chalcedony. When the chert was viewed after being crushed to less than 250 sieve size, however, the

EXPLANATION OF PLATE I

Differential Thermal Analysis (DTA) Curves

- A. DTA curve of M bed chert showing strong quartz blip with peak of quartz inversion at 590°C.
- B. DTA curve of OPQ bed chert showing strong quartz blip with peak of inversion at 590°C.
- C. DTA curve of R bed showing strong quartz blip with peak of inversion at 600°C.
- D. DTA curve of Florence chert showing a very weak quartz inversion point.
- E. DTA curve of Schroyer chert showing no definite quartz inversion.
- F. DTA curve of Threemile chert showing no definite quartz inversion.



silica grains showed no tendency to have fibrous or wavy extinction. Grains down to about .004 mm. could be seen clearly. It was concluded that the apparent wavy extinction had been due to grains, other than the one being examined, going to extinction. Since the grains were smaller than the thickness of the slide, and since all optical orientations were present, the grains above and below a particular grain had caused it to appear to have wavy extinction.

When crushed fragments of the local cherts were examined, the fibrous nature of the silica could be seen even in grains which were less than .004 mm. in size.

Besides the difference in extinction characteristics, there was a difference in index of refraction. The index of refraction for all fragments of Tri-State chert which were examined, was very close to 1.55, being slightly higher than 1.55. No fast and slow directions could be determined due to the random orientation of the grains. The index of 1.55 indicated quartz.

The index of refraction for fragments of local chert varied more than that of the Tri-State chert. This was attributed to the effect of glass in the chert. The fragments which were composed of anisotropic silica, showed an index of refraction of 1.53, which indicated chalcedony.

On the basis of these findings it was concluded that in most

cases a good aggregate could be separated from a poor one. If the chert in question is crushed to less than 250 sieve size and is examined for index of refraction and for extinction position, a chert which is seen to be composed almost entirely of microcrystalline quartz might be safely used as an aggregate.

There may exist cherts which are gradational between the quartz chert of the Tri-State and the predominately chalcedony chert of the Manhattan area. Such cherts would be difficult to evaluate. Before such petrographic evaluation as that described above can enjoy much success, some standards must be set up. A method of measuring quartz to chalcedony ratio must be devised. The percentage of chalcedony which can be accepted in an aggregate will probably have to be determined experimentally.

RESUME OF CONCLUSIONS

Origin of Tri-State Chert

The evidence of replacement of limestone in the Tri-State chert was abundant. This investigation has shown both cavity filling and replacement. Fowler and Lyden (1935) have shown the source of silica to be outside the limestones which contain chert nodules or beds. It was concluded that the first stage of chert formation was replacement of limestone with silica derived from connate waters in the adjoining or nearby

shales. The second stage of chert formation derived its silica from deeper formations and the third stage, which accompanied mineralization, derived silica from both a magmatic source and from connate waters.

Origin of Local Chert

Evidence of replacement was abundant in the local cherts. There was also conclusive evidence of the existence of volcanic glass. It was not clear what percentage of silica was contributed by volcanic glass and what amount by normal sedimentary processes. In view of the world wide coincidence of volcanism and chert formation, and in view of the apparent abundance of volcanic glass, it was concluded that the local cherts were largely the result of contemporaneous deposition of volcanic ash and lime sediments. The chert beds represent ash deposits which fell in marine waters, were partially dissolved, and remained as an unconsolidated mass while lime was deposited above it. The overlying and underlying lime deposits became consolidated before the silica and as compaction proceeded, replacement of the limestones proceeded until the available supply of dissolved silica was exhausted.

Chert as an Aggregate

Studies of various minerals have shown that opal, chalcedony, and silica glass tend to form alkali silicates when used with a high alkali cement. These silicates are gels, which form on the surfaces of aggregate particles. They cause expansion and failure in the concrete. Tests on quartz and cherts composed of microcrystalline quartz have shown no reaction with high alkali cement.

This investigation showed the Tri-State chert to be composed almost entirely of microcrystalline quartz. The local cherts were predominately composed of chalcedony, with appreciable amounts of volcanic glass. It was concluded that this petrographic difference is the main reason Tri-State chert is a good aggregate while other cherts are poor aggregates.

Differentiation of Good and Poor Aggregate

Differential Thermal Analysis. The differential thermal analysis curves showed a greater quartz when Tri-State chert was tested than when local chert was tested. If a proper study were made to determine how much of a quartz inversion indication is required for a siliceous aggregate to be considered good, this method could probably be used to differentiate between good and poor aggregate. Obviously much work must be

done before this method will be useful.

Petrographic Method. By examining thin sections of the cherts it was possible to distinguish between quartz and chalcedony when the grains were about .030 mm. or greater in size. Unfortunately most of the grains were .010 mm. or less in dimension.

When fragments of the cherts were crushed to less than 250 sieve size, the extinction could be seen clearly in grains down to about .004 mm. The quartz of the Tri-State chert showed definite extinction while the chalcedony which, dominated in the local chert, could be seen to be fibrous.

The index of refraction for the fragments of the Tri-State cherts was determined by oil immersion. It was a very consistent 1.55, the index of quartz. The index of refraction of fragments of the local cherts was more variable but for the most part was greater than 1.53 and less than 1.54. This is the index of refraction of chalcedony.

It is believed that any competent petrographer, by determining index of refraction and by study of extinction positions of the fine grains, can give a rough estimate of the percentage of quartz to chalcedony (or other mineral) of a particular chert. Assuming that quartz is non-reactive and that chalcedony, opal, and glass are reactive, a reasonable evaluation of a particular chert could be made.

Improvement of petrographic methods and testing of aggregates studied would increase the accuracy of this method.

ACKNOWLEDGMENTS

To Prof. A. B. Sperry, head of the Department of Geology and Geography and the authors major instructor, sincere gratitude is expressed for arousing the authors interest in the cherts, and for his continued interest and cooperation. Also, to John D. McNeal and Carl F. Crumpton of the Kansas State Highway Department, appreciation is expressed for their interest and assistance.

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MINERALOGY OF CHERTS AS A FACTOR IN THE
USE OF SILICEOUS AGGREGATES FOR CONCRETE

by

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B. S., Kansas State College
of Agriculture and Applied Science, 1950

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Geology and Geography

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1953

The cherts of the Tri-State mining district have been used as concrete aggregate for many years and the concretes in which they have been used have fine service records, almost without exception. Elsewhere, cherts have caused considerable trouble when used as concrete aggregate. It was the purpose of this investigation to determine differences between Tri-State cherts and other cherts which would account for this difference. Also it was desired to devise or discover methods of distinguishing between a good chert aggregate and a poor chert aggregate before its use.

During the course of the investigation, certain facts were revealed and conclusions drawn concerning the origin of the cherts being studied. These were included in the report.

Samples were collected from the Blue Goose mine at Picher, Oklahoma. These samples were similar to the great quantities of chert commonly used as aggregate in that district.

For comparison with the Tri-State cherts, local chert samples were taken from the Wreford and Barnston formations in the Manhattan, Kansas area.

Studies were made of the cherts by use of the ore microscope, the petrographic microscope, and by differential thermal analysis.

The petrographic study consisted of both thin section studies and crushed fragment studies. A thin section was cut from each member studied and these sections studied to determine mineral relationships. The crushed fragment study proved to be more useful in actual mineral identification than thin sections. After examination of the fragments, the relationships of minerals in the thin sections became clearer. For the crushed fragment study the cherts were crushed to less than 250 sieve size, and a bromoform separation made. The bromoform was adjusted to a specific gravity of 2.45. The fragments were then studied as light fractions and heavy fractions.

Differential thermal analyses were made in an attempt to identify the particles of less than .004 mm. diameter, which were abundant in all cherts examined. The analyses failed in this identification, but showed a difference in quartz content of the various cherts which proved to be significant.

This investigation showed the Tri-State cherts to be composed largely of microcrystalline quartz. The local cherts were predominately chalcedony with appreciable amounts of volcanic glass. Tests by other investigators have indicated that opal, chalcedony, and glass, react with high alkali cements to form alkali silicates, which in turn cause expansion and failure in concrete. Other tests have indicated

that quartz is inert when used with such cement. It was concluded that this mineralogical characteristic, of the Tri-State cherts, explained the difference between cherts when used as aggregate.

On the basis of evidence revealed by this investigation in addition to evidence presented by other authors it was concluded that the Tri-State cherts were formed partially by metasomatic replacement of limestones and partially by hydrothermal cavity filling.

Of importance in this investigation was the identification of volcanic glass in the local cherts. There were indications that the cherts had been largely volcanic glass at one time. The conclusion was reached that the local cherts were the result of penecontemporaneous deposition of lime and volcanic ash.

It was shown that differential thermal analysis may ultimately be useful in evaluating a chert for use as an aggregate. It was also shown that petrographic examination can probably be used at present for such evaluation.