Petrology and Stable Isotope Geochemistry of Pleistocene and Holocene Calcite Cement in Kame Terrace Gravel, Central New York State

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ABSTRACT: Wisconsin-age kame terrace gravel in south-central New York State contains post-depositional calcite cement (~4500 bp radiocarbon). Clasts of cemented gravel conglomerate are also present in these deposits, suggesting that pre-Late Wisconsin cementation occurred to form conglomerates that were eroded and re-deposited. In situ CaCO3 cement exhibits phreatic and vadose fabrics. Multi-layer cements show internal dissolution and re-growth surfaces. Phreatic cement above the present water table suggests either a higher water table in the past or groundwater ponded above low-permeability zones as ephemeral ‘perched’ water table aquifers. Vadose cement post-dates phreatic zone cement in samples where both are present. Conglomerate clast cements are commonly single-layer ispachous prismatic calcite.

14C values suggest that carbonate ion in calcite was derived from a mixture of isotopically lighter (more negative) soil organic C, and heavier atmospheric CO2 or marine limestone carbonate. The heaviest carbon isotope signatures are found in vadose calcite cement, suggesting an atmospheric source of carbon. 18O data from in situ cements are consistent with precipitation of calcite at local groundwater temperature (11-13°C) from waters having a δ18Owater of ~8.5‰; modern local groundwater has δ18Owater of ~10.7‰. The precipitation of calcite cement at ~4500 bp is consistent with a drier climate at that time, which might correlate with heavier isotopic signatures in meteoric water. Cement from transported clasts resembles in situ phreatic cements in terms of δ18O, but is ~2-3‰ heavier in δ18O. This suggests that the clast cements precipitated from isotopically heavier waters or at lower temperatures than in situ cements.

INTRODUCTION

Precipitation of calcium carbonate cement from soil water and shallow groundwater provides a potential record of environmental conditions via the crystal fabrics and textures preserved (James 1985; James and Choquette 1987; Moore 1989) and the stable isotope geochemistry of the carbonate (Hudson 1975; Allain and Mathews 1982). Recent studies of pedogenic carbonate and groundwater concretionary carbonate indicate that combined petrographic and stable isotope study can provide important information regarding local environmental conditions. Cerling (1984) demonstrated that variations in the carbon isotope content of soil carbonate could be used to distinguish forest and grassland soil systems because of the differences in the isotopic values of organic matter from C3 (forest) vs. C4 (grassland) plants. The oxygen isotope values of ancient soil carbonate were controlled by the local hydrologic regime, allowing paleoclimatological inferences to be drawn (Cerling 1984; Cerling et al. 1989; Hays and Grossman 1991). Concretionary calcite cement formed in shallow groundwater has also been shown to record soil carbon sources and the oxygen isotopic variation in precipitation (Quade and Roe 1999).

Kame moraine and kame terrace deposits are characteristic Late Wisconsin depositional features of the Appalachian Upland in south-central New York (Cadwell 1972; Fleisher 1991). Stream-transported gravel and sand formed ice-contact deposits adjacent to stagnant ice masses within the major north-south ‘through valleys’ (Fig. 1). This phase of late glacial deposition is thought to have occurred immediately prior to the development of the Valley Heads moraine system (Cadwell 1972). Irregular masses and discontinuous layers of calcite-cemented gravel are common in kame terrace sediment (Fig. 2). Termed ‘cement rock’ by local drillers and contractors, carbonate-cemented zones are best developed near the valley floor margins of terrace gravel deposits. Within these same terrace gravel, rounded clasts of calcite-cemented conglomerate are also found. The conglomerate cement and clast composition closely resembles the host gravel.

In situ cemented glacial gravel and transported clasts of pre-Holocene conglomerate in Quaternary deposits of the Appalachian Upland have been known for some time. Holmes (1939) and Schmidt (1947) described the distribution of both features, and recognized that the transported conglomerate clasts represented a phase of pre-Late Wisconsin cementation followed by subsequent erosion and transport. Aber (1979) described the distribution and petrographic character of cemented zones and the relationship of cementation to modern weathering horizons. He interpreted the bulk of the cementation as vadose in origin, based upon the location of most cemented zones well above the modern water table. Aber also described minor occurrences of aragonite cement within in situ cemented zones. Schmidt (1947) and Aber (1979) described the occurrence of clasts in a variety of late Wisconsin deposits in the area, including within lodgement till at two upland exposures. Aber (1979) described multi-generation clasts which contained clasts of earlier conglomerate. He interpreted the earlier cementation phase as Sangamon, with the older cemented clasts incorporated in a mid-Wisconsin conglomerate that was eroded and redeposited in late Wisconsin time. An isolated conglomerate mound near Syracuse, New York, approximately 65 km north-northwest of the Norwich locality was also described by Aber (1979), who
suggested that the anomalous deposit was cemented prior to late Wisconsin glaciation, and thus may have served as a source for conglomerate clasts in that area.

In this paper we describe the petrographic and stable carbon and oxygen isotope character of calcite from in situ cement and transported clast cement in a kame terrace system near Norwich, New York (Fig. 1). The oxygen isotope systematics of the cements are interpreted in the context of the stable isotope character of modern groundwater in the region.

**REGIONAL SETTING AND FIELD OCCURRENCE**

The study area (Fig.1) lies south of the Valley Heads Moraine system on the Appalachian Plateau in south-central New York. The area is underlain by upper Devonian marine shale and sandstone. To the north lie older Devonian and Silurian units, including widespread marine limestone. Wisconsin-age glacial deposits include upland lodgement and ablation till, kame terrace ice-contact drift and valley train outwash deposits (Cadwell 1972). Holocene floodplain, marsh and lake sediments also are present.

The Norwich, NY kame terrace system consists of an elongate complex of broad valley-margin terraces that rim the western margin of the Chenango River Valley (Fig. 1). Most of the material for this study came from a small gravel pit immediately west of the Norwich Airport on Route 12 approximately 2 miles north of the Norwich city limit. The Norwich system has been mined extensively for aggregate and road fill, and excellent, fresh exposures abound. The sediments consist of well-sorted matrix-free gravel, moderately well-sorted matrix-supported sandy gravel and well-sorted gravelly sand (Fig. 2). Beds dip toward the valley center at approximately 10 degrees. The gravel clast composition is dominated by local middle and upper Devonian siltstone and sandstone (30-60%), limestone derived from Devonian and
Calcite cement in kame terrace gravel, central New York

Figure 2. A. Typical exposure of kame terrace gravel with cemented masses (arrows). B. Discontinuous cemented masses following gravel horizon. C. Rounded conglomerate clast in uncemented gravel, Norwich locality.

Ordovician strata to the north (15-25%), Devonian, Silurian and Cambrian red and white sandstone (5-15%) and Adirondack or Canadian Shield-derived igneous and metamorphic rocks (1-5%).

In situ cemented masses are common throughout the Norwich complex (Fig. 2), and cemented conglomerate clasts are regularly encountered (Fig. 2c). In situ masses may be confined to particular stratigraphic horizons in an exposure, or irregularly distributed. Most cemented masses are not laterally continuous for more than a few meters. Thick rinds of white or yellowish calcite are commonly visible in coarser, matrix-free facies of the cemented gravel (Fig. 3a). In matrix-rich facies, cement is distributed in the matrix.

Multiple layers of rind cement are common in matrix-free coarse gravel (Fig. 3b), and may form cement masses up to 5 cm thick. Within these multi-layer masses, small (2-5 mm) stalactites and downward-pointing aggregates of cement are found within remaining pore space. The most well-developed multi-layer cement in the Norwich locality occurs immediately above a horizon of fine, cemented sand near the quarry floor. In the exposures examined in the Norwich kame terrace system cemented masses occur 2-12 meters above the modern water table.

Clasts of calcite-cemented conglomerate in the Norwich exposure are 2-20 centimeters in diameter, and range from sub-angular to rounded, with cement and constituent lithic fragments truncated by abrasion during transport (Fig. 2c). The lithic fragment composition of the clasts is similar to the surrounding kame terrace gravel. Some clasts found within otherwise unoxidized gravel bear lithic fragments that are heavily oxidized, suggesting some chemical weathering of the clasts prior to transportation. As noted by earlier workers, the composition, texture and fabric of the clasts resemble in situ cemented gravel found in the Norwich locality and elsewhere on the Appalachian Plateau.

Methods

Samples for petrographic and isotopic studies were taken from undisturbed exposures at the level of the main quarry floor level, located 3-5 meters below the pre-excavation level.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Material</th>
<th>Age (¹⁴C yr B.P.; ¹³C corrected)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP-9-4</td>
<td>Isopachous single-layer phreatic in situ cement</td>
<td>4,510 ± 85 (GX-25896)</td>
</tr>
<tr>
<td>AP-9-34</td>
<td>Multilayer phreatic in situ cement</td>
<td>4,475 ± 85 (GX-25895)</td>
</tr>
<tr>
<td>AP-13-C</td>
<td>Isopachous single-layer clast cement</td>
<td>&gt;32,710 (GX-26234)</td>
</tr>
</tbody>
</table>
surface and 3-5 meters above the modern water table. The most prominent zone of calcite cement in the quarry is immediately above a relatively continuous layer of lightly cemented fine sand. Twenty-nine thin-sectioned samples of in situ cement and six conglomerate clasts were studied from the Norwich locality.

Samples for stable isotope analysis were selected by hand-picking lightly crushed materials for clean, unaltered calcite. Phreatic and vadose cement from in situ cemented gravel, and clast cement samples were powdered and roasted at 300°C to remove organic carbon. Calcite samples were analyzed for carbon and oxygen stable isotopes at SUNY Albany’s Stable Isotope Ratio Mass Spectrometer (SIRMS) Laboratory in the Department of Earth and Atmospheric Sciences. Samples of powdered calcite were placed in small septum-capped glass chromatography V-vials and loaded into a heated rack controlled to ±0.1°C. A needle sequentially punctures each vial’s septum, injecting 100% phosphoric acid into the sample vial. The carbon dioxide that is evolved during acid digestion of the calcite is passed to a Micromass Optima gas-source triple-collector mass spectrometer for isotopic ratio determination. Replicate sample analyses indicate that carbon and oxygen SIRA were performed at a precision of +/- 0.05 per mil.

Two samples of prismatic rind cement from in situ cemented masses and one sample of transported clast cement were analyzed using conventional ¹³C techniques at Geochron Labs.

Groundwater samples from central New York collected in mid-summer of 2000 were analyzed for oxygen and hydrogen isotopes to provide a framework for interpretation of the stable isotope values of the calcite cement in the Norwich locality. Water samples were analyzed using standard techniques at University of California Davis Stable Isotope Facility. The samples analyzed in this study were from municipal water supplies that depend on large aquifers.
Figure 4. Thin section photomicrographs of cement from Norwich locality. Scale bar in each image is 1.0 mm. A, B. Plane light and cross-polars view of thick, multilayer isopachous prismatic phreatic rind with later microcrystalline vadose cement exhibiting pendant geometries (arrow). C, D. Plane light and cross-polars view of single layer prismatic isopachous phreatic cement from pre-Late Wisconsin clast, Norwich locality. E. Multilayer prismatic cement with numerous truncation-dissolution surfaces. F. Higher magnification view of (D) Darker zones are formed by abundant inclusions of organic matter, suggesting flushing of soil-derived material into shallow groundwater.
RESULTS

Petrographic Observations

Two varieties of calcite cement were observed in hand specimens and thin sections: ‘rind’ cement and ‘microstalactitic’ cement. Rind cement forms continuous, isopachous coatings on detrital grains and consists of single or multiple layers of prismatic, elongate calcite crystals 2-5 mm in length that exhibit competitive growth fabrics (Fig. 4a, b). Multilayer rind cement (Fig. 4e, f) is characterized by internal dissolution and regrowth surfaces. The rind cements are interpreted as having formed in water-saturated conditions - a phreatic environment (James and Choquette 1987) - based on the continuous, isopachous character and the lack of geopetal features. Multilayer cements suggest episodes of cement precipitation alternating with periods of dissolution. Microscopic dark inclusions of organic material decorate dissolution surfaces in some multilayer cement (Fig. 4e, f).

Pendant, crustose, microstalactitic cement (Fig. 3a, b; Fig. 4a,b) post-dates rind cement, and consists of multiple thin laminae of equant calcite crystals 10-60 m in diameter. This cement is interpreted as vadose in origin based on the small crystal size, geopetal geometries and occurrence limited to the undersides of clasts or underside of earlier phreatic cement rinds.

Cement in the six conglomerate clasts examined was limited to the prismatic rinds interpreted as phreatic in origin (Fig. 4c,d). Cement in clasts often shows evidence of abrasion or dissolution-truncation of rinds (Fig. 4f, arrow).

The distribution of cemented masses and cement types at the Norwich locality suggests that while the cements are phreatic in origin, the present water table is well below the exposures of cemented gravel. This suggests that either the water table was higher in the past during phreatic cement precipitation, or that local ‘perched’ phreatic lenses developed during periods of high recharge.

Stable Isotope Data - Carbonate

$^{13}$C and $^{18}$O data (Table 2, Fig. 5) reveal three important trends:

1. A consistent difference of 2-3\(\%\) between in situ and clast cements in terms of $^{18}$O, with clast cements more positive. This suggests that clast cements precipitated from isotopically heavier water or at cooler temperatures than younger in situ cement.

2. Overall, the range of $^{13}$C (-10.5 to -6.5\(\%\)) is similar to temperate climate soil carbonate reported by other workers (e.g. Cerling 1984) but the relatively larger range of values suggests that more than one carbon source is involved. Vadose in situ cements generally contain heavier carbon than phreatic in situ cements.

3. In situ cement $^{13}$C and $^{18}$O data plot as a linear array with a slight positive slope, suggesting mixing of two reservoirs of carbon with different $^{13}$C values, with heavier carbon values found in samples with the heaviest water isotope signature. The covariance suggests that water in the vadose zone was slightly heavier (e.g. more evaporated?) or that precipitation in the vadose zone took place under slightly lower temperatures.

Stable Isotope Data – Water

The range of $^{18}$O and D in groundwater samples is illustrated
Figure 5. Plot of $^{13}$C vs $^{18}$O for all calcite cement samples from the Norwich locality. Note linear array formed by the in situ cement samples, suggesting mixing of two different carbon isotope reservoirs. Note also the heavier oxygen isotopic signature of the clast cement vs. in situ cement.

Figure 6. $^{18}$O of municipal groundwater samples arrayed on a north-south transect in central New York State. See inset map for location of transect.
Table 3. Stable isotopes - Municipal Groundwater.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Municipality</th>
<th>δD</th>
<th>δ¹⁸O</th>
</tr>
</thead>
<tbody>
<tr>
<td>THS-07242000</td>
<td>Theresa</td>
<td>-76.4</td>
<td>-11.24</td>
</tr>
<tr>
<td>LAM-07242000</td>
<td>LaFargeville</td>
<td>-75.7</td>
<td>-11.04</td>
</tr>
<tr>
<td>PHS-07242000</td>
<td>Philadelphia</td>
<td>-85.1</td>
<td>-12.27</td>
</tr>
<tr>
<td>EMH-07242000</td>
<td>Evans Mills</td>
<td>-85.0</td>
<td>-12.31</td>
</tr>
<tr>
<td>ACM-07242000</td>
<td>Adams Center</td>
<td>-76.5</td>
<td>-11.16</td>
</tr>
<tr>
<td>CRC-07242000</td>
<td>Croghan</td>
<td>-80.9</td>
<td>-11.86</td>
</tr>
<tr>
<td>BOS-07242000</td>
<td>Boonville</td>
<td>-77.5</td>
<td>-11.35</td>
</tr>
<tr>
<td>MXK-07252000</td>
<td>Mexico</td>
<td>-80.8</td>
<td>-11.90</td>
</tr>
<tr>
<td>PAC-07252000</td>
<td>Parish</td>
<td>-80.7</td>
<td>-11.74</td>
</tr>
<tr>
<td>LFM-07212000</td>
<td>Lafayette</td>
<td>-80.4</td>
<td>-11.54</td>
</tr>
<tr>
<td>HAL-07252000</td>
<td>Hamilton</td>
<td>-78.6</td>
<td>-10.92</td>
</tr>
<tr>
<td>HMB-07212000</td>
<td>Homer</td>
<td>-77.1</td>
<td>-11.21</td>
</tr>
<tr>
<td>CLK-07212000</td>
<td>Cortland</td>
<td>-77.3</td>
<td>-11.19</td>
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<tr>
<td>SHM-07202000</td>
<td>Sherburne</td>
<td>-76.2</td>
<td>-11.03</td>
</tr>
<tr>
<td>NWW-07202000</td>
<td>Norwich</td>
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<td>-10.72</td>
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<tr>
<td>OXB-07202000</td>
<td>Oxford</td>
<td>-72.9</td>
<td>-10.57</td>
</tr>
<tr>
<td>GRM-07202000</td>
<td>Green</td>
<td>-71.9</td>
<td>-10.33</td>
</tr>
<tr>
<td>WPH-07202000</td>
<td>Whitney Point</td>
<td>-72.4</td>
<td>-10.32</td>
</tr>
<tr>
<td>CFS-07202000</td>
<td>Chenango Forks</td>
<td>-68.0</td>
<td>-9.76</td>
</tr>
</tbody>
</table>

in Figure 6 (Table 3). The samples analyzed in this study were from municipal water supplies that depend on large aquifers. The data are plotted from north to south, with sampling locations shown in the inset map. Modern precipitation in this area is strongly influenced by the “lake effect”, resulting in waters that are isotopically lighter than regional precipitation derived from maritime-sourced weather systems (Gatt et al. 1999). The north to south variation in δ¹⁸O reflects the change in mean annual temperature along the transect and the influence of moisture derived from Lake Ontario. Samples from municipalities closest to Lake Ontario (Fig. 6) show the most depleted groundwater values. This effect diminishes to the south, but since lake effect precipitation is carried from the northern edge of the Appalachian Plateau by south-flowing rivers, the isotopic value of groundwater along these rivers is likely influenced by lake effect in a minor way. Norwich lies at the southern edge of the region of significant lake effect snow, but the municipal well aquifer is likely partially recharged from the nearby Chenango River, the headwaters of which are within the lake effect zone. One sample of Norwich municipal well groundwater, collected in mid-summer 2000, has δ¹⁸O of -10.72‰ vsSMOW.

Radiocarbon Dates

The Holocene ages for the in situ cements are unsurprising and these ages suggest the calcite does not contain a significant proportion of ‘dead’ carbonate from dissolution of Paleozoic limestone clasts. The older age of the clast cement is consistent with the suggestion of Aber (1979) that the clasts were cemented during a mid-Wisconsin or earlier interglacial episode, but provides no useful constraint on the age of mid-Wisconsin or older interglacials in the area. The timing of the late Wisconsin advance into the Appalachian Upland is not well-understood, but clast cements could have formed during the Farmdale or Port Talbot phases of Karrow et al. (2000), which represent relatively warm intervals at ~32,000 – 24,000 ybp and ~60,000-45,000 ybp, or during the Sangamon Episode of ~135,000 -95,000 ybp.

DISCUSSION

Hydrology and Isotopic Composition of Calcite-precipitating Waters

The precipitation of calcite cement in the Norwich locality involved the generation of acidic soil waters by interaction of downward-fluxing meteoric waters with soil organic matter. As these waters reacted with the host gravel, dissolution of limestone and reaction of waters with unstable silicate minerals raised alkalinity and pH. We suggest that calcite cementation occurred as the waters reached lower levels in the gravel pile, and modest evaporation or degassing of CO₂ occurred, promoting carbonate precipitation. The occurrence of in situ phreatic cement fabrics above the present water table in the Norwich locality indicates that on occasion the system was flooded with recharged meteoric water. The multilayer nature of the cement, with crystalline layers terminated by smooth dissolution surfaces followed by new isopachous cement suggests a series of flooding events that initially carried undersaturated waters, followed by precipitation of calcite. In the Norwich locality, we suggest that water was temporarily ponded above a low permeability zone defined by a fine sand layer just below the modern quarry flow. This ephemeral, perched phreatic zone remained watersaturated long enough to permit formation of the isopachous rind cement observed.

The temperature of calcite precipitation can be determined from the δ¹⁸O values of calcite if the isotopic composition of the precipitating waters is known. Correspondingly, if the temperature of precipitation is known, the δ¹⁸O of precipitating waters can be determined. With regard to the calcite cement in the Norwich locality, the modern groundwater (as measured in the summer of 2000) δ¹⁸O is -10.72‰ vsSMOW, and the groundwater temperature is in the range 11-13°C, based on water well measurements made in the vicinity of the Norwich site. Using the constants of O’Neil et al. (1969), calcite precipitating from modern groundwater in the Norwich area should have δ¹⁸O in the range ~9.5 to ~9.8‰. Figure 7 shows the calculated values of δ¹⁸O in calcite for a range of temperatures and water isotope values.

In situ phreatic calcite cement in the Norwich locality has δ¹⁸O in the range -8 to ~9‰, suggesting precipitation from waters cooler by 2-5°C, or slightly heavier waters than the measured modern groundwater. Since the in situ phreatic cement formed above the modern water table, apparently
from waters temporarily stored in a 'perched' phreatic zone, slightly heavier waters, derived from local rain and snowmelt which has a minor lake effect input, might be expected. Likewise, the heavier isotopic signature of vadose cement samples is consistent with locally-derived, and perhaps slightly evaporated meteoric water. Alternatively, precipitation of calcite at lower temperatures than modern groundwater would also account for heavier isotopic calcite than predicted.

Since formation of calcite cement would be favored under drier climatic conditions, slightly heavier meteoric waters would be expected due to higher temperature during rainfall and enhanced evaporation of soil water. If the ~4500 ybp radiocarbon age for in situ cement is broadly representative of the time of in cement precipitation, our data is most consistent with a climate that is warmer and drier than today's. Mid-Holocene warm/dry intervals are well documented in the climate records of mid-continent lakes (Yu et al. 1997; Dean et al. 1996) and a particularly strong period of drought in the interval 6000-4500 ybp is reflected by the history of sand dune migration in the U.S. Great Plains (Forman et al. 2001).

$^{18}O_{\text{PDB}}$ of clast cement is in the range $-5.2$ to $-6.7\%_{\text{oo}}$, significantly heavier than the in situ Holocene cement. This difference calls for isotopically heavier waters or much lower temperatures of precipitation for the pre-Holocene clast cement. Assuming the lowest possible temperature of clast cement precipitation is 0°C, waters in equilibrium with clast cement would have had $^{18}O > -9.0\%_{\text{Osmow}}$. If the clast cements formed at the 11-13°C of modern groundwater, the equilibrium waters were in the range of $-6$ to $-7\%_{\text{Osmow}}$ (Fig. 7). In either circumstance, the pre-Late Wisconsin waters that formed the clast cement must have been isotopically heavier than Holocene waters that gave rise to the in situ cements.

Modern groundwater influenced by recharge from lake effect precipitation in central New York is isotopically lighter than regional precipitation derived from maritime-sourced weather systems (Gutt et al. 1994). The heavier isotopic signature of the pre-Late Wisconsin clast cements in the Norwich terrace gravels indicate groundwater with less significant lake-effect precipitation, suggesting a climatic regime dominated by maritime-derived precipitation. Alternatively, the Great Lakes basins may have been smaller and thus exerted a less significant effect on local precipitation, or regional wind patterns may have been more zonal, limiting lake effect precipitation.

**Source of Carbon in Cement Carbonate**

The range of $^{13}C$ (-10.5 to $-6.5\%_{\text{oo}}$) in the Norwich calcite cements suggests that the carbonate was derived from more than one source. The lighter carbon reservoir was most likely CO$_2$ derived from decay of plant organic matter in the soil system. Modern forest vegetation in the Norwich area is dominated by C$_3$ plants which provide carbonate (by decay and release of CO$_2$) in the range $^{13}C = -19$ to $-12\%_{\text{oo}}$ (Cerling et al. 1989). Assuming that the surface vegetation system was similar during precipitation of the Norwich cements, a source of isotopically heavier carbon is required. Heavier carbon could have been derived either from dissolution of Paleozoic carbonate rocks found abundantly in the gravel or from atmospheric CO$_2$. Paleozoic limestones to the north of
the Norwich area have $^{13}$C in the range -2 to +4 $\%_{oc}$ (Popp et al. 1986; Simonsen and Friedman 1991). Alternatively, atmospheric CO$_2$ dissolved in soil waters could also provide heavier carbonate with $^{13}$C in the range +4 to +7 $\%_{oc}$ (Cerling et al. 1989). Since dissolution of limestone and mixing with atmospheric CO$_2$ both take place in the vadose zone, a heavier carbon isotope signature might be expected for vadose cements, as is the case for three of the four vadose cement samples (Fig. 5).

**SUMMARY**

1. *In situ* phreatic calcite cement in the Norwich area kame terrace gravel is of Holocene age and precipitated from meteoric waters slightly heavier in terms of $^{18}$O than modern municipal groundwater as measured in the summer of 2000. Heavier $^{18}$O of calcite-precipitating waters is consistent with a relatively drier climate that would likewise favor precipitation of calcite from evaporated groundwater. If the radiocarbon dates are broadly representative of the time of calcite cement precipitation, then generally drier conditions existed in central New York at -4500 bp.

2. Calcite cement fabrics in conglomerate clasts resemble *in situ* phreatic cement, but are pre-Late Wisconsin in age. Clast cement precipitated from isotopically water heavier than the *in situ* cements. The isotopically heavier waters of the pre-Late Wisconsin hydrologic system suggest that the region received relatively less lake effect precipitation or had a warmer climate dominated by maritime-derived moisture than the Holocene system.

3. Carbonate in the cements was derived from organic respiration and decay, plus minor contributions from dissolution of Paleozoic limestone clasts in the gravel and/or dissolution of atmospheric carbon dioxide in recharging groundwater.

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**REFERENCES**


HOLMES, C.D., 1939, Pleistocene Geology of the region south of Syracuse, N.Y. PhD Dissertation, Yale University.


SIMONSEN, J. and FRIEDMAN, G.M., 1991, Deep-burial limestone diagenesis of the lower Devonian Becraft Formation (Helderberg Group) of the Hudson River Valley area: *North-
YU, A., MCANDREWS, J. H., and ELCHLIN, U., 1997, Middle
Holocene dry climate caused by change in atmospheric
circulation patterns: Evidence from lake levels and stable