A Petrographic Study of Devonian Teeth from Clinton County, Pennsylvania

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Introduction:

Fossils are our record of past life on the Earth and are the basis of our understanding of geological time. Although a lot of effort has been directed at correlation between the marine and terrestrial records, this effort is hampered by the incompleteness of the rock record and the rare interfingering of marine and terrestrial deposits. If vertebrate fossils could be dated, this would provide a powerful test for correlations since in many cases these are the very foundations for the correlations. Our ultimate goal is to test the potential for U-Pb dating of fossil bone material. It is clear from many studies of Cenozoic fossils that U uptake is a complex process in bones. For young bones researchers have had to make models for the U uptake and in most cases the results are ambiguous and can be clearly erroneous. In some cases uranium uptake appears to have occurred over many tens of thousands of years (Grun et al., 1999). This protracted history makes dating very young fossils challenging, but if the fossils become closed to U uptake after the fossilization process they could potentially provide fairly precise ages for much older deposits. The incorporation of U in fossils may depend on the fossilization rate and how uranium is incorporated in the fossils. Although bones are originally hydroxyapatite they are almost always converted to francolite, a F bearing apatite. The interpretation is that F replaces the OH group in the apatite. This process may beautifully preserve the original structures of the bones and teeth and this suggests that fossilization may proceed geologically rapidly. By learning more about the fossilization process and examining fossils on a microscopic scale we hope to learn more about the replacement processes and its relationship to U uptake in the fossil. In this study we compare teeth of Osteolopiformes from an oxidized facies and from a reduced facies of the Red Hill Bed of the Duncannon Member of the Catskill Formation in Clinton County, Pennsylvania to learn more about the process of fossilization. Teeth were chosen because they are known to be one of the most durable remains of vertebrate organisms.

Geological History:

In the late Devonian, the super continent Pangea had already begun to form. The Acadian mountains, produced by this tectonic activity in upstate New York and neighboring Pennsylvania, were being eroded to form a series of alluvial, deltaic and marine deposits along the eastern shore of Laurasia. These deposits are referred as the Catskill Clastic Wedge or Catskill Delta. At the time of their deposition they were located south of the Paleoequator, around 30º S. The mountains in the area affected the local climate causing wet, dry or desert climates.

For this study, the alluvial deposits at Red Hill, central Pennsylvania, were targeted due to its rich vertebrate fossil remains. Red Hill belongs to the Duncannon Member of the Catskill Formation. The sedimentary environment of the Red Hill is interpreted to have been a meandering river in a low relief alluvial plain. The fining upward cycles, between 5-10 meters, include red mudstone, greenish gray mudstone, and very fine-grained and flat laminated gray sandstone. There are several groups of vertebrate fish found within the formation. Additionally, an early tetrapod fossil from the Catskill Formation extended the temporal range of tetrapods in North America and suggests that they attained a virtually global equatorial distribution by the end of the Devonian (Daeschler et al., 1994). In the Devonian, plant life began to have more of a presence on land. Red Hill, on the basis of palynology, is considered Famennian, the last epoch in the Devonian (Woodrow et al., 1995). The teeth used in this study are Osteolepiforms, probably from the Tristchopteridae or Eusthenopteridae family. These conical teeth have a complexly folded enamel structure (labyrinth structure) that is a shared trait between Osteolepiforms and Paleozoic tetrapods.

Techniques:

The samples were first examined in the rock matrix as they were found (***Figure 1A, 1C***). The type, color and the grain size of the rock were noted. Thin sections were cut to expose the cross-sections of each sample. Thin sections were studied using plane-polarized light and cross-polarized light and with incidental light using the white card technique (Folk, 1987).

Autoradiography, a type of phosphor imaging, was used to estimate the concentration of radioactive elements such as U and Th (***Figure 1B, 1D***). Autoradiography detects strong β, γ and X-radiation emitted from U or Th concentration of the sample and causes Eu^{2+} to oxidize (Cole et al., in review). The image is then detected by a Phosphor Imager at the University Microscopy Imaging Center at the State University of New York at Stony Brook.

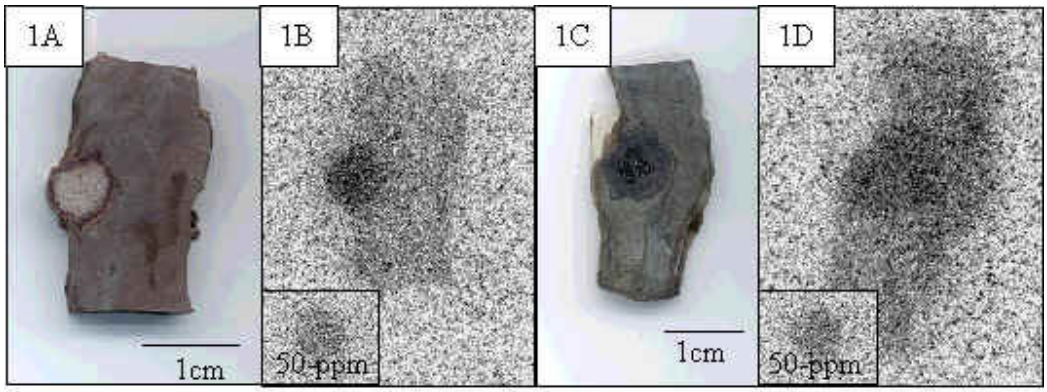

Figure 1: Hand specimens and autoradiographs. For semi-quantitative comparison a 50-ppm uranium standard is used. ***1A)*** Sample TCAT in cross-section, notice the lemon shape of the sample. ***1B)*** Autoradiograph of sample TCAT shows the uranium distribution, the darker areas indicate higher U concentrations. The sample is clearly more enriched than 50 ppm based on the noticeably darker image. ***1C)*** Sample SCAT in cross-section, notice the lemon shape of the sample. ***1D)*** Autoradiograph of sample SCAT shows that the tooth has similar U concentrations to that in TCAT. The rock in which SCAT is enclosed in clearly more enriched in radioactive elements than TCAT.

Results:

The two fossil teeth samples are structurally similar. In cross section the teeth are lemon shaped (***Figure 1A & 1C***). The complex folding between the dentine and pulp cavity identifies the folded tooth labyrinth structure (***Figure 2A & 2C***). Each sample has a thin layer of enamel (***Figure 2B & 2D***), which is the hard outer coating of the tooth. The dentine is the fibrous layer under the enamel (***Figure 2B & 2D***). The center of the teeth contains the pulp cavity (***Figure 2A & 2C***), which was the living tissue that served as the blood and nerve supply for the tooth. The tubular holes (***Figures 2B & 2D***) in this cavity are the pathways for blood vessels.

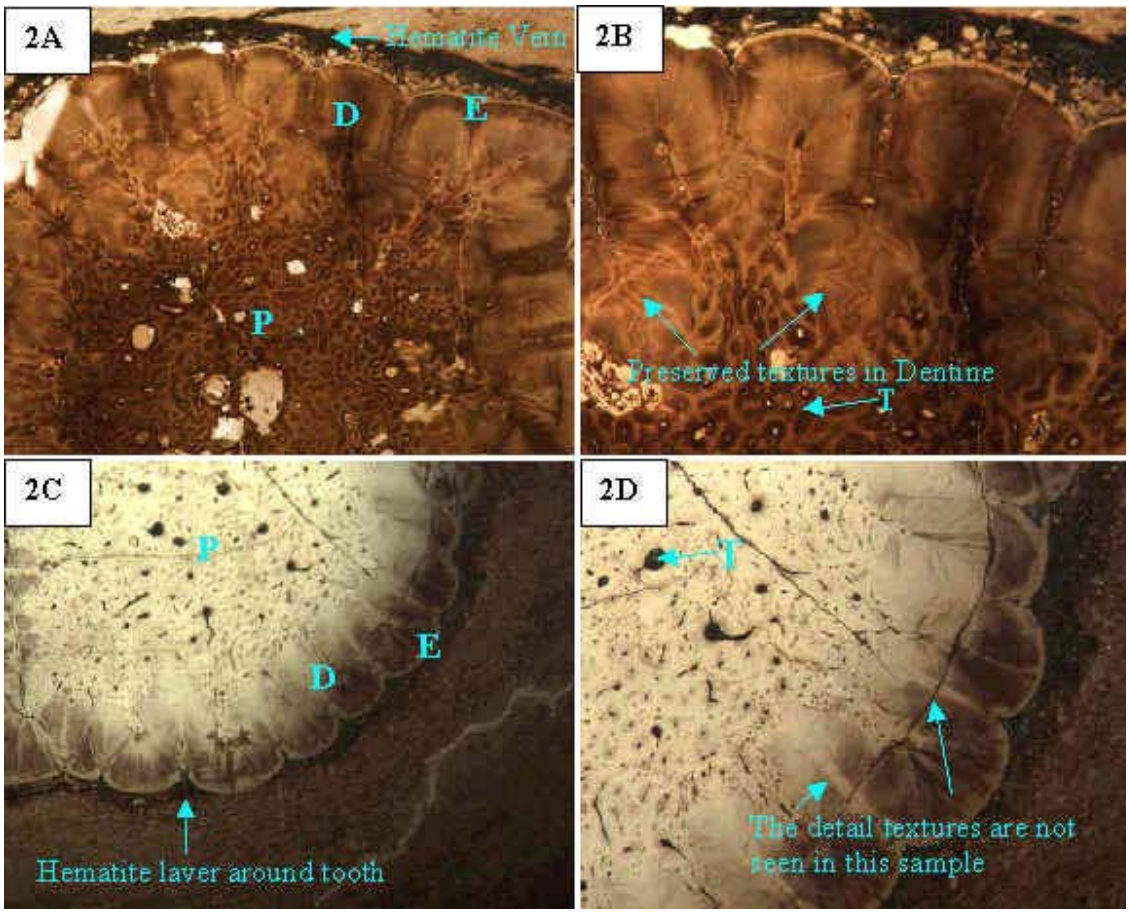

Figure 2: Photomicrographs of teeth under a incidental light microscope. The labels on the photographs represent a different feature in the teeth. **E**, is the enamel, **D**, is the dentine, **P**, is the pulp cavity and the tabular canal where the blood once flowed is represented by the **T** and arrow. ***2A)*** Sample SCAT, 9mm across base of photo. ***2B)*** Sample SCAT 4mm across the base of the photo. Brown organic coloring throughout sample SCAT is easily seen. ***2C)*** Sample TCAT, 9mm across the base of the photo. ***2D)*** Sample TCAT, 4mm across.

Sample SCAT was found in a gray-brownish mudstone. This color indicates a reducing environment, with low oxygen levels and likely high organic matter preservation. These conditions probably also resulted the brown coloring seen in this tooth (***Figure 2A and 2B***). Sediments were compacted around the tooth (***Figure 1A***). Thin section examination reveals that the rock consists mostly of a mudstone, however, in the area around the tooth there are floating quartz grains (***Figure 3A***). Within the rock there is a vein of specular hematite that partially surrounds the tooth (***Figure 2A***). The tooth does not appear to be crushed by the compaction, possibly suggesting that the replacement of the fossil occurred before the compaction event. The enamel is a semi-translucent, white, thin layer, which is most easily viewed with Folk's (1987) lack card technique (***Figure 3A, Figure 5A***). There are cracks that break the enamel layer (***Figure 3A and 3B***), but the enamel is not discolored and does not appear to have complex alteration history. In cross-polarized light the apatite has fans of micro-crystals that seem

to maintain a primary morphology. The dentine area has been broken by micro-fractures, which appear to have provided pathways for diagenetic fluids (***Figure 3A***). Some of these micro-fractures are filled with hematite (***Figure 3B***). With increasing distance from the cracks, the alteration appears much less pronounced. The pulp cavity of the tooth has a light brown and dark brown pattern (***Figure 3C***). The pulp cavity contains blood vessel tubules that are a series of round shapes. The material that originally permineralized the tooth no longer occupies the tubules in the pulp cavities (***Figure 3C***), and the tubules are left empty. The material surrounding the tubule holes is light brown and contains tiny capillary features in a radial pattern (***Figure 3C***). These features are not always easily seen in this specimen. Between the folded structures of the outer tooth, we see lines of holes (***Figure 2B***). These holes connect to a zigzag pattern, with alternating colors the center (***Figure 3D***). The zigzag pattern is also seen in the center of the folds (***Figure 3D***). Layers seen within the dentine, mostly parallel the enamel layer tend to be darker near the enamel (unless altered by a micro-fracture) and lighten as they near the pulp cavity (***Figure 2B***). We interpret these layers as growth bands.

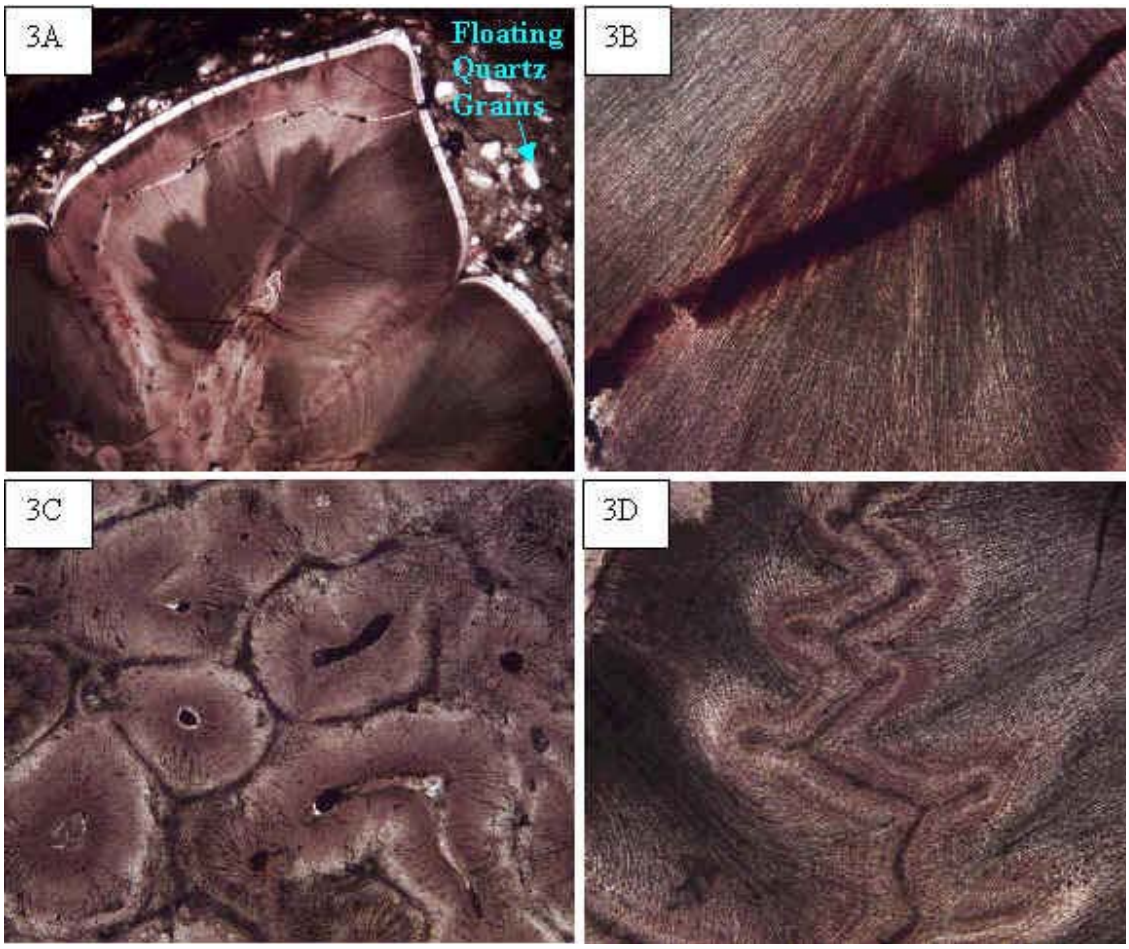

Figure 3: Photomicrographs of sample SCAT in plane light. 3A) 1.2 mm across. This picture demonstrates the micro fractures along which diagenesis altered the dentine fibers. Although the enamel does not appear altered, the micro fractures break it as well as the underlying dentine. ***The scales of 3B, C & D, are all 0.5 mm across. 3B)*** A micro

fracture filled with hematite and alteration of the nearby dentine fibers. ***3C)*** Tabular structures of the pulp cavity where blood vessels and nerves resided. Around each hole are radiating capillary tubes, which are thought to be an original structure within the tooth. The structures surrounding the tabules, like the rest of the tooth, are a brown color, with a thin white rim. ***3D)*** Within the crease of the folds in SCAT there are very well preserved zigzag feature in the dentine fibers that appear to have growth layers.

Sample TCAT was found in a red mudstone. This color indicates an oxidizing environment; as a result we can see plenty of hematite. The enamel is a semi-translucent white (***Figure 5C***), and does not show evidence that it was diagenetically altered near the micro fractures, but these breaks provides a pathway for fluids to enter the tooth. The dentine is red near the enamel and becomes whiter towards the pulp cavity (***Figure 2C&D***). In this specimen, as in sample SCAT, fluids appear to have used micro fractures in the tooth to preferentially alter the tooth (***Figure 4B***). The dentine fibers appear to have been coated with or replaced by hematite. The pulp cavity is off-white, and the centers of the tubules are filled with specular hematite. A radiating pattern of fine capillary like tubes, filled with hematite, extends from the center to the rim of the tubular structures (***Figure 4A)***. Hematite permineralization appears to have accentuated these capillary like tubes in sample TCAT so that they are far more visible than they are in sample SCAT, although overall the preservation appears to be less in sample TCAT.

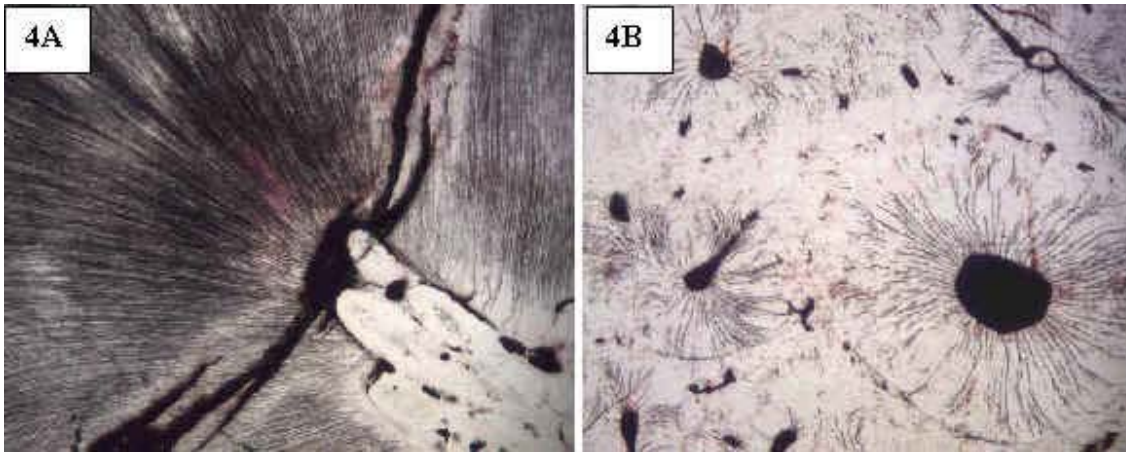

Figure 4: Photomicrographs of sample TCAT. Scale for both A and B is 0.5 mm across. 4A) Similar to SCAT, TCAT has hematite filled micro-fractures that cut the tooth. While the dentine is stained red by the hematite near the micro fractures, the pulp cavity does not exhibit this alteration. ***4B)*** The tubular structures in the pulp cavity are filled with hematite. The hematite also is in the structures radiating from the tubules.

From this study alone we are able to find areas within the teeth that may be more favorable for dating then others. Sample SCAT, from the reducing environment seems to have preserved more textures. By using the white card technique the original growth patterns are easily seen (***Figure 5B***). In contrast, sample TCAT from the oxidizing environment does not have the detailed preservation of growth textures. This is likely the result of the organic matter which makes SCAT brown not been preserved in TCAT

because oxidizing conditions break down organic matter. However, alteration associated with micro fractures within the dentine may have also modified the U-Pb on this part of the tooth. Based on the apparent preservation, we believe the best parts of the tooth to target for U-Pb dating are: 1) the enamel in both TCAT and SCAT; and 2) the tubular structures in SCAT.

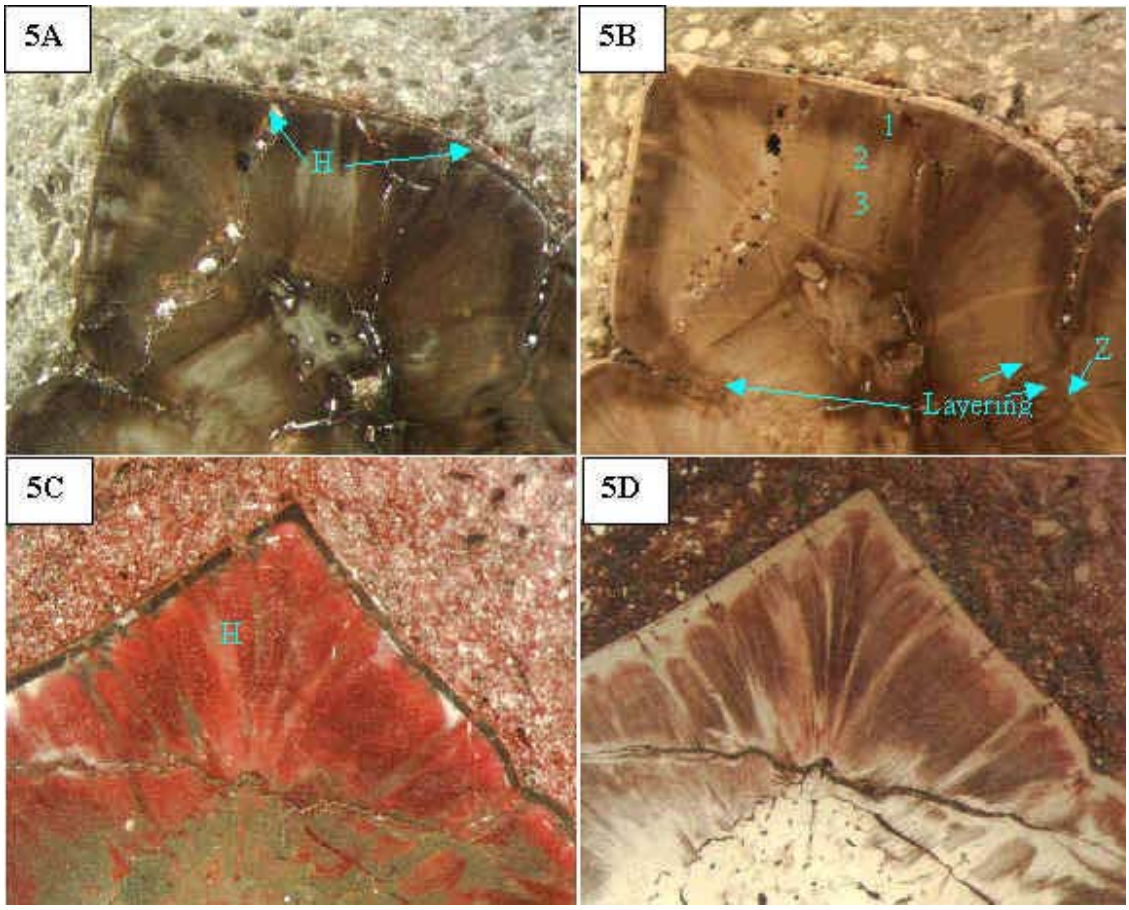

Figure 5: Photomicrographs using incidental light and the black and white card technique of Folk (1987). Scale is 3mm across. In sample SCAT: 5A) The black card technique shows micro-fractures that were filled with a lighter material. The enamel is translucent as demonstrated by the black background showing through. The hematite is easily detected by the bright red color (H), and there is not much of it. ***5B)*** The white card technique emphasizes the preserved growth layering. A few of the layers are marked with *1, 2,* and *3)*. The layering parallels the contact of the dentine and enamel. The layering can also be seen within the zigzag patterns (Z). In sample TCAT: ***5C)*** The black card technique brings out the very abundant hematite in the dentine layer (H). ***5D)*** The white card technique shows the bleached pulp area. There is no color layering preserved within the dentine as seen in SCAT.

Based on autoradiography, both teeth appear to have similar concentrations of U. This suggests that the local conditions of the surrounding rock may not play a large role in the uptake of U in fossils. This seems reasonable because U travels as the oxidized

uranyl species and even in reducing conditions, U is not easily reduced. In our future studies of these teeth we will perform synchrotron micro-diffraction studies of the enamel, dentine, and pulp cavities to determine the mineralogy. We will also use synchrotron X-ray fluorescence to map trace elements such as U, Th, Pb, REE, Fe, and Mn, which will help us to further constrain the diagenetic history of fossilization. Finally we hope to use synchrotron X-ray absorption spectroscopy to determine the oxidation state of the U. In a previous study of bones we found U in the reduced state in one bone and in mixed oxidation states in another (Nienstedt et al., 2001). We hope to combine petrographic analyses with synchrotron techniques to allow for better sampling for U-Pb dating.

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