A PETROGRAPHIC COMPARISON OF TRIASSIC CALICHES FROM THE GETTYSBURG AND HARTFORD BASINS

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Introduction:

Caliches are calcite deposits formed in soils by evapotranspiration of plants causing local supersaturation. Caliches are formed in places where evaporation exceeds precipitation at least seasonally and are generally considered to reflect semi-arid conditions when seen in the rock record. Thus these are soil deposits and as such they form during the time that the sediments are subaerially exposed. Wang et al. (1998) showed that some calcite from caliches have favorable U/Pb ratios for dating and presented a precise age from one petrographically well characterized caliche from the New Haven Arkose of the Hartford Basin. The Hartford Basin is one of the Triassic Basins that line the eastern margin of North America and caliches are recognized from a number of these basins. We have chosen to further examine the caliches from the Hartford Basin in the framework established by Wang et al. (1998) and to compare these caliches with the wider variety of caliche types that have been recognized by deWet et al. (1998) from the Gettysburg Basin. The incentive for this study is to refine our understanding of the diagenetic fluids that might be responsible for concentrating U in a soil with the ultimate goal of exploiting this tool to date the time of sedimentation for terrestrial environments. In this investigation we first established the field relationships of the caliches and then examined the samples petrographically with transmitted light, cathodoluminescence and fission track mapping.

Geological Setting

In the late Triassic the supercontinent Pangea began to break apart, forming a string of rift basins along the present day eastern margin of North America. Approximately fifteen Triassic-Jurassic rift basins lie from the region of Nova Scotia to South Carolina. Among these are the Hartford and Gettysburg Basins. At the time of rifting, these basins were located near the palaoequator. As Laurasia shifted northward, a shift in climate occurred as the continent moved from a tropical climate to a more arid climate. Some rapid humidification also occurred, associated with a sea level rise as Laurasia drifted (Olsen, 1997). As a result, many sedimentary environments were created and altered over time. These changes are recorded in the sedimentary rocks that were deposited in the basins. Alluvial fan, fluvial, palustrine, lacustrine, playa, marine, and eolian deposits all occur in the Triassic-Jurassic sequences of the rift basins. For this study, the deposits within the Hartford and Gettysburg Basins containing caliches are the main focus. The caliches are mainly in the fluvial sequences, which are recognized as cycles of channel sand deposits followed by overbank clay deposits. The caliches are most notably developed in the overbank deposits.

The Hartford Basin is a north-trending basin located in central Connecticut. The New Haven Arkose is interpreted as a fluvial sequence and consists of 2000 m of sandstone and red mudstone that make up the lower portion of the approximately 4000m thick clastic fill of the Late Triassic-Early Jurassic Hartford Basin (Wang et al., 1998). The rocks used for this study are from an outcrop near Meridan from which the precise U-Pb age of Wang, et al. (1998) were obtained. The age results from the New Haven Arkose indicate that not all generations of calcite are datable. U-Pb data for the first generation pure micritic calcite from a horizontal sheet calcrete in sedimentary rocks gives an age of 211.9 ± 2.1 Ma and is consistent with its interpreted stratigraphic position some 2000 m below the Triassic-Jurassic boundary (Wang et al., 1998). The second generation of calcite is a blocky non-luminescent calcite that is closely associated with internal sediment. The third generation calcite is brightly luminescent, blocky calcite that followed the deposition of the internal sediment and can be seen crosscutting the first and second generation calcites and fills the remaining void space. A cement filled rhyzolith that is interpreted as the third generation of calcite cement was dated at 81 ± 11 Ma (Wang et al., 1998). These results illustrate both the great potential for dating the rock record and the complexity that must be understood in any soil horizon before geochemical analyses can be interpreted.

The Gettysburg Basin is located in southeastern Pennsylvania, and western Maryland (de Wet, et al., 1998). The caliches studied are from a core drilled near Thomasville, PA, known as the Rife Farm core. The core has 142 m of cyclical sandstone-mudstone fluvial deposits similar to those of the Hartford Basin. The cycles begin with a coarse grained sandstone, fine upward into a siltstone, and are overlain by mudstone which contains the caliches (de Wet, et al., 1998). Although the main focus of their paper was not the caliches, de Wet et al. did note that the calcite cement precipitated in two different episodes. The first generation filled the rims of fractures, in the form of non-ferroan low-Mg calcite micrite. The second filled the remaining pore space and is ferroan low-Mg calcite. These are just some of the appearances of caliches in the lacustrine unit.

Petrographic Techniques

First we examine each slide under plane light to examine the variety of fabrics in the caliches. The caliches are also examined for obvious alteration that would have an effect on dating.

Cathodo-luminescence (CL) is a technique commonly used for the study of diagenesis of carbonates because trace elements such as Fe and Mn quench and excite luminescence in a sample. Often this technique shows generations of calcite that could not have been recognized with standard petrographic examination. Additionally, since the mobility of Fe and Mn is controlled by the redox state of the fluid (Meyers, 1974) the CL technique allows a qualitative evaluation of the redox changes at the time that the calcite was precipitated.

Fission tracks provide a map of the distribution of uranium. These maps are obtained by neutron bombardment of a mirror-polished sample that is placed on a detector such as Lexan plastic. The detector records the induced fission of ^{235}U, and etching with NaOH accentuates the tracks so that they can be seen with plane transmitted light. The samples from the Gettysburg Basin were irradiated by a flux of 10^{16} N/cm^2 at the Kansas State University reactor. The samples from the Hartford Basin were irradiated at the Oregon State University reactor at a flux of 10^{17} N/cm^2 as recommended by Swart (1988). We have found that for samples that have 1 ppm uranium or more, the greater neutron flux is not necessary. Comparison of fission tracks with thin sections and rock chips provides a way to evaluate relative differences in the uranium concentration of the different generations of calcite in the palaeosols and their host rocks.

Results and Discussion

Petrography of the caliches in the New Haven Arkose shows three generations of calcite (Wang et al., 1998). The first is a dull-luminescent micritic calcite. Micrite refers to fine grained calcium carbonates when the particles are less then 4µm across (Folk, 1959). This first generation of calcite has abundant features that are recognized as the result of plant and soil processes including: alveolar structures, rhizoliths (organosedimentary structures produced in roots), as filling the cracks and as dense nodules (Wang, 1998). The second generation of calcite is a non-luminescent blocky calcite, which occurs as cements in pores of rhizoliths, alveolar structures and cracks. These first two generations of calcite are considered to have formed during soil formation (Wang et al., 1998). The third generation is a bright-luminescent blocky calcite that fills pores left behind by the previous two generations and also crosscut these first two generations of calcite (Wang, 1998). The fission track distribution shows that uranium is associated with the first and second generation of calcite (around 1-14 ppm and that the third generation of calcite has low abundances. For this study, we chose to study the Meridan section because of the precise age reported from this section by Wang et al. (1998). We decided to look "backwards" at one cycle in this section to try to understand how the generations of calcite that Wang et al. (1998) recognize relate to both caliches in overbank shales that he studied and to the calcite cemented base of the overlying channel sand deposit. At the base of the sandstone, within the mudstone, is where the caliches occur. CL reveals micritic and blocky calcite cements at the base of a channel sandstone layer of the New Haven Arkose. Our interpretation is that the sandstone layers are permeable layers that meteoric water can easily percolate through and that the passage of water is slowed by the underlying mudstone layers that act as aquitards. This creates a perched water table and the water becomes supersaturated with respect to calcite probably due to evaporation. Some of this supersaturated water also makes its way into the mudstones, especially through the sheet cracks and this may be the reason that caliches occur at the top of the overbank deposits. This interpretation is supported by the observation that the sandstone is bleached at the base and the sheet cracks in the underlying overbanks deposits have bleached halos. If this interpretation is correct, there should be similarities of the calcite within a sandstone layer and a mudstone layer. CL helps to support this idea because we see a dull-luminescent micritic calcite and a bright luminescent blocky calcite (Figure 1). Although Wang et al. (1998) recognized the

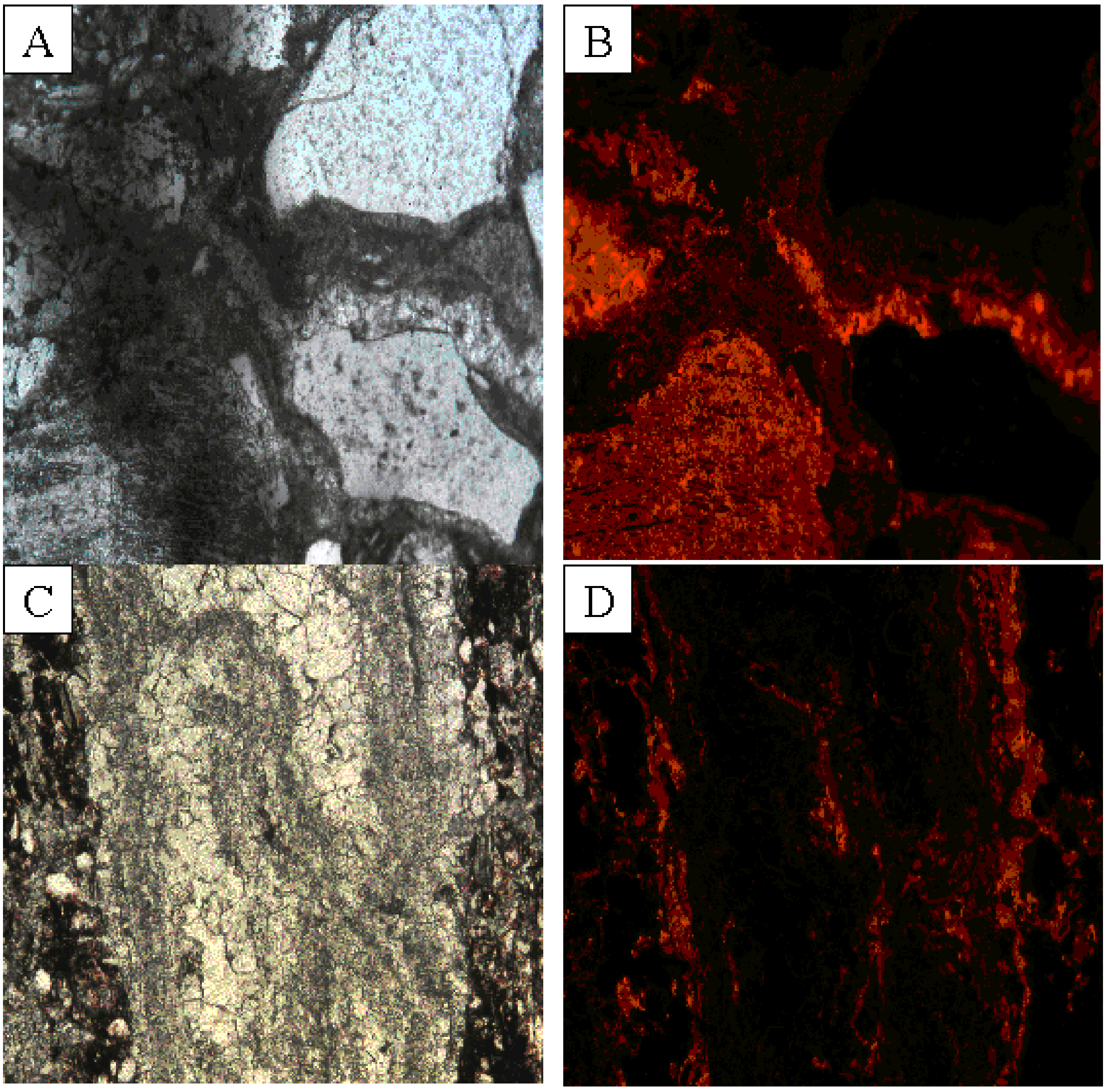

Figure 1. *Hartford Basin petrography:* **A)** Plane light photomicrograph (PL) of a sandstone with two generations of calcite including micrite calcite and blocky calcite; **B)** catholuminescence photomicrograph (CL) of the same area as A showing dull-luminescent micrite calcite followed by brightly-luminescent blocky calcite that also replaces some grains (lower left corner). **C)** PL shows alternating generations of blocky calcite followed by micritic calcite. **D)** CL of the same area as C showing dull-cathodoluminescent micritic calcite and brightly-luminescent blocky calcite. Scale of all photomicrographs is 1 mm across.

micrite calcite as first generation, in some of the overbank deposits and in the sandstone we see a blocky calcite is precipitated first and this is followed by the micrite calcite. The blocky calcite that Wang et al. (1998) recognized as the second generation of calcite is non-luminescent while the blocky calcite we observe has bright luminescence.

The caliches within the fluvial sediments of the Gettysburg Basin exhibit many different features and some of these are summarized in Table 1. The first generation of calcite that Wang et al. (1998) recognized in the Hartford Basin was micrite. The micrite seen in the Rife Farm core samples is also early but occurs dominantly in nodules (Figure 2 A, B). Although they are dull luminescent like those of the Hartford Basin, they incorporate the host clay. Wang et al. (1998) demonstrated that greater than 5% insoluble residue in the caliche samples limited the utility for U-Pb dating. In the Hartford Basin micrite also occurs as the first generation of calcite in horizontal sheet cracks and this micrite was relatively free of insoluble residue. In the Rife Farm core, cracks that are similar macroscopically have as the first generation of calcite a blocky calcite that might be equivalent to the second generation of calcite that was recognized by Wang et al. (1998). However, unlike the second generation calcite in the sheet cracks of the Hartford Basin, which are non-luminescent, the CL of the blocky calcite in the Rife Farm sheet cracks has zoned luminescence and non-luminescence (Figure 2 A-D). The zoning suggests that this calcite formed under fluxuating redox conditions probably near the water table. Further study of this banding compared with fission tracks may help determine the role that Eh plays in the incorporation of U in soil calcite. In many of the sheet cracks, one or more zones of hematite occurs within the zoned blocky calcite and U is highly concentrated in

Table 1: Initial results of the petrographic study of caliches from the Rife Farm core, Gettysburg Basin, PA.

Type of Caliche	Cathodo luminescence	Fission Tracks	Location
Blocky Calcite	1) Non luminescent	On a very small scale	Cracks
	2) Luminescent		
Micrite	Dull Luminescent	Small amounts	Nodules, few cracks
Flower shaped Calcite	Brightly luminescent	Not yet interrupted	Grows into shape
Calcite with Hematite	Hematite non luminescent	Follows the hematite	Hematite growth
	Calcite tends to be one	Calcite shows small	follows the outline of
	of the types of blocky calcite	amounts	caliche
			*Chart based solely on this study.

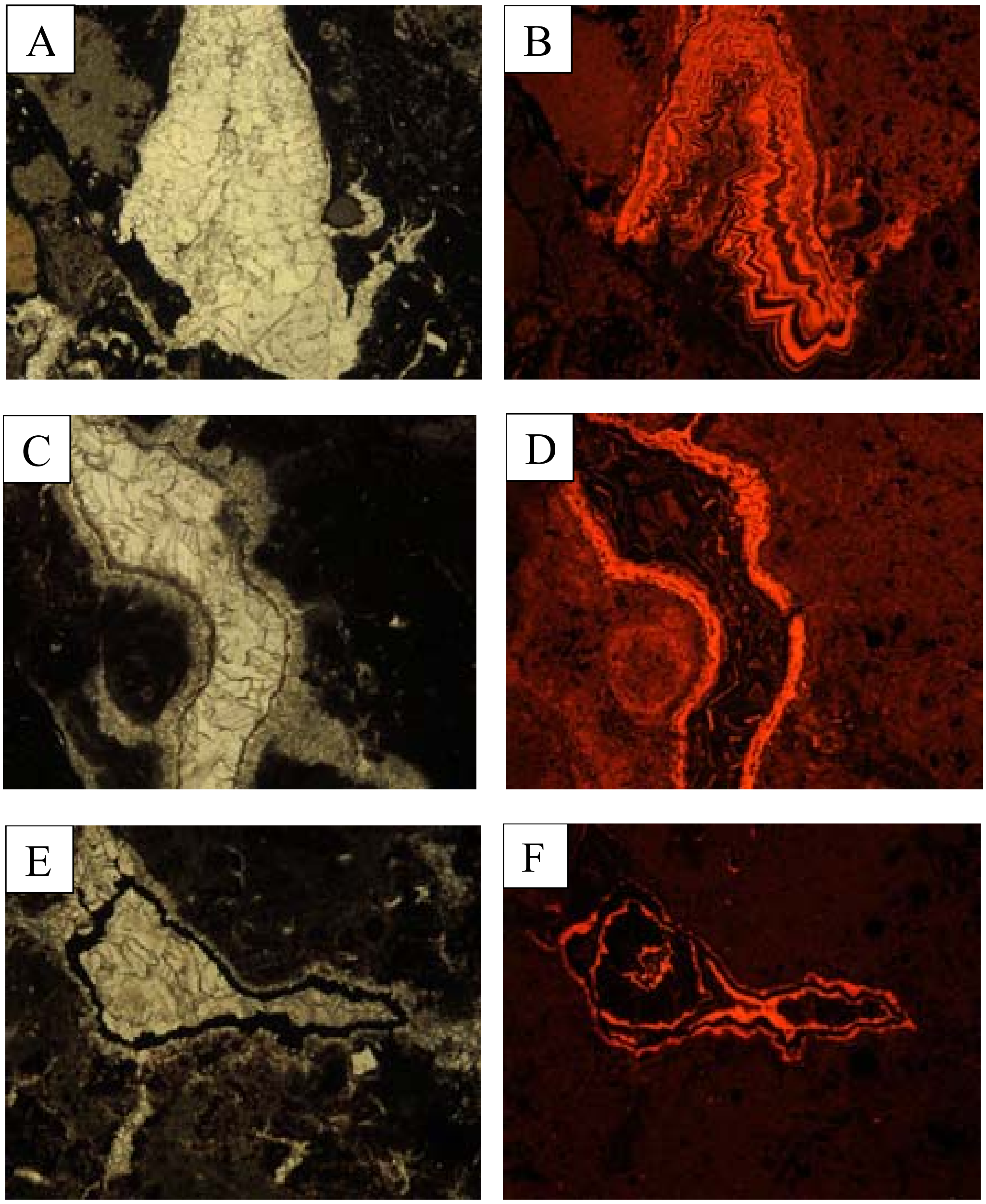

Figure 2. *Gettysburg Basin petrography:* **A)** Plane light photomicrograph (PL) showing nodular calcite followed by a vein that is filled with blocky calcite. **B)** Cathodo-luminescence photomicrograph (CL) of the same area as A showing the dull luminescent micrite and zoned blocky calcite. **C)** PL of vein filling calcite showing an early generation of finer crystals of blocky calcite followed by a thin hematite layer and finally filled with a course crystalline blocky calcite. **D)** CL of C showing the bright luminescence of the first generation of blocky calcite and fine scale zoned luminescence in the course blocky calcite. **E and F)** PL and CL of vein filling calcite with a hematite layer that separates non-luminescent calcite from zoned luminescent calcite with that are much wider than those seen in C and D. Scale of all photomicrographs is 1 mm across.

this phase. Although Rasbury et al. (2000) showed that hematite from other palaeosols has complicated U-Pb systematics, they were unable to demonstrate when the hematite formed relative to the soil calcite. In the case of the Rife Farm hematite (Figure 2 C-F), the intercalation within the zones of calcite requires that the hematite formed in the soil zone. Thus this phase is worth considering for U-Pb analyses. This type of hematite was not recognized in the petrographic study of the caliches in the Hartford Basin.

This study has led to many possibilities for understanding the geochemistry of fluids that are responsible for the precipitation of the variety of caliche types we recognize. Although the caliches of the Hartford and Gettysburg Basins are macroscopically similar, microscopically they exhibit distinct differences. With the variety of textures and differences in the chemistry of the waters from which the calcites precipitated based on different CL properties, we hope to gain more insight into the processes that are important for U incorporation in soil calcite with the ultimate goal of using the U-Pb system to date the time of sedimentation of these terrestrial sequences.

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