Calcite Cementation of Pleistocene Glacial Deposits in Southwest Michigan

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CALCITE CEMENTATION OF PLEISTOCENE GLACIAL DEPOSITS IN SOUTHWEST MICHIGAN

by

Robert Lee Tolliver

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Master of Science
Department of Geology

Western Michigan University
Kalamazoo, Michigan
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Six calcite-cemented glacial deposits in southwest Michigan were studied to determine the conditions of calcite precipitation. Samples from two of the sites contain only pore-filling equant cements, indicating cementation in the phreatic zone. Cements from the other locations all display cement morphologies characteristic of the vadose zone, including abundant meniscus cements and irregular grain coatings. Pore-filling cements occur only in smaller pores at these sites.

Stable isotope analysis of cements from all locations ($\delta^{13}C$ from -9.20 to -3.67, $\delta^{18}O$ from -7.96 to -5.49) indicates that the cements were not precipitated by glacial melt waters and that the carbon originated from a mixture of soil-CO$_2$ and detrital carbonate. Comparison of $\delta^{18}O$ for a water sample and the cement from a well in Kalamazoo County indicates that the present water did not precipitate the cement. A $^{14}C$ age of 11,495 ± 140 years BP was obtained for one sample. These three factors suggest that significant precipitation of calcite cement is not occurring at present.

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Robert Lee Tolliver
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Calcite cementation of pleistocene glacial deposits in southwest Michigan

Tolliver, Robert Lee, M.S.
Western Michigan University, 1992
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INTRODUCTION

Coarse-grained glacial deposits in Michigan are commonly indurated. These deposits, commonly referred to as "crag," are found in many other formerly glaciated regions including Indiana (Henderson, 1973), New York, and Vermont (Friedman and Kolesar, 1971). The degree of cementation ranges from extremely friable to fully indurated. Some exposures include both cemented and noncemented deposits. Other exposures are completely cemented, although they usually contain variations in the degree of cementation.

Previous Work

There have been few studies of cemented Pleistocene glacial deposits. Friedman and Kolesar (1971) looked at cemented glacial gravels in Proctor, Vermont and Troy, New York. These deposits are cemented by low-magnesium calcite. The cements fill pores with crystal sizes increasing away from grain boundaries and crystals are commonly bladed. For the Proctor, Vermont cements, they attributed the source of the calcium carbonate to a metamorphic dolostone underlying the glacial drift based on the observation that cement was present only where the deposits were overlying this dolostone. The source of the calcium carbonate

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for the Troy, New York cements was not determined.

Henderson (1973) examined outwash deposits in Indiana. His samples showed variations in the degree of cementation with finer-grained deposits being more intensely cemented. The cements occurred as pore-fillings, films surrounding grains, and at grain contacts. He suggested that the source of the calcium carbonate was glacial till, and that cementation was the result of increase in water temperature, evaporation, pressure release.

James (1985) did a detailed study of a cemented outwash deposit in St. Joseph County, Indiana. Greater than 98% of the cement was calcium carbonate, with minor limonite and gypsum cement present. He determined that four factors controlled cement formation and distribution: primary stratification, sediment grain size, framework grain composition, and proximity to near-surface processes. Cement growth occurred primarily parallel to lamination, with the dimension of cement zones normal to laminae being rarely greater than 0.25 percent of the dimension parallel to laminae. Coarser-grained strata contain grain contact and pore-lining cements, while finer-grained zones contain pore-filling cements. There is a lower percentage of free surface area on silicate grains adjacent to carbonate fragments than on isolated silicate grains. The carbonate fragments may act as seeds for the nucleation and spread of
crystal growth. However, he found no overall correlation between percent carbonate cement and percent carbonate grains. Finally, all of the cemented deposits are within 7 meters of the surface, suggesting a relationship to soil-forming processes.

Research Objectives

The purpose of this study is to determine the factors controlling the occurrence and distribution of cements within Pleistocene glacial deposits. The sparse literature on these deposits does not adequately address this problem.

The first objective of this study is to determine the mineralogy of the cements present in these deposits. Previous studies have found that the cements in glacial drift deposits are predominantly calcite.

The second objective is to determine what physical and hydrological factors control the occurrence of cements within glacial deposits. Are there textural and/or structural features of the deposits themselves which are controlling the distribution of cement? Porosity and permeability relationships will have an important effect on the amount and rate of water available to precipitate cements. Does the hydrologic setting of these sediments control the distribution of cements? The crystal morphologies of calcite cements found in the vadose zone can be very different.
from those found in the phreatic zone (Longman, 1980).

The third objective is to determine what chemical factors control the occurrence of cements in these deposits. What is the source of ions available for precipitation of cements? What are the driving mechanisms of precipitation? The Ca$^{2+}$ and CO$_3^{2-}$ ions must be available in sufficient quantity to form calcite, and some driving mechanism must create waters oversaturated with respect to calcite allowing it to precipitate out of solution.

The final objective was to attempt to place constraints on the timing of cementation. Were the cements precipitated during deglaciation, are they precipitating today, or were they precipitated sometime in between? It is also possible that they have been precipitating throughout the last 14,000 years.

Research Methods

Cemented deposits were examined at six localities in southwest Michigan (Figure 1). These sites included three outwash deposits, one channel deposit within a clay till, an esker, and a lacustrine sand. The sedimentary features and relationships were described, along with the site location relative to major regional geomorphic structures such as moraines. Of particular importance was the relationship between degree of cementation and sediment type and/or
Figure 1. Location Map of Study Sites.
structures.

Thin sections were prepared for examination with a petrographic microscope from samples taken at each site. Due to the friability of these deposits, most samples were impregnated with epoxy. The epoxy was dyed blue to show porosity. Two thin sections from each site were stained with Alizarin Red-S and potassium ferricyanide to identify calcite (Dickson, 1966). In addition, two thin sections from each site were polished for cathodoluminescence microscopy.

Examination of thin sections with a petrographic microscope was used to determine cement mineralogy and morphology, and to determine the relationship between the cements and the sediments in which they reside. The scanning electron microscope was also used to supplement the thin section examination. Cathodoluminescence microscopy was used to determine changes in water trace element composition during cementation. Thin sections were point counted to determine percentage of detrital carbonate.

Stable isotopes were used to identify the geochemical conditions of precipitation. Three microsamples of cement were taken from each site. These were obtained using a dental drill at the University of Michigan. They were analyzed for both $^{13}$C and $^{18}$O isotopes. Water samples from well SA-2 in Kalamazoo County were sent to the University of 
Waterloo, Waterloo, Ontario for analysis of stable isotopes of carbon and oxygen. These results were compared with the results for the cements from this well to determine if they were in equilibrium.

Additional analyses include carbon-14 dating of the cements at one site and X-ray diffraction of till samples and clay clasts to determine the presence of calcite.
GEOLOGY

Regional Geology

The entire state of Michigan was covered by glaciers during much of the Pleistocene epoch. The advance and retreat of these glaciers eroded the existing bedrock and left behind thick deposits of unconsolidated sediment. These deposits now cover almost all of southern Michigan. The thickness of this glacial drift exceeds 500 feet in some parts of the state (Farrand and Eschman, 1974).

The last glaciation, the Wisconsinan, occurred between approximately 110,000 and 10,000 years before present (BP) (Sugden and John, 1976). The maximal extent of glaciation occurred around 18,000 years BP (Andrews, 1987), during the Late Wisconsinan. During this period, ice extended as far south as southern Indiana and Ohio (Flint, 1971). It is from this episode of glaciation that the majority of Michigan’s glacial deposits are derived.

During the Late Wisconsinan, the glacial sediments in southwest Michigan were deposited by two ice lobes (Figure 2). The Lake Michigan lobe occupied what is now Lake Michigan and the surrounding area. The Saginaw lobe advanced southwestward through Saginaw Bay towards Kalamazoo County. During their retreat, these lobes formed a series
Figure 2. Michigan and Saginaw Lobes During the Late Wisconsinan (after Leverett and Taylor, 1915).
of moraines which coalesce along a line running north from eastern Kalamazoo County (Figure 2). Between these moraines, meltwater deposited additional sediments.

The moraines, which mark periods of stagnation during glacial retreat, are composed of sediments deposited directly from the ice and sediments deposited by fluvial action. Sediments deposited directly from glacial ice, without fluvial transport, are commonly referred to as till. Because of this lack of transport, till is poorly sorted, lacks bedding structures, and often contains a large clay fraction. Sediments deposited by meltwater transport are better sorted and contain sedimentary structures such as bedding and climbing ripples. These sediments deposited in front of the glacier due to fluvial processes are referred to as outwash. Two additional types of deposits important to this study are eskers and lacustrine sands. Eskers are sorted, stratified sands and gravels deposited by interglacial or subglacial streams. Lacustrine sands, deposited by lakes formed at the margins of glaciers, are well sorted and contain crossbedding and ripples.

It is the sorted, stratified deposits of sand and gravel that are of importance to this study. Their high porosity and permeability allow sufficient transmission of water for the precipitation of calcite cements.
Site Geology

Four of the sites in this study occur in glaciofluvial deposits on or near a moraine. One site is located in an esker, formed by deposition in an inter or sub-glacial stream. And the last site is located in a lacustrine sand along Lake Michigan. Each of the six study areas will be discussed in detail in the following sections.

Balkema Quarry

The Balkema Quarry (Figure 3) is located southwest of Kalamazoo in Texas Township, Kalamazoo County (E 1/2, NW 1/4, NW 1/4, sec. 4 T4S R12W). The quarry exposes sediments deposited at the front of the Outer Kalamazoo Moraine. This site is located near the top of the glaciofluvial fan described by Steinmann (in progress).

Sediments are predominantly massive, coarse-grained sands and gravels (Figure 4). These sands and gravels are poorly sorted with grain sizes from 0.5 mm to 100 mm. Grains are sub- to well rounded. Thin lenses of well sorted sand, up to 15 cm thick, are also present. These sands contain both horizontal and cross-bedding.

The cemented zone is located along the north and east walls of the quarry, approximately 0.5 to 3 meters below the surface. This zone of cementation is approximately one
Figure 3. Surficial Geology of Allegan, Kalamazoo, and Van Buren Counties (after Farrand and Bell, 1982).
Figure 4. Balkema Quarry in Kalamazoo County.

meter thick and extends horizontally around the north and east walls. Within this zone the coarse-grained sands and gravel are cemented, while the fine-grained, well sorted sands are not. Cemented sands and gravels are well cemented, but not fully indurated. Some samples could be broken apart by hand.

**Bloomingdale Pit**

The Bloomingdale Pit is located south of Bloomingdale in Van Buren County (SW 1/4, NE 1/4, SE 1/4, sec. 29 T1S R14W), between the inner and outer Valparaiso Moraines, but closest to the inner moraine (Figure 3). Most of the quarry is composed of outwash sands and gravels. Monaghan, Larson, and Gephart (1986) measured a section on the south wall. They found three tills with outwash at the bottom and between the top and middle tills. These tills are not exposed throughout most of the rest of the quarry. A discontinuous lacustrine clay was present near the land surface, however most of this has been excavated.

Most of the north half of the quarry is composed of coarse-grained sands and gravels. Sands and gravels are interbedded with both horizontal bedding and cross-bedding present. The gravels are poorly sorted with some interbedded well-sorted sands. These gravels tend to be moderately to well cemented, while the well-sorted sands...
are not cemented.

The south half of the quarry is predominately cross-bedded, well sorted sands with some interbedded gravels. These sands are generally not cemented, however some thin lenses of cementation were found. The gravels in this part of the quarry are occasionally loosely cemented.

One area along the west wall is predominantly poorly sorted gravel with thin lenses of well sorted, coarse-grained sands (Figure 5). Grains are sub-rounded to well rounded, grain sizes ranging from 0.5 mm to 50 mm. This is the most extensively cemented area with some layers completely indurated. Bedding is present with alternating coarser- and finer-grained layers. There is no bedding within layers of the same grain size. Samples discussed in this study were taken from this area. One feature noted, which is characteristic of other study areas as well, is that within a cemented zone, finer grained layers are more extensively cemented than coarser layers.

In the upper northeast area of the quarry, cemented ledges of well-sorted sand occur in the top five feet of sand, directly beneath the lacustrine clay. The unique feature of this zone of cementation is the presence of clay clasts and laminated carbonates (Figure 6). These two features are commonly associated, with laminated carbonates appearing to spread laterally away from the clasts.
Figure 5. Bloomingdale Pit in Van Buren County.

(A) Interbedded sands and gravels. Hammer for scale. (B) Close up of interbedded sands and gravels. Hammer for scale.
Figure 6. Laminated Calcite and Clay Clasts, Bloomingdale Pit. Hammer for scale.
Laminated zones are usually about 2 to 5 mm thick, are discontinuous, and contain floating grains from the surrounding sand.

Blue Ridge Esker

The Blue Ridge Esker (Figure 7) is located south of Jackson in Jackson County (NE 1/4, NE 1/4, NW 1/4, sec. 6 T4S R1E). This esker is the result of deposition by a subglacial or intraglacial stream. The study area is a gravel quarry.

The esker is composed of well-sorted sands with channels of coarse-grained sand and gravel present throughout (Figure 8). The channel deposits are intensely cemented. They are composed of massive gravels with boulders up to 1.5 meters in diameter, and cross-bedded sands and gravels. The cross-bedded sands and gravels display alternating layers of different grain size. The finer grained layers range in grain size up to 6 mm, and are more indurated than the coarser-grained layers. The massive gravels are also well indurated. The finer-grained sands comprising the rest of the esker are poorly cemented. Weathering of these zones made them impossible to sample.

Glen Haven Shores

The Glen Haven Shores study area (Figure 3) is located
Figure 7. Surficial Geology of Jackson County (after Farrand and Bell, 1982).
Figure 8. Blue Ridge Esker South of Jackson.

(A) Cross-bedded sands and massive boulders. Massive boulders form steep faces. (B) Contact between Cross-bedded sands and massive boulders.
along Lake Michigan south of Glenn in Allegan county (NW 1/4, NW 1/4, NW 1/4, sec. 7 T1N R16W). Figure 9 shows a cross-section of the study area. Most of the bluff is composed of very well-sorted, cross-bedded, fine-grained sand. Grain size ranges from 0.1 to 0.5 mm, with grains being rounded to well rounded. The top 3 to 5 meters is a clay-rich till. Larson and Monaghan (1988) suggest that the sand may represent a subaqueous fan deposit or a mid- and lower delta forsets of a proglacial lake. The top 3 to 5 meters of the sand is well cemented. However, due to bluff erosion, much of the cemented zone is severely weathered, leaving only a small area of outcrop exposed (Figure 10). Large blocks of this fully indurated sand can be found along the lake shore at the base of the bluff (Figure 11).

Lowell

This study area (N 1/2, NE 1/4, sec. 8 T6N R9W) is located east of Grand Rapids, Michigan, near the town of Lowell, in Kent County (Figure 12). The exposure is a cross-bedded, coarse-grained sand and gravel channel deposit within a clay-rich till (Figure 13). The cross-beds consist of alternating beds of sand and gravel up to 10 cm thick. The finer-grained layers are moderately sorted, while the coarser layers are poorly sorted. The entire
Figure 9. Stratigraphic Section at Glen Haven Shores.
Figure 10. Bluff, Glen Haven Shores, Allegan County.

(A) Cross-bedded sands. (B) Close up of cross-bedded sands. Hammer for scale.
Figure 11. Shoreline, Glen Haven Shores, Allegan County.

(A) and (B) Large blocks of cemented sands which have fallen from the eroding bluff. Hammer for scale.
Figure 12. Surficial Geology of Kent County (after Farrand and Bell, 1982).
Figure 13. Study Site near Lowell in Kent County.

(A) Cross-bedded sands and gravels. (B) Close up of cross-bedded sands and gravels. Hammer for scale.
channel deposit is cemented, with the finer grained beds more tightly cemented. The lower beds also contain till clasts from the surrounding till.

Wells SA-1 and SA-2

Wells SA-1 and SA-2 (Figure 3) are located southwest of Kalamazoo in Kalamazoo County (NE 1/4, SE 1/4, NW 1/4, sec. 4 T4S R 12 W). They are nested wells located approximately 1/4 mile from the Balkema Quarry, at the top of the glaciofluvial fan studied by Steinmann (in progress) and Barrese (1991). Figure 14 shows a cross section of the wells. This section is predominantly sand and gravel with approximately 1.5 meters of till at the top. A cemented zone occurs between 7.5 and 9 meters below the surface. This section is composed of moderately sorted coarse sand and gravel and is very well cemented. Grain size in this zone is from 0.1 to 50 mm and grains are sub- to well rounded.
Figure 14. Stratigraphic Sections for Wells SA-1 and SA-2 in Kalamazoo County.
PETROLOGY

Preparation

Thin sections were prepared from hand samples taken from each of the six study locations. Most of the samples were impregnated with epoxy to prevent plucking of grains during grinding. The epoxy was dyed blue to delineate original porosity. The rock chips were then mounted on glass slides and ground to a thickness of approximately 30 microns. Twelve slides, two from each study location, were polished with a silica polishing compound, in preparation for cathodoluminescence microscopy.

Some thin sections were then stained to determine the type of minerals present as cement. Alizarin red S and potassium ferricyanide were used according to the method of Dickson (1966). This stain will distinguish between calcite, ferroan calcite, and dolomite. Staining indicated that all of the cements were calcite.

Sample Description

Thin sections from all locations were examined for grain size, sorting, and roundness using a petrographic microscope. Detrital composition was determined by use of a point-counting stage. Two hundred points were counted on
each thin section. Detrital composition was plotted on a ternary diagram as Quartz vs. Carbonates vs. Lithics + Feldspars. These results are summarized in Figure 15. This method of plotting the detrital composition was used to determine possible correlation between detrital carbonate and the presence of calcite cement. Volume percentage of cement and porosity were also included determined. The results of this analysis are discussed below. Cement morphology will be discussed in more detail in the next section.

Balkema Quarry

The samples from the Balkema Quarry are poorly sorted gravels. There is no bedding present at hand sample or thin section scale. Samples from this quarry are poorly cemented and quite friable. Grain sizes range from 0.5 mm to 100 mm. Grains are sub- to well rounded. Detrital composition is divided fairly evenly between quartz, rock fragments, and carbonates, with quartz being slightly more abundant in most samples (Figure 15). Feldspars are rare. Original porosity (cement + porosity) ranged from 17.5 to 36 percent of the total volume. Calcite cement comprises approximately 11.5 percent of the total volume, with a range of 9.5 to 14 percent. Porosity is in the range of 10.5 to 24 percent.
Figure 15. Ternary Plot of Modal Composition. Quartz(Q) vs. Carbonates(C) vs. Feldspar + Lithics(F + L).
**Bloomingdale Pit**

The cemented samples from this site are mostly poorly sorted sands and gravels, with some lenses of well-sorted sand. All samples are well cemented. Grains in all samples are sub- to well rounded. Grain sizes range from 0.5 mm to 50 mm. Within hand samples of the same grain size and sorting, no bedding features are observed. Detrital composition is fairly evenly divided between quartz, rock fragments, and carbonates, but with some variation between thin sections (Figure 15). There is also variation in the percentage of cement present. Percentages range from 10.5 to 28.5% of the total volume. Porosity ranges from 7 to 22.5 percent. Original porosity ranged from 17.5 to 40.5 percent.

**Blue Ridge Esker**

Cemented samples from this site fall into two distinct groups: massive, poorly-sorted gravels and cross-bedded, well-sorted, coarse sands. The gravels are well cemented with grain sizes ranging from 0.2 mm to approximately 300 mm. The sands have grain sizes from 0.5 mm to 6 mm. The cross-bedding forms alternating layers, approximately 4 to 6 mm thick, of different grain size. The coarser layers are less tightly cemented then either the finer-grained cross-beds or the massive gravels. Grains in all samples
are rounded to well rounded.

Point counting reveals a detrital composition of predominantly carbonate rock fragments (Figure 15). Carbonate rock fragments comprise between 44 and 66% of the total detrital content in all samples. Other rock fragments are generally more abundant than quartz. Cements comprise only 10 to 17% of the total volume. Porosity falls into two groups: the poorly-sorted gravels have a porosity near 2%, while the well-sorted, coarse sands have porosities greater than 15%. Likewise, original porosity falls into two groups, with the gravels at approximately 15% and the coarse sands at approximately 35% of the total rock volume.

Glen Haven Shores

The Glen Haven Shores samples are well sorted, fine-grained sand. These samples are well cemented. Planar cross bedding is common. Grains are from 0.1 to 0.5 mm and rounded to well rounded. Layers of magnetite following the cross bedding can be seen in both hand sample and thin section. In thin section these layers appear to be two or three grains thick, with the magnetite interspersed with the other detrital components.

The detrital composition is predominantly quartz (Figure 15). Quartz comprises at least 80% of the detrital
content in all samples. Neither detrital carbonates, rock fragments, or feldspars comprise more than 12% each. Calcite cements occupy a large percentage of the total volume, approximately 35%. Porosity is less than 17%, some of which is due to grain plucking during preparation of the thin sections. As a result of the well-sorted and well-rounded nature of these samples, original porosity was greater than 39% of the total volume.

Lowell

Cemented samples from this location are moderately to poorly sorted gravels. Samples are moderately to poorly cemented. Cross bedding alternates coarser-grained, poorly sorted layers with less coarse, moderately sorted layers. The coarser layers are less tightly cemented. Clasts from the surrounding till are abundant in samples from the outer margins of the channel.

Detrital composition is predominantly carbonate rock fragments (Figure 15). Carbonate grains comprise between 51 and 71.5% of the detrital content of the sample. Quartz and non-carbonate rock fragments are present in approximately equal, but varying amounts. Total cement present is variable, from 10 to 25% of the volume. Porosity is less than 20 percent, with original porosity less than 34%.
**Well SA-1**

Samples obtained from well SA-1 are tightly cemented, moderately sorted, fine gravels. Grain sizes are from 0.1 to 50 mm, with grains sub- to well rounded.

Detrital composition is quite variable (Figure 15). Quartz is generally most abundant; however, carbonates are also quite abundant. Calcite cement comprises approximately one quarter of the total volume, with values of from 20 to 32 %. Porosity is very low at less than 8 % in all samples. However, original porosity ranges from 20 to 38.5 %.

**Cement Morphology**

**Background**

Examination of cement morphology is an important tool for determining the hydrologic setting in which calcite cementation took place. Cement morphology can be used to determine if a cement was precipitated in the phreatic zone or the vadose zone (Harris, Kendall, and Lerche, 1985; Longman, 1980).

In the vadose zone, pores contain both water and air. Water is held at grain contacts and beneath grains. Water at grain contacts is held by capillary forces and forms a meniscus. Cements precipitated at these locations will also form a meniscus shape (Longman, 1980), with cement...
crystals growing out to the air/water interface (Figure 16). Gravity will cause water to accumulate on the underside of grains. Cements may precipitate from these droplets forming pendant (microstalagtitic) shapes (Longman, 1980; Moore, 1989). This is shown in the middle block of Figure 16. These two cement morphologies indicate precipitation in the vadose zone.

In the phreatic zone, the pores are completely filled with water. Therefore, cements may precipitate at an equal rate from all points on the grain surface. This causes precipitation of two cement morphologies: equant and elongate. Equant cements grow at approximately the same rate along all crystal axes with crystals increasing in size towards the center of the pores (Longman, 1980). These cements may fill all pore space. Elongate cements grow fastest along the c-axis. These cements appear as blades in thin section, and are often referred to as bladed cements (Harris et al., 1985; Longman, 1980). These cements tend to grow as circumgranular crusts which do not entirely fill all pore space (Figure 16).

Study Locations

Both vadose and phreatic cements were found in the locations studied. Four of the sites contained primarily vadose cements. These locations were the Balkema Quarry,
Figure 16. Variation in Calcite Cement Morphology Within the Meteoric Environment.

(A) Meniscus cements at grain boundaries. (B) Meniscus cements plus gravity cements on bottom of grains. (C) Circumgranular crusts surrounding grains (from Moore, 1989).
the Bloomingdale Pit, the Blue Ridge Esker, and the Grand Rapids site. The other two study sites, Glen Haven Shores and well SA-1, contained only phreatic cements. Descriptions of these cements are given below.

**Balkema Quarry**

Calcite cement morphologies present at this study location include meniscus, pore-filling equant, and rare irregular micritic coatings. Pore-filling equant cements occur in pores smaller than 0.1 mm in diameter. These pores were small enough to be filled entirely with water (Figure 17A). Meniscus cements occur in larger pores (Figure 17B). Micritic cements occur as irregular grain coatings and menisci. Equant or elongate cements often occur on top of the micritic cements, indicating a change in the local hydrologic conditions.

**Bloomingdale Pit**

Meniscus, equant, and elongate cements are present at this location. Smaller pores and fine-grained sand lenses contain pore-filling equant cements. In some cases distinct suture lines are present between crystals growing from opposing grain surfaces. Meniscus cements line the larger pores. The relationship between cement type and pore size is shown in Figure 18A. Circumgranular elongate
Figure 17. Photomicrographs of Balkema Quarry Samples.

(A) Small pores are completely filled with calcite (C), while larger pores (P) only contain cement at grain boundaries forming meniscus shapes (M). Plane light. Sample BQ-2-1. (B) Large pores (P) with meniscus cements (M) at grain contacts. Plane light. Sample BQ-5.2.
Figure 18. Photomicrographs of Bloomingdale Pit Samples.

(A) Equant calcite (E) fills smaller pores while meniscus cements (M) form at grain contacts in large pore (P). Crossed nichols. Sample BP-7.3. (B) Example of circum-granular elongate cements (C). The center of the pore (P) is free of cement. Crossed nichols. Sample BP-7.3.
cements were present in a thin lens less than 1 cm across (Figure 18B). Some micritic cement may be found beneath the elongate crystals. They occurred above a lens of well cemented fine-grained sand. These cement crystals were up to 0.1 mm in length.

Some unique calcite precipitates were found in the upper 1.5 meters of sand along the north face of the quarry. These sands contain clasts of the overlying lacustrine clay. Layers of wavy laminated micrite (Figure 19A) are present and are often correlated with the presence of the clay clasts. The micrite contains "floating" detrital grains and possible organic matter. These layers are separated by cemented sands with morphologies similar to those discussed in the preceding paragraph. Rare needle fiber calcite cements are found adjacent to the laminated micrite (Figure 19B). These two features are commonly associated with caliche profiles. However, other features characteristic of caliche, such as nodules and rhizoliths, were not present.

Blue Ridge Esker

Meniscus cements, irregular micritic grain coatings, and minor amounts of pore-filling equant cements are present at this location. This location contains the best examples of gravity cements, commonly containing microsta-
Figure 19. Photomicrographs of Bloomingdale Pit Samples.

lagtite/microstalagmite pairs (Figure 20A). The gravity cements, irregular grain coats and some of the meniscus cements are composed of very fine-grained calcite crystals (Figure 20B). These cements are often overlain by coarser-grained cements. Reduction in pore space by the earlier cements may have created conditions favorable to the precipitation of coarser crystals, including pore-filling equant and circumgranular equant to slightly elongate cements (Figure 21A and B).

At this location, there is a distinct alternation of coarser and finer-grained layers in the cross-bedding. In these cases, the finer-grained zones are more tightly cemented and contain a higher percentage of the pore-filling and circumgranular equant cements.

Lowell

Meniscus cements, gravity cements, irregular grain coatings, and circumgranular equant to slightly elongate cements are present at this location (Figure 22A). Here numerous micritic grain coatings are adjacent to or overlain by coarser-grained meniscus and circumgranular cements (Figure 22A and B). The circumgranular cements are composed of equant to slightly elongate crystals and rarely fill entire pores. Suturing between crystals on adjacent grains is often present. Like the Blue Ridge Esker, this
Figure 20. Photomicrographs of Blue Ridge Esker Samples.

(A) Variations in cement morphology within a sample. Smaller pores are filled with cement (C) while larger pores (P) contain meniscus cements (M) at grain contacts. Gravity cements (G) are commonly present as stalagtite/stalagmite pairs. Crossed nichols. Sample BRE-3.1. (B) Meniscus cement (M) at grain contacts surrounding an open pore (P). Crossed nichols. Sample BRE-1.3.
Figure 21. Photo- and Scanning Electron Micrographs of Blue Ridge Esker Samples.

(A) Micritic calcite (M) overlain by larger equant crystals (E) with central pore free of cement (P). Plane light. Sample BRE-1.3. (B) Circumgranular elongate crystals (C) overlying micritic crystals (M). Sample BRE-5.
Figure 22. Photo- and Scanning Electron Micrographs of Lowell Samples.

(A) Variation in cement morphology within a single sample. Cement morphologies present include equant (E), meniscus (M), and micrite overlain by circumgranular elongate crystals (C). Crossed nichols. Sample GR-1.1. (B) Micrite (M) adjacent to larger equant (E) crystals. Sample GR-3.
location has alternating coarser- and finer-grained zones of cross-bedding, with the finer-grained zones being more tightly cemented.

**Glen Haven Shores**

Cements in this location are entirely pore-filling equant (Figure 23A and B). Increase in crystal size towards the center of the pores is noticeable in some pores. Suturing of crystals between adjacent grains is also present. Syntaxial overgrowths are present on echinoderm fragments (Figure 23B). The pore space is almost entirely filled with cement.

**Well SA-1**

Cements in this location are entirely pore-filling equant (Figure 24A and B). Increase in crystal size towards the center of pores is distinctively noticeable. Indications of crystal growth starting as circumgranular crusts is present around some grains. Crystal growth around some carbonate rock fragments began as circumgranular elongate crystals (Figure 24B), instead of the more common equant crystals. Syntaxial overgrowths on echinoderm fragments are also present (Figure 25).
Figure 23. Photomicrographs of Glen Haven Shore Samples.

(A) Pore filling equant calcite crystals (E). Half crossed nichols. Sample GHS-3.1. (B) Pore filling equant crystals and syntaxial overgrowth (S) on a detrital carbonate grain (D). Half crossed nichols. Sample GHS-1.2.
Figure 24. Photomicrographs of Well SA-1 Samples.

(A) Pore filling equant calcite crystals (E). Crossed nichols. Sample SA-1-1. (B) Pore filling equant calcite crystals (E) with crystal size increasing towards the center of the pores. Circumgranular elongate crystals (C) occur around detrital carbonate grain in center of photomicrograph. Crossed nichols. Sample SA-1-1.

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Figure 25. Photomicrograph of Well SA-1 Sample.

Pore filling equant calcite crystals (E) and syntaxial overgrowth (S) on echinoderm fragment. Sample SA-1-1.2.
Discussion

The Balkema, Bloomingdale, Blue Ridge Esker, and Lowell samples all show cement morphologies characteristic of cementation in the vadose zone. Meniscus cements, composed of both micrite and larger equant crystals, are found at each of these sites. Pore-filling and/or circum-granular cements, suggestive of water filled pores, are also present at these sites. It is common for meniscus cements to be overlain by these latter cements (Figures 21A, 21B, and 22B). There are two possible causes for this relationship. First, an increase in the amount of infiltration may allow pores which contained both water and air to become saturated with water. Secondly, the growth of calcite crystals may reduce the effective pore volume to the point where it can maintain water saturation. Within each site, there is a correlation between pore size and the presence of meniscus cements. Smaller pores do not contain meniscus cements or they are overlain by other cements, while larger pores contain only meniscus cements, gravity cements, or irregular micrite coatings. This relationship is apparent within adjacent pores (Figures 17A, 17B, 18A, 20A, and 22A).

Meniscus cements, gravity cements, and irregular grain coats are often composed of very small crystals (Figures 20A, 20B, 22A, and 22B), commonly termed micrite. Within
the vadose zone, because of the slow rate of supply of ions to nucleation sites, crystals grow very slowly. An increase in the supply of ions will lead to the precipitation of larger crystals, as seen in some samples (Figures 17B and 18A). Micritic crystals are sometimes overlain by larger crystals (Figures 21A and B). In this case, the early crystal growth causes a decrease in pore size. Consequently, given no change in the rate of infiltration or concentration of ions, the same volume of water is now passing over a smaller area of nucleation sites. This allows for the precipitation of larger crystal sizes due to a higher rate of supply of ions.

It was noted previously that there is a variation in the degree of cementation within cross-beds composed of different grain size. Finer-grained cross-beds are more intensely cemented than adjacent coarser-grained cross-beds. The finer-grained layers, because of their smaller pore size, are able to maintain a higher water saturation than the coarser-grained layers. This allows cements to fill a larger percentage of the pore space. Complete cementation of fine-grained layers may cause the development of a perched water table. In this perched water table, the increased lateral flow of water may allow the precipitation of large, circumgranular, elongate cements (Figure 18B), as opposed to the more common equant crys-
tals. In this situation, the increased supply of CO$_3^{2-}$ due to rapid degassing of CO$_2$ from moving waters allows for enhanced crystal growth along the c-axis (Given and Wilkinson, 1985). Elongate to acicular crystals are also found in "micro"-phreatic zones along the top of some large grains (Figure 26).

In summary, for cements precipitated in the vadose zone, variation in pore size controls the degree of water saturation within the pores. The degree of water saturation in turn controls the morphology of the cements being precipitated. Crystal size is controlled by the rate of fluid flow. The relationship between sediment fabric and sedimentary structures, which controls the distribution of pores sizes, controls the distribution of cement morphologies and the degree of cementation.

In contrast to the vadose cements, the cements precipitated in the phreatic zone show little variation. Pores are completely filled with equant crystals. Grain sizes increase towards the center of pores creating a druzy mosaic characteristic of phreatic, meteoric cementation. The only variation is the presence of circumgranular, elongate crystals surrounding some carbonate rock fragments, and the presence of syntaxial overgrowths on echi-noderm fragments.

There are three features which must be discussed in
Figure 26. Photomicrograph of Blue Ridge Esker Sample.

This sample shows an example of cementation within a "micro"-phreatic zone. Circumgranular elongate (C) and acicular (A) crystals are precipitated in small pores along the top of a large grain. Larger pores (P) at upper right only contain meniscus (M) cements at grain contacts. Crossed nichols. Sample BRE-1.3.
more detail. These are the laminar and needle fiber calcites at the Bloomingdale site (Figure 19A and B), and the irregular micritic coats found at the four vadose zone sites. These features are commonly observed in caliche profiles (Esteban and Klappa, 1983; Wright and Tucker, 1991).

Laminar caliche may form when infiltrating water encounters an impermeable layer or through biological activity (Wright and Tucker, 1991). In the Bloomingdale samples the wavy laminations of calcite occur as thin, discontinuous lenses within cemented sands. The laminations contain floating detrital grains (Figure 19A), indicating that the precipitation of the calcite has pushed apart the sand trapping some grains within the growing calcite laminae. The laminations are often associated with clay clasts, in which cases they appear to thin as they spread away from the clasts. X-ray analysis indicates the presence of calcite in these clasts, suggesting that carbonate within the clasts is being dissolved and reprecipitated in the surrounding area. The presence of possible organic matter suggests that some biological activity may have played a role in the precipitation of the calcite.

Rare needle fiber calcite is found adjacent to the laminar calcite (Figure 19B). This calcite morphology has been shown to be the result of fungal activity (Knox, 1977;
Wright, 1986; Wright and Tucker, 1991). This suggests that in the top meter of sand, biological activity was playing some role in the precipitation of calcite.

The last feature that needs to be discussed is irregular micrite coats on detrital grains. These features are particularly common at the Balkema Quarry, Blue Ridge Esker, Lowell sites. Irregular coats along the bottom of grains often occur within the vadose zone (Longman, 1980; Moore, 1989). These cements are the result of water accumulating at the bottom of grains due to gravity. They may sometimes be accompanied by an accumulation of cement on the top of the underlying grain, forming a microstalag­
tite/microstalagmite pair. The samples in this study do appear to show examples of these stalagtite/stalagmite pairs (Figures 18B, 20A, and 22A). They are particularly common at the Blue Ridge Esker site. However, in many cases the coatings show protuberances in various directions that cannot be accounted for by gravitational effects. Calvert and Julia (1983) and Wright (1986) have found irregular micritic coats resulting from fungal activity. This was indicated by the presence of elongate filaments preserved within the grain coatings. In this study, scan­ning electron micrographs (Figures 21B and 22B) do not show conclusive evidence of fungal activity.
Cathodoluminescence microscopy was used to identify changes in water chemistry during cementation, in particular oxidizing or reducing conditions. Cathodoluminescence is dependant primarily on the relative amounts of Mn$^{2+}$ versus Fe$^{2+}$ incorporated in the crystal lattice. The Mn$^{2+}$ is an activator, causing luminescence (Miller, 1988). The Fe$^{2+}$ acts as a quencher, reducing the intensity of the luminescence (Miller, 1988). Under reducing conditions both of these ions, if present in the water, are readily incorporated into the crystal lattice. However, under oxidizing conditions, Fe is present in the Fe$^{3+}$ state. This ion is too large to be incorporated into the crystal lattice.

All of the cements in this study were precipitated either in the vadose zone or in shallow unconfined aquifers, and were probably precipitated under oxidizing conditions. This would create cements which would not luminesce due to the lack of incorporation of Mn$^{2+}$. However, if there were reducing conditions present at any time, cements precipitated at this time may display luminescence.

The results of cathodoluminescence suggest that all of the cements were precipitated under oxidizing conditions, where iron was present as the larger Fe$^{3+}$ ion. None of the cements luminesced, indicating that smaller Mn$^{2+}$ and Fe$^{2+}$...
ions were not sufficiently abundant to be incorporated into the crystal lattice.
GEOCHEMISTRY

Stable Isotopes

Purpose

The analysis of stable isotopes has become an important technique for investigating geological processes. In this study the ratios of stable isotopes of carbon and oxygen in the cements were analyzed. This analysis served three purposes. First, carbon isotopes can be used to determine the source of the carbon that is being incorporated into the calcite cement. Second, a comparison of the carbon and oxygen isotope ratios between sites may indicate if the cements were precipitated under similar environmental conditions. And third, a comparison between the oxygen isotopes in the cements and the pore water can indicate whether or not the cements were precipitated from the present water.

Background

Isotopes of an element contain different numbers of neutrons, and therefore, have slightly different masses, or atomic weights. Stable isotopes are those isotopes of an element which do not spontaneously decay over time. Stable
isotopes are useful for the study of geochemical reactions due to fractionation between the different isotopes of an element.

Because isotopes of an element have the same number of electrons and the same ionic radius, all isotopes of an element are involved in the same chemical reactions. However, because of the small difference in atomic weight, one of the isotopes of the element will be preferred in specific chemical reactions. This is known as fractionation.

Isotopes of carbon and oxygen are the most important isotopes used in studying carbonate cements (Moore, 1989). The only two stable isotopes of carbon are $^{12}\text{C}$ and $^{13}\text{C}$. The percentage of each isotope present on earth is 98.89% for $^{12}\text{C}$ and 1.11% for $^{13}\text{C}$ (Hoefs, 1987). The two most abundant stable isotopes of oxygen are $^{16}\text{O}$ and $^{18}\text{O}$. The percentage of each isotope on the earth is 99.763% for $^{16}\text{O}$ and 0.1995% for $^{18}\text{O}$ (Hoefs, 1987). These are the isotopes that will be used in this study.

To study the amount of a particular isotope present in a sample, the ratio of two isotopes of an element are compared with the ratio of those two isotopes in some standard. In the case of carbon and oxygen in sedimentary carbonates, the standard is the Pee Dee Belemnite (PDB). For water samples, the standard for carbon is again PDB and
for oxygen it is Standard Mean Ocean Water (SMOW).

Ratios of isotopes are reported as δ-values. This is calculated as:

\[ \delta(x) = \left( \frac{R_x - R_{std}}{R_{std}} \right) \times 10^3 \]

where \( R_x \) is the isotopic ratio of the sample and \( R_{std} \) is the isotopic ratio of the standard (Anderson and Arthur, 1983).

The ratio of carbon isotopes is calculated as \(^{13}C/^{12}C\), and the ratio of oxygen isotopes is calculated as \(^{16}O/^{18}O\). The isotope ratios are reported as the ratio of the heavier isotope to the lighter isotope. If \( R_x > R_{std} \), then the δ-value will be positive; and if \( R_x < R_{std} \), then the δ-value will be negative (Anderson and Arthur, 1983).

**Carbon**

There are two reaction mechanisms which affect the fractionation of carbon isotopes: a kinetic effect during photosynthesis which concentrates \(^{12}C\) in organic matter, and a chemical exchange effect between atmospheric \( CO_2 \) and dissolved \( HCO_3^- \), which concentrates \(^{13}C\) in the bicarbonate (Hoefs, 1987). The precipitation of calcium carbonate involves \( HCO_3^- \) through the reaction:

\[ CO_2 + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^- \]

Consequently, calcium carbonate precipitated from marine waters, involving bicarbonate, tend to have carbon isotope ratios of δ=0 to +3, while organic matter has carbon iso-
tope ratios of δ=-15 to -30 (Figure 27). These are the two major, potential sources for the carbon in calcite cements. Therefore, the δ-value for the cements can be used to determine the possible processes which may have led to its precipitation.

**Oxygen**

Oxygen isotope ratios vary in nature due to both equilibrium and kinetic fractionation effects (Hoefs, 1987). Of most importance to the study of carbonate precipitates is the effect of temperature. If the δ¹⁸O value is known for the precipitate and the water it precipitated from, then the temperature of precipitation can be determined. This relationship is often used to determine paleo-ocean temperatures based on the following equation:

$$T^°C = 16.0 - 4.14 (\delta_c - \delta_w) + 0.13 (\delta_c - \delta_w)^2$$

where δ_c is the value for the calcite reported relative to PDB and δ_w is the value for the water reported relative to SMOW (Anderson and Arthur, 1983; Craig, 1965; Epstein, Buchsbaum, Lowenstam, and Urey, 1953). Decreasing the temperature or increasing the δ¹⁸O of the water will cause an increase in the δ¹⁸O of the calcite precipitated, while the opposite changes will cause a decrease in the δ¹⁸O of the calcite precipitated (Faure, 1991).
Figure 27. Carbon Isotope Compositions Within the Meteoric Environment.

The ranges of isotope compositions are given for the primary carbon sources within the meteoric environment and the resulting values for calcite precipitated from fresh water. (from Morse and MacKenzie, 1990; after Allan and Matthews, 1982).
Geographic effects are important for fresh water carbonates. As water evaporated from the ocean passes over a continent and water precipitates out, the remaining water becomes lighter because $^{16}$O is preferentially incorporated in the precipitation. This is due to the Raleigh distillation process (Anderson and Arthur, 1983). Thus, precipitation is increasingly lighter further inland and at higher latitudes.

Evaporation also affects the oxygen isotope ratios. During evaporation the lighter $^{16}$O isotope is preferentially evaporated, making the remaining water isotopically heavier. Any carbonates precipitated from this water will have correspondingly heavier oxygen isotope values than carbonates precipitated from the original water. With increasing evaporation, the $\delta^{18}$O value of calcite being precipitated will become progressively heavier.

**Meteoric Calcite Line**

Because of the factors mentioned in the previous portion of this chapter, fresh water calcite precipitated at a particular geographic location will display a characteristic pattern when the $\delta^{13}$C-values are plotted against the $\delta^{18}$O-values (Lohmann, 1988; Meyers and Lohmann, 1985). This is shown in Figure 28. Carbon isotope values show a significant variation, while the oxygen isotope values show
Figure 28. Idealized Variation in $\delta^{18}O$ and $\delta^{13}C$ for Meteoric Carbonates (from Lohmann, 1988).
very little variation. Thus, the isotope values plot along a vertical trend, creating a pattern referred to as the meteoric calcite line (Lohmann, 1988). The variation in carbon isotope values is due to variations in the mixture of CO₂ derived from the weathering of detrital carbonates versus that derived from soil-CO₂, and possibly differences in the amount of CO₂-degassing (Gonzalez and Lohmann, 1988; Lohmann, 1988) which preferentially concentrates ¹³C in the remaining fluid. The lack of variation in the oxygen isotope values is due to the strong dependence of oxygen isotopes on temperature. Evaporation, however, will cause precipitates to be heavier than those from the original waters. The effects of CO₂-degassing and evaporation on calcite precipitation can be seen in Figure 29.

Results

Stable isotope analysis was performed on cement samples from all six study areas, and on a water sample from well SA-2 in Kalamazoo County. The cement samples were analyzed by the University of Michigan Stable Isotope Laboratory in Ann Arbor. Three samples from each location were run for statistical purposes. The water sample was analyzed by the Environmental Isotope Laboratory at the University of Waterloo in Ontario, Canada. Two analyses were performed on this sample. The results are discussed
Figure 29. Effect of CO₂-Degassing and Evaporation on $\delta^{18}O$ and $\delta^{13}C$ Values of Meteoric Carbonates (from Lohmann, 1988).
in the following sections.

**Cement**

The results of the carbon and oxygen isotope analysis for the cements are plotted in Figure 30. They show a pattern characteristic of meteoric carbonates with very little variation in the oxygen isotopes and a greater variation in the carbon isotopes (Lohmann, 1988; Meyers and Lohmann, 1985). The carbon isotope values range from $\delta^{13}C = -9.20$ to $-3.67$, with a total range of 5.53 per mil. The oxygen isotope values range from $\delta^{18}O = -7.96$ to $-5.49$, with a total variation of 2.47 per mil. These values are reported relative to the PDB standard.

Data from each study location, with the exception of the Blue Ridge Esker, also display the pattern of large variations in carbon isotopes and small variations in oxygen isotopes. The anomalous results of the Blue Ridge Esker samples may be the result of precipitation over a longer period of time involving precipitation under varying climatic conditions, or the effects of large variations in the amount of evaporation.

One important feature to note is the similarity in oxygen isotopes between the Glen Haven Shores samples and the Samples from well SA-1. The total variation is 0.63 per mil. This strongly suggests that they were precipitat-
Figure 30. Plot of $\delta^{18}$O vs. $\delta^{13}$C for the Calcite Cements From This Study.

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ed at approximately the same time.

The Balkema Quarry study area and the nested wells SA-1 and SA-2 are located approximately 1500 feet apart. There is a similarity in the carbon isotopes at these two sites. The Balkema Quarry samples were precipitated in the vadose zone, while the samples from well SA-1 were precipitated in the phreatic zone. The similarity in carbon isotopes may suggest precipitation at the same time. The variation in oxygen isotopes may be a result of greater evaporation during the precipitation of the vadose cements.

Source of the Carbon

One important use of stable isotopes is to determine the source of the carbon. There are two primary sources for the carbon which is being incorporated into the calcite crystal lattice. One source is from dissolution of pre-existing carbonates. The other is from soil derived CO₂. These two sources can be distinguished using the carbon isotope ratios (Allen and Matthews, 1982; Hudson, 1977; Lohmann, 1988).

The detrital carbonate grains present in the glacial deposits are predominantly of marine origin. Marine carbonates have a relatively heavy carbon isotope signature (Figure 27). Carbonates precipitated from marine waters have δ¹³C values ranging from approximately -2 to +5. Soil-
CO₂ has δ¹³C values between approximately -10 and -20. This is due to the fact that biological processes preferentially incorporate the lighter ¹²C isotope. Because of the different δ¹³C values of these two carbon sources, it is possible to determine the relative contribution of each in the precipitation of meteoric calcite cements.

Two settings for the precipitation of these cements were considered: precipitation from glacial melt water prior to development of plant cover, and precipitation after the development of plant cover under hydrologic conditions not related to glacial meltwater.

Carbonate precipitates associated with glacial melt-water have been described in the literature (Aharon, 1988; Dreybrodt, 1982; Ford, Fuller, and Drake, 1970; Magaritz, 1973). These precipitates include both surficial coatings and speleothems. Under these conditions the primary source of carbon is from the dissolution of preexisting marine carbonates. Cold meltwaters dissolve calcium carbonate until the water becomes saturated with respect to calcite. Later, warming of the water causes oversaturation and calcite precipitates out of solution (Dreybrodt, 1982). These precipitates have δ¹³C values of approximately 0 or higher (Dreybrodt, 1982; Magaritz, 1973).

The carbon in most meteoric calcite precipitates is from a mixture of marine carbonate dissolution and soil-CO₂.
The result of this mixing of carbon sources is $\delta^{13}C$ values falling somewhere between that of the two sources (Figure 27).

The results of the carbon isotope analysis on the cements in this study indicate a mixture of carbon from both marine carbonate dissolution and soil-CO$_2$. Vegetation must have been present during the period of cementation. This eliminates the possibility of cementation from glacial meltwaters.

Water

Water samples were taken from well SA-2 for stable isotope analysis. The samples were analyzed for $^{18}O$ obtained from H$_2$O. The results were then compared with the isotope values for the cements obtained from well SA-1 to determine if the cements were precipitated by present waters.

Of particular importance are the $^{18}O$ isotope results. Because the fractionation of oxygen isotopes during the precipitation of calcite is very temperature dependant (Anderson and Arthur, 1983; Hoefs, 1987), if the $\delta^{18}O$ for both the calcite and the water it precipitated from are known, the temperature of precipitation can be determined.

In this study, the $\delta^{18}O$-values were determined for both the calcite cements and the water. The possible range of
water temperature throughout the year is also known. If the cements were precipitated by the present waters, then plugging the $\delta^{18}O$-values into the appropriate equation should give a temperature value within the range of possible temperatures. If the value falls outside this range, either the present waters were not responsible for the cements or they were precipitated by a non-equilibrium reaction.

The equation used was that of O’Neil, Clayton, and Mayeda. (1969). The equation is as follows:

$$10^3 \ln a_{\text{calcite-water}} = 2.78 \times 10^6/T^2 - 2.89$$

where $a$ is the fractionation factor between calcite and water and $T$ is the temperature in degrees kelvin. $a$ is determine by the formula:

$$a = \frac{(1000 + \delta_{\text{calcite}})}{(1000 + \delta_{\text{water}})}$$

The $\delta$-values are reported as SMOW, so the values for the calcite samples must be converted from PDB using the formula:

$$\delta^{18}O \text{ (SMOW)} = 1.03086\delta^{18}O \text{ (PDB)} + 30.86$$

From these formulas, if two of the three variables are known the third can be determined.

The water samples from well SA-2 were obtained on January 12, 1991. They were sent to the University of Waterloo, Waterloo, Ontario where stable isotope analysis was performed by the Environmental Isotope Laboratory.
resulting values for $\delta^{18}O$ were -10.80 and -10.66. This gives an average value of -10.77. This is similar to an average value for all glacial drift aquifers of -10.25 calculated from data compiled by Dannemiller and Baltusis (1990).

The average for the water sample from well SA-2 was used, along with the cement average for well SA-1 of $\delta^{18}O$ = -6.72, to determine the temperature of precipitation. The temperature value obtained was -0.35°C. This is far lower than the actual temperature of 11°C or the possible range of temperatures from approximately 7 to 14°C (Kehew, personal communication) that would be expected in the zone of cementation. Therefore, the calcite cements are not in equilibrium with the present groundwater.

Using the formula of O'Neil et al. (1969), a graph of $\delta^{18}O$ of the water vs. temperature was generated. This graph (Figure 31) shows the possible combinations of water and temperature required to precipitate a cement with the observed $\delta^{18}O$-value. To precipitate the observed cements would require water with a $\delta^{18}O$-value heavier than approximately -9.00.

Water Chemistry

Barrese (1991) studied the water chemistry of the Schoolcraft Aquifer, which includes wells SA-1 and SA-2.
Figure 31. Plot of Temperature vs. $\delta^{18}$O of Water.

This plot shows the possible combinations of temperature and $\delta^{18}$O of water required to precipitate a calcite cement with the observed value from well SA-2.

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He used the WATEQF software package (Plummer, Jones, and Truesdell, 1976) to determine chemical equilibria for the ground water in this aquifer. One of the chemical calculations which this software package performs is the calculation of saturation indices for various minerals. The saturation index indicates whether the water is undersaturated or oversaturated with respect to a particular mineral. Water undersaturated with respect to a particular mineral would dissolve the mineral if it were present in the aquifer, while an oversaturated water would precipitate the mineral out of solution.

Of particular importance to the present study are the saturation indices for calcite, dolomite and aragonite. The Saturation Index is reported as Log IAP/KT. The results from Barrese (1991) are shown in Figure 32. The median Saturation Index for calcite was 0.0234 with a range of -0.1537 to 0.2634. The value for well SA-1 was 0.0444, and for well SA-2 it was 0.0381. This indicates that the waters in wells SA-1 and SA-2 are slightly oversaturated with respect to calcite and could, therefore, precipitate calcite out of solution.

The Dolomite S. I. had a median value of -0.2683, with a range of -0.6842 to 0.2378. The values for wells SA-1 and SA-2 were -0.0448 and -0.1550, respectively. The ground water is undersaturated with respect to dolomite
Figure 32. Calcite S.I. vs. Dolomite S.I. for Groundwaters in the Schoolcraft Glaciofluvial Fan (from Barrese, 1991; after Langmuir, 1971).

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throughout most of the area of Barrese's study. Aragonite is also undersaturated in wells SA-1 and SA-2, with values of -0.2592 and -0.2641 respectively. Any detrital dolomite or aragonite encountered by these undersaturated waters would begin to dissolve.

The results of Barrese’s study suggest that calcite could be precipitating from present waters in much of the aquifer, while any dolomite or aragonite encountered should be dissolving. The S. I. values for these three minerals are in agreement with the presence of a zone of extensive calcite cementation in wells SA-1 and SA-2. However, the results suggest that authigenic calcite should be present in many of the other wells also (Figure 32). This lack of calcite cement is difficult to explain.

Radiometric Dating

The calcite cement from the Glen Haven Shores location was age dated using $^{14}$C to determine when it was precipitated. A sample from this site was chosen because of the low percentage of detrital carbonate in this deposit (Figure 15), and because the results of the $^{14}$C dating could be compared with past high lake levels.

Because of the low detrital carbonate content and low variability between samples, the percentage of "dead" carbon, carbon older than 40,000 years BP, could be accounted
for when determining the actual age of the cement. This 
"dead" carbon would have the effect of giving a greater age 
than the actual age, so it would be important to be able to 
determine what percentage of the actual carbon was detrital 
and what percentage was cement. The other study areas had 
higher percentages of detrital carbonate and, more impor-
tantly, the percentage of detrital carbonate was highly 
variable (Figure 15). This made samples from the other 
study locations virtually impossible to accurately date.

A sample was analyzed by Krueger Enterprises, Inc. in 
Cambridge, MA. The age determined was 11,900 ± 140 years 
BP. This age was then corrected for detrital carbonate 
based on an average of 7.15 % of the total carbonate being 
detrital. This percentage was based on point count data 
from thin sections. The corrected age is 11,495 years BP. 
The correction based on point count data introduces an 
additional small error due to the uncertainty as to the 
exact percentage of detrital carbonate present in the 
sample used in the analyses. This additional error should 
be less than 200 years.

This date correlates with the Calumet phase of glacial 
Lake Chicago (Figure 33), which occurred between 11,800 and 
11,200 years BP (Hansel, Mickelson, Schneider, and Larson, 
1985). During this phase the level of Lake Chicago rose to 
a high of 620 feet. The present level of Lake Michigan is
Figure 33. Stratigraphic Section at Glen Haven Shores. Age dates given for cements along with past and present lake levels.
approximately 580 feet. The cement zone in the bluff is between approximately 620 and 640 feet. Due to erosional retreat of the bluff and the tendency for the elevation of the water table to rise away from the point of discharge, the elevation of the cemented zone above the probable lake level is expected.

There is a potential problem with the above date. Ground water passing through carbonate rocks, or sediments containing carbonate grains, picks up 'dead' carbon from the dissolution of the carbonates (Freeze and Cherry, 1979). Calcite precipitated from the ground water will incorporate that "dead" carbon, giving an older $^1$C date than the actual time of precipitation. The actual age may be thousands of years younger than the $^1$C age. As can be seen from the $\delta^{13}$C values (Figure 30), there is a significant quantity of detrital carbon included in the cements from this study. The age determined for the Glen Haven Shores cements may, at best, be the oldest possible time of precipitation.

Discussion

The carbon isotopes show that the carbon came from a mixture of dissolved detrital carbonate and soil-CO$_2$. This precludes precipitation from glacial meltwaters. The cements from well SA-2 are not in equilibrium with present
waters based on oxygen isotopes. The similarity in oxygen isotope values for the cements at all of the sites studied, and the similarity of the oxygen isotope value for the groundwater with that of other glacial drift aquifers in southern Michigan (Dannemiller and Baltusis, 1990), suggest that none of these cements are in equilibrium with present waters. The $\delta^{18}O$-value of groundwater necessary to precipitate these cements may indicate precipitation during a period of slightly higher mean annual temperature. Such a period of warmer temperatures occurred between approximately 6000 and 3000 years BP. Edwards and Fritz (1986, 1988), based on stable isotopes, determined that this was a period of very warm, moist conditions (Figure 34). The heavier $\delta^{18}O$ values that they found for this period are consistent with the values needed to precipitate the cements in the present study (see Figure 31). This was also a time of high lake levels which would correlate with the location of the cements at Glen Haven Shores. Although this contradicts the $^{14}$C date of the cements, as discussed in the previous section, this date may be too old.

Another factor which may be relevant to the timing of cementation is vegetation change during and after deglaciation. Before 11,000 years BP, upland moss species and pollen data suggest a dry, nonforest habitat with sparse spruce woodlands (Miller, 1980). The moss species present
Figure 34. Inferred Paleoclimatic Conditions during the Late Wisconsin and Holocene at Brampton, Ontario (from Edwards and Fritz, 1988).
also indicate that soils were generally alkaline. Through the early Holocene, the warming climate led to the northward migration of mixed conifer-hardwood forests (Delcourt and Delcourt, 1987), which would create more acidic soils and increase leaching. This correlates well with the inferred climatic changes of Edwards and Fritz (1986, 1988), and suggests that changes in vegetation may have played a role in the precipitation of calcite cements.

Barrese (1991) found that the ground water in most of his study area was near saturation with respect to calcite, and that approximately half of the wells sampled were above saturation. But the presence of calcite cemented zones was only noted for the two wells included in the present study. These two wells were nearest the top of the glaciofluvial fan in his study area, and near the beginning of the local flow path. It is unclear why cement is present only in these two wells. The lack of cement in the other wells may be related to a decrease in grain size down the fan (Kehew, personal communication). This lack of correlation between calcite saturation and the presence of calcite cement does suggest that calcite saturation alone is not enough to cause the precipitation of appreciable quantities of calcite.

Although most ground water in local glacial outwash deposits are at or near saturation with respect to calcite,
some driving mechanism may be necessary to precipitate substantial quantities of calcite cement. The three primary mechanisms driving precipitation of calcite in meteoric environments are evaporation, degassing of CO$_2$, and warming of the water. CO$_2$-degassing and evaporation are probably the primary driving mechanisms in the vadose environments. Warming of recharging groundwater may be important in the phreatic environment. Biological activity may have played a role in the precipitation of some cements.
CONCLUSIONS

1. The cements found in this study are calcite. Based on cement morphology and staining using the technique of Dickson (1966), no other cementing minerals are present in appreciable quantities.

2. Examination of cement morphology indicates that the cements at the Balkema, Bloomingdale, Blue Ridge Esker, and Lowell sites were precipitated in the vadose zone. This conclusion is based on the presence of meniscus cements at each site and irregular micritic coatings at the Blue Ridge Esker and Lowell. The cements at Glen Haven Shores and in wells SA-1 and SA-2 are all pore-filling equant calcite, suggesting precipitation in the phreatic zone.

3. The textural and bedding features of the sediments are an important factor controlling the distribution and intensity of cementation in the vadose zone. Pore size determines whether a pore is completely filled with water, or if it contains both water and air. Smaller pores are filled with water due to surface tension and may become completely filled with cement. Larger pores contain air in the center of the pores. In these pores cements grow until they reach the water/air interface, forming meniscus shapes.
near grain contacts.

The relationship between pores of different sizes is most often controlled by bedding features. Because bedding planes represent separate intervals of sedimentation, and current strength may vary from one interval to another, alternations in grain size between bedding planes creates a strong control on the distribution of cements. Finer-grained bedding planes, which contain only water within the pores, are more intensely cemented than coarser-grained bedding planes, which contained both air and water within the pores. The cementation of very fine-grained sand lenses may create a perched water table. This type of structural control also occurs on a small scale from one pore to the next.

4. Modal analysis of the detrital composition of these sediments suggests that they contain sufficient detrital carbonate to account for the cements. The only exception is the Glen Haven Shores site. The cemented sand at this site is overlain by approximately ten feet of till which must be the source of the Ca\textsuperscript{2+} ions.

5. Stable isotopes of carbon indicate a mixture of weathering of detrital carbonates and soil generated CO\textsubscript{2} as the source of the CO\textsubscript{3}\textsuperscript{-} ions. The cements have $\delta^{13}$C values between -9.20 and -3.67.

6. Variations in carbon and oxygen isotopes within
each site suggest CO₂-degassing and evaporation as driving forces for precipitation of calcite. Variations in the amount of CO₂-degassing cause the variation in the δ¹³C values, while variations in the amount of evaporation cause the variation in the δ¹⁸O values. Warming of infiltering water upon entering the phreatic zone may be an important driving force for precipitation at Glen Haven Shores and in wells SA-1 and SA-2.

7. Comparison of stable isotopes of oxygen between the calcite cement and the groundwater in well SA-1 indicates that the present groundwater did not precipitate the calcite cement. Based on the fractionation equation of O'Neil, et al. (1969), precipitation of the calcite present would require a temperature below freezing from waters with the present chemistry. Precipitation of these cements, as well as those in the other sites in this study, would require groundwater with δ¹⁸O heavier than approximately -9.00. This suggests that the cements were precipitated during a period when the mean annual temperature was warmer than at present. There was a period of warmer temperatures between approximately 3000 and 6000 years BP which may have had ground water of the required isotopic composition. Vegetation changes during this time, which increased soil acidity and leaching, may have contributed to the precipitation of the cements.
8. Carbon-14 dating of the calcite cement at Glen Haven Shores gave a date of 11,495 years BP. Due to the incorporation of "dead" carbon from the weathering of detrital carbonate grains, this is the oldest possible age for the precipitation of the cements at this site. They may be thousands of years younger.
Appendix A

Western Michigan University
Monitoring Well Logs
### WATER WELL AND PUMP RECORD

#### 1. LOCATION OF WELL
- **County**: Kalamazoo
- **Township**: Branch
- **Range**: 2
- **Section**: 17
- **Township Range**: 35
- **Street Address & City of Well Location**: Schoolcraft
- **Locator with "0" in Section Below**: Test Well #1 SA-1

#### 2. FORMATION DESCRIPTION
- **Thickness of Stratum**
  - Soft Brown clay & gravel: 5 ft.
  - Coarse gravel (water): 20 ft.
  - Coarse Gravel, Gravel: 5 ft.
  - Ape Gravel, Cobbles: 5 ft.
  - Coarse Sand & Gravel: 10 ft.
  - Coarse Sand: 30 ft.
  - Soft Gray Clay: 22 ft.
  - Soft Gray Clay & Gravel: 3 ft.
  - Soft Gray Clay: 6 ft.
  - Soft Gray Clay & Sand: 5 ft.
  - Coarse Gravel (water): 8 ft.
  - Fine Muddy Sand: 10 ft.
  - Fine Gray Silt: 12 ft.
  - Sand & Gravel (water): 5 ft.
  - Coarse Sand: 15 ft.
  - Fine Sand & Gravel: 4 ft.

- **Depth to Bottom of Stratum**
  - Coarse gravel (water): 25 ft.
  - Coarse Gravel, Gravel: 30 ft.
  - Ape Gravel, Cobbles: 35 ft.
  - Coarse Sand & Gravel: 45 ft.
  - Coarse Sand: 70 ft.
  - Soft Gray Clay: 97 ft.
  - Soft Gray Clay & Gravel: 100 ft.
  - Soft Gray Clay: 105 ft.
  - Soft Gray Clay & Sand: 110 ft.
  - Coarse Gravel (water): 114 ft.
  - Fine Gray Silt: 140 ft.
  - Sand & Gravel (water): 145 ft.
  - Coarse Sand: 150 ft.
  - Fine Sand & Gravel: 154 ft.

#### 3. OWNER OF WELL
- **Geology Dept**: Western Ill. University
- **Address**: Kalamazoo, 49007

#### 4. WELL DEPTH
- **228 ft.**
- **11-21-85**
- **Replaced Well**

#### 5. USE
- **Domestic**
- **Type I Public**
- **Type III Public**
- **Filling Well**
- **Type I Public**
- **Type III Public**

#### 6. SCREEN
- **Steel**
- **3.0 ft. above grade**
- **Screen Diameter**: 124 ft.

#### 7. CASING
- **Diameter**: 124 ft.
- **Height Above/Dwelling**: 0 ft.
- **Staggered**: 124 ft.
- **Weight**: 124 ft.
- **What**: 124 ft.
- **Material**: 124 ft.
- **Type of Screen**: 124 ft.

#### 8. STATIC WATER LEVEL
- **10 ft.**

#### 9. STATIC WATER LEVEL
- **10 ft.**

#### 10. PUMPING LEVEL
- **10 ft. after 1 hrs. pumping at 50 G.P.M.**
- **10 ft. after 1 hrs. pumping at 50 G.P.M.**

#### 11. WELL HEAD COMPLETION
- **Pressurized**: Yes
- **Basement drain**: Yes
- **Drain pipe**: Yes

#### 12. WELL GROUTED
- **No**
- **4 ft.**: From 0 to 125 ft.
- **No**
- **No**
- **No**
- **No**
- **No**

#### 13. NATURE OF GROUTING
- **Type**: Cement
- **Material**: Portland Cement
- **Quantity**: 250 lbs.

#### 14. PUMP
- **Type**: Centrifugal
- **Manufacturer**: Western Pumps
- **Model number**: 250 HP
- **Volute**: 250
- **Length of Discharge**: 250 ft.
- **Capacity**: 250 G.P.M.
- **Type of Submersible**: 250 ft.
- **Jet**: 250 ft.
- **Pressure Tank**: 250 ft.
- **Manufacturer**: Western Pumps
- **Model number**: 250 ft.
- **Capacity**: 250 G.P.M.

#### 15. REMARKS
- **Remarks, elevation, source of data, etc.**
- **Owner Took Permit**

#### 16. WATER WELL CONTRACTOR'S CERTIFICATION
- **This well was drilled under my jurisdiction and this report is true to the best of my knowledge and belief.**
- **Authority**: Act 399 PA 1976
- **Registration No**: 78-147647
- **Address**: 78-147647
- **Date**: 11/23/86

#### IMPORTANT
- **File with deed.**
**WATER WELL AND PL**

### LOCATION OF WELL

<table>
<thead>
<tr>
<th>County</th>
<th>Township Name</th>
<th>Fraction</th>
</tr>
</thead>
</table>

**Distance And Direction From Road Intersection**

- [Diagram: Test well #1 Deep]

**Street Address & City of Well Location**

- [Diagram: Sketch Map]

### FORMATION DESCRIPTION

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<tr>
<td>Fine gray silt (water)</td>
<td>20</td>
<td>180</td>
</tr>
<tr>
<td>Hard gray clay &amp; gravel</td>
<td>15</td>
<td>195</td>
</tr>
<tr>
<td>Hard gray clay</td>
<td>5</td>
<td>200</td>
</tr>
<tr>
<td>Hard gray clay &amp; gravel</td>
<td>38</td>
<td>238</td>
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</table>

**Note - Casing pulled back to 172'**

**Note - Screen set between 174' & 175'**

**Note - Total Depth of hole 238'**

### Remarks, elevation, source of data, etc.

**WATER**

This was to the br

**ADDRESS**

Signed:

**DATE** 12/15

**IMPORTANT:** File with deed.

**WELL OWNER**
**WATER WELL AND PUMP RECORD**

### LOCATION OF WELL
- **County**: Kalama 200
- **Township**: Prairie Rowe
- **Range**: 4
- **Section**: 5W N/E NW
- **Fraction**: 1/4
- **Township Name**: Kalama 200
- **City**: Westport
- **State**: WA
- **Distance and Direction from Road Intersection**: 1/2 mi S.W.
- **Location of Well**
  - **County**:
  - **Township**:
  - **Range**:
  - **Section**:
  - **Town Number**:
  - **State**:
  - **Street Address & City of Well Location**: Schodroft
  - **Sketch Map**:
  - **Depth**:
  - **Well Completion**
    - **Date of geologic interpretation**:
    - **Date of completion**:

### FORMATION DESCRIPTION
- **Formation**:
  - **Sand & gravel**: 65 ft
  - **Coarse gravel**: 20 ft
  - **Coarse cemented gravel**: 10 ft
  - **Gravel & sand (water)**: 37 ft

### WATER WELL CONTRACTOR'S CERTIFICATION
- **Name**:
- **Address**:
- **Date**:

**IMPORTANT**: File with deed.
Appendix B

Point Count Data
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CC- circumgranular crust, PF- pore-filling equant, VA- meniscus and irregular coatings

All data based on 200 points per thin section.
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Calcite

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Appendix C

X-Ray Diffraction Traces
Bloomingdale Pit Clay Clast

Relative Intensity

°2θ

Quartz
Calcite
Dolomite
Quartz & Illite
Illite
Dolomite
Quartz
Appendix D

Stable Isotope Data
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Appendix E

Radiocarbon Data
Our Sample No. GX-16798  Date Received: 05/22/91
Your Reference: letter of 05/16/91  Date Reported: 06/29/91
Submitted by: Robert L. Tollliver
Dept. of Geology
W. Michigan University
Kalamazoo, MI 49008

Sample Name: Pleistocene sandstone. Sample A.
Calcite cement.

AGE = 11,900 +/- 140 C-14 years BP (C-13 corrected).
( 22.2 +/- 0.4) % of the modern (1950) C-14 activity.

Description: Calcite cemented sandstone.

Pretreatment: The total carbonate content was hydrolyzed, under vacuum, with dilute HCl. The evolved carbon dioxide gas was collected and analyzed.

Comment: Correcting for 7.15% of the total carbonate being detrital and without C-14 activity, the cement age becomes 11,495 C-14 years BP.

\[ \delta^{13}C_{org} = -7.4 \%
\]

Notes: This date is based upon the Libby half life (5570 years) for \(^{14}C\). The error stated is +1σ as judged by the analytical data alone. Our modern standard is 95% of the activity of N.B.S. Oxalic Acid. The age is referenced to the year A.D. 1950.
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Steinmann, W.K., The geological and hydrogeological characterization of the Schoolcraft Aquifer, Schoolcraft, Michigan: Master's thesis in preparation, Western Michigan University, Kalamazoo, MI.


