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Phosphate Mineralization at Nonconnah Creek, Memphis, Tennessee

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Abstract—Vivianite, a colorful rare iron phosphate mineral, was recently found in a point bar of Nonconnah Creek, a stream which flows along the southern edge of the city of Memphis, Tennessee. We believe this is the first reported occurrence of vivianite in western Tennessee. In contrast to the predominant siliceous water-worn sediments in the creek, vivianite crystals here are often angular and show good crystal form. Consequently, vivianite is interpreted to have formed locally without significant transport by the stream. Local biological and anthropogenic sources of phosphate are evaluated, as well as the possibility of biologically mediated vivianite precipitation.

Introduction

Herein we report the discovery of a new location of the mineral vivianite and the research conducted to determine why it occurs in an unusual place, a creek within the city limits of Memphis, Tennessee. In this paper we 1) review the geology of the locality where vivianite is found; 2) discuss the mineralogy of vivianite and the procedures used to identify it; 3) report field observations which have driven our interpretation for the processes that led to the formation of the vivianite crystals; and 4) evaluate the involvement of biogeochemical processes in the formation of vivianite at Nonconnah Creek and its potential implications for phosphate fixation and water quality control.

Background and Methods

The Geological Setting of Nonconnah Creek—Memphis sits beside the Mississippi River in Shelby County, Tennessee, within the north-central Mississippi Embayment, a low-lying body of land that stretches from the Gulf Coastal Plain to southern Illinois. The embayment is a broad, shallow sedimentary basin filled approximately 1 km deep with Cretaceous through Holocene sediments (Cushing et al., 1964). The basin-fill sediments are capped in western Tennessee by alluvial terrace gravels (Van Arsdale et al., 2008) and loess, a glacially-derived wind-blown sediment of Pleistocene age (Snowden and Priddy, 1968).

Nonconnah Creek is a tributary of the Mississippi River that drains a large portion of the southern area of Shelby County plus portions of southwestern Fayette County, Tennessee, and northern Marshall and Tate counties, Mississippi (Fig. 1). Exposed along the banks of Nonconnah Creek are strata consisting of silt, sand, gravel, and clay. Blue-gray clay at some locations along the creek contains compacted organic matter: trees, leaves, nuts, acorns, and seeds, as well as the remains of fauna ranging from snails and insects to a mastodon (Brister et al., 1981).

The study site on Nonconnah Creek is in the southeastern part of the city of Memphis (Fig. 2). Here at the contact between the loess and fluvial deposits occurs a horizon of iron-stained sediment and deposits of organic matter in a blue-gray clay layer between the loess and a lower gravel layer. Gravel deposits in the creek primarily consist of siliceous lithologies including chert, jasper, geodes, agate, and silicified fossils such as bryozoans, crinoids, corals, brachiopods, and rare cephalopods and trilobites. The fossils found here are dominantly of Mississippian period species.

Circumstances of the Discovery of Vivianite—On several collecting trips to Nonconnah Creek about five years ago, the first author discovered some unusual crystals on a gravel point bar

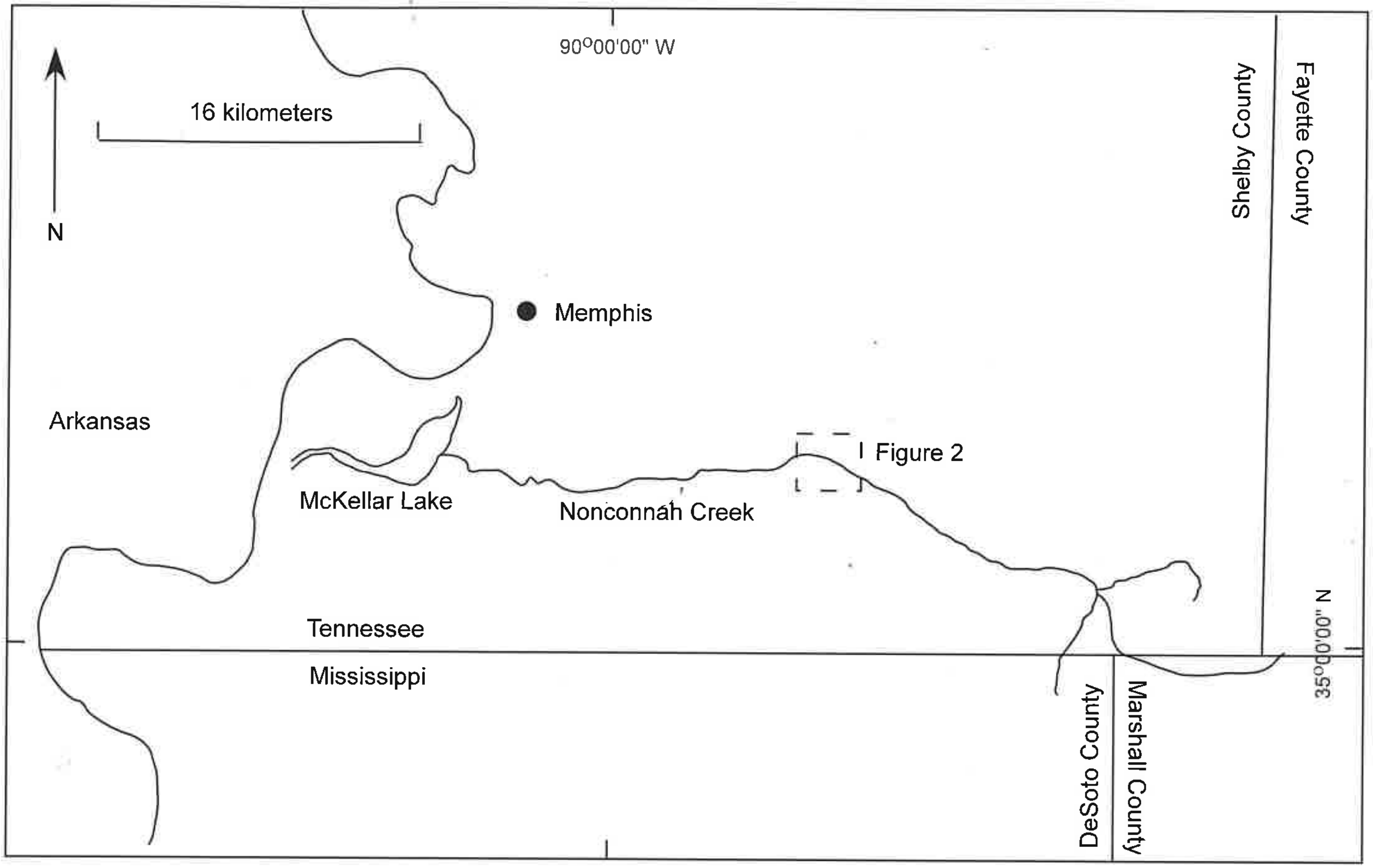

Fig. 1. Location map of Nonconnah Creek in southwestern Tennessee. Note that the Tennessee–Arkansas border (shown) closely follows the course of the Mississippi River (not shown).

behind Halle Park, located on Mt. Moriah Road. At the March 2006 meeting of the Memphis Archaeological and Geological Society he showed some of the best crystals to the speaker of the evening, William Prior, an Arkansas Geological Survey geologist. Mr. Prior conducted simple tests on them that indicated that the crystals were vivianite. Mr. Prior and others encouraged the first author to show the crystals to someone at the University of Memphis (UofM), so he contacted the second author.

Mineralogy of Vivianite—Vivianite, $Fe_3(PO_4)_2 \cdot 8(H_2O)$, hydrated iron phosphate, can occur as clear monoclinic crystals when first exposed to surface conditions, but usually changes to shades of green and then blue to black over a period of days to weeks. This color change reflects changes in the chemical composition of vivianite that involve some Fe^{+2} altering to Fe^{+3}. However, sometimes conflicting statements in the literature suggest that the controls on the color change need further study. Vivianite occurs in several geological settings including coarsely crystalline igneous bodies called pegmatite and sedimentary strata where it occurs as microscopic to centimeter size individual crystals or aggregates. In the sedimentary setting, vivianite formation has been associated with bacterial reduction of iron oxide and oxidation of organic material in anoxic sediment (Zachara et al., 1998).

Analytical Techniques—Specimens were observed with a binocular microscope and analyzed by powder X-ray diffraction (XRD, Bruker AXS D8 instrument in the UofM Department of Physics and Philips instrument in the Department of Earth Sciences) and energy dispersive spectrometry (EDAX, Philips XL 30 environmental scanning electron microscope with energy dispersive spectrometer in the UofM Integrated Microscopy Center).

Results

Field Observations—All specimens collected from the surface of the modern point bar on

Fig. 2. Google Earth image with the vivianite-bearing point bar marked on Nonconnah Creek. Coordinates of the point bar are 35°04′50″ N, −89°52′39″ W.

Nonconnah Creek between 2005 and late 2009 were dark purple to nearly black. Many crystals show the characteristic one direction of perfect cleavage of vivianite (Fig. 3), but some samples are irregular microcrystalline aggregates. The often well-formed individual crystals range in maximum dimension from less than 1 mm to about 1 cm. The crystals and crystal aggregates are found on the surface of and in pits on chert and other siliceous pieces of gravel of the point bar. The host gravel particle surfaces are variously smooth, knobby, or irregular, but all show signs of being thoroughly water worn. No macroscopic crystals have been found on anthropogenic materials such as concrete or glass. Many of the macroscopic dark purple to black crystals are angular and many display good crystal faces. Some crystals show evidence of some abrasion and partial dissolution. Blue to purple cryptocrystalline encrustations, also believed to be vivianite, have been found on the clay sediments of the river bank just upstream from the point bar and on gravel on the point bar. A piece of brick found on the point bar has a

Fig. 3. Vivianite sample on silicified fossiliferous limestone cobble from Nonconnah Creek. The 3-mm crystal is olive green in the interior grading to black toward the exterior.

patch of a microcrystalline aggregate on it that also may be vivianite. Specimens collected from the gravel bar and immediately adjacent creek channel in late 2009–early 2010 are often similar to those collected previously, but many were initially very light green, translucent, and often as larger crystals up to 2 × 5 × ½ cm, that were not abraded or partially dissolved. Some of these exhibit beautiful penetration twins.

Mineral Identification—Optical observation and XRD analysis of the dark purple to black crystals indicated that the specimens are related to the vivianite group of minerals, such as baricite (a magnesium iron phosphate mineral), bobierrite (a magnesium phosphate), and vivianite. XRD data were not definitive (Table 1) due to the similar d-spacings of these minerals. A specimen was then subjected to EDAX analysis, to obtain the material's chemical composition (Table 2). In combination with the XRD results, this test confirmed that the dark purple to black crystals are samples of the mineral vivianite.

Discussion

Potential Sources of Iron and Phosphate—Numerous vivianite crystals have only been found in and on one point bar along Nonconnah Creek. Crystals have been found loose in the sand and gravel, but most crystals occur attached to gravel-size particles of the point bar. Crystals attached to gravel have been found on the submerged shoulder of the point bar in the creek, on the exposed top of the point bar, and buried within the point bar. The vivianite crystal finds have been more abundant with proximity to the upstream end of the point bar, but samples have come from all parts of the point bar. After some high water events, vivianite specimens have been left distributed, presumably by the receding water line, in trails roughly following the contours of the point bar. Vivianite is rather soft with a Mohs Hardness between 1.5 and 2. Consequently, the angular crystals of vivianite that don't show evidence of being water-worn cannot have been transported far by the creek. Furthermore, since vivianite can change color within days of exposure from clear or light green to dark purple or black, the light green crystals found during the 2009–2010 interval suggest that they had been excavated from the subsurface and deposited on the gravel bar or formed on the gravel over a very short period of time. The nearly exclusive restriction of the vivianite crystals to this one point bar on the creek suggests that the sources of iron and/or phosphorus for vivianite are local.

Iron is fairly abundant in the sediments of Nonconnah Creek as oxide, hydroxide, and sulfide minerals, and in the groundwater of the Memphis aquifer (Brahana et al., 1987), the primary municipal source of water located approximately 30 m below the Halle Park area (Strom, 1997). Iron oxide/hydroxide mineralization along bedding and stratigraphic surfaces exposed along the creek banks indicates that groundwater within the shallow unconfined aquifer contains reduced iron. Some of the iron oxide/hydroxide mineralization may result by dissolution of pyrite and other iron-bearing sulfide minerals in the sediments and precipitation as oxide/hydroxide upon contact with oxygenated water or the atmosphere. Although unconfirmed in the present study, it seems reasonable that some iron may be locally reduced by bacteria such as *Thiobacillus* or *Shewenella* (Glasauer et al., 2003). Anthropogenic sources of iron may also exist. Indeed, low concentrations of iron in wastewater from the nearby Lichterman Pumping

Table 1. Comparison of powder XRD data of ASTM standards and Nonconnah sample.

Baricite		Vivianite		Nonconnah	
29–705		30–662		Sample	
d	Int	d	Int	d	Int
7.9	25	7.93	13	7.82	3
6.71	100	6.73	100	6.65	100
4.87	20	4.9	12	4.86	5
4.51	5	4.558	5	4.532	2
4.33	15	4.341	2		
4.07	10	4.081	12	4.052	2
3.832	20	3.849	7	3.824	2
		3.768	<1		
3.61	5				
3.341	1	3.361	1		
		3.343	2	3.326	1
3.196	40	3.21	16	3.195	4
		2.985	10	2.977	2
2.956	60	2.96	8	2.943	1
		2.77	4	2.758	1
		2.728	9	2.722	4
2.699	70	2.706	9		
2.626	10	2.637	6	2.627	1
		2.593	4		
2.526	50	2.53	8	2.521	1
		2.514	3		
		2.448	1		
2.418	35	2.421	6	2.413	1
2.311	15	2.321	7	2.314	2
		2.296	1		
2.275	5	2.279	1		
2.217	30	2.233	5	2.227	1
		2.194	5	2.187	1
2.179	10	2.173	2		
		2.108	1		
2.066	20	2.075	4	2.069	2
		2.039	<1		
2.001	5	2.012	2		
1.959	5	1.964	2		
1.922	10	1.936	2		
1.886	5	1.886	2		
1.878	1				
		1.816	2		
		1.793	1		
		1.786	3		
1.768	10	1.772	2	1.769	2
1.676	30	1.681	6	1.678	2
+ 20 add'l		+ 4 add'l			

Table 2. Instrumental chemical analysis of Nonconnah vivianite. (Qualitative chemical analysis by EDAX/ESEM).

Ideal vivianite: $Fe^{+2}{}_3(PO_4)_2 \cdot 8H_2O$		
Anhydrous part of the formula: $Fe^{+2}{}_3(PO_4)_2$		
	Anhydrous element weight % calculated	Element weight % analyzed
Fe	46.9	43.6
P	17.3	16.4
O	35.8	40.0 (by difference)
Total	100.0	100.0

Station (which pumps water from the Memphis aquifer) have occasionally entered drainage channels that empty into Nonconnah Creek (US EPA, 2012). The abundance of iron in the environment around Nonconnah Creek precludes the necessity of identifying a particular point source for use in the formation of vivianite.

Sources of phosphate in sufficient abundance are less clear. In general, phosphate occurs in natural organic materials such as decaying plant and animal tissues, animal wastes, bones and shells, in natural inorganic forms such as the mineral apatite, and in anthropogenic compounds and human wastes. In archaeological studies, microcrystalline encrustations of vivianite have been reported on buried animal remains. A 39,000-year-old Alaskan steppe bison carcass was called the 'Blue Babe' because of the vivianite coating its fur (Guthrie, 1990). In the forensic setting, vivianite was observed on the remains of three American casualties of the Vietnam War missing in action for 28 years (Mann et al., 1998). Vivianite has also been reported on the remains in mass graves from the Bosnian conflict, demonstrating vivianite formation in only three years (Wright et al., 2007).

Nonconnah Creek flows through residential and commercial urban areas, suburbs, and agricultural areas. A number of potential sources of anthropogenic phosphate occur upstream from the vivianite locality including laundromats and car washes (possible former or current sources of phosphate detergents). However, inquiries made to city engineers resulted in the response that sewer lines in southeast Memphis do not run close to Nonconnah Creek. Pollutants in storm drains and agricultural runoff (phosphatic fertilizer) were also considered. The apparent localization of vivianite on one gravel bar along Nonconnah Creek suggests that a point source of phosphate should be sought. An old dump or fill site could be a potential point source. The Director of the Solid Waste Management Memphis Field Office (Tennessee Department of Environment and Conservation) informed us that there are no regulated landfills or dumps in the study area today, but that the state has no records for the period before regulations were implemented. Low quality fill to prepare the area for development could also have been a source of phosphate. Our examination of the flanks of Nonconnah Creek in the vicinity of the vivianite-bearing point bar did not identify evidence of dumps or fill, but they could exist unexposed near the creek.

A survey of water quality a decade ago along Nonconnah Creek (Molavi and Grubaugh, 2000) found that phosphate was an environmental concern throughout the Nonconnah Creek drainage system. But very elevated phosphate (0.54 mg/L as orthophosphate) occurred at only one of 15 sites sampled on Nonconnah Creek about two km downstream from the present study site. This elevated phosphate site was located about 600 m downstream from a locality described below which produced mastodon bones. Unfortunately, no water samples were taken near the present study site during the survey a decade ago.

Hundreds of samples of vivianite have been found on the gravel bar near Halle Park. Two specimens were found at the cut bank immediately upstream from the Halle Park point bar, one specimen has been reported from the next point bar upstream, two specimens have been reported from the next point bar downstream, and one specimen from a location about 750 m further downstream. Thus, the overwhelming majority of vivianite specimens have been located at the one gravel bar close to Halle Park. Consequently, the 50 or 60 m of creek channel and banks between the Halle Park point bar and the next gravel bar upstream are the most likely source of phosphorus for vivianite formation. As noted in the introduction, an organic-rich clay horizon in the cut bank sediments of Nonconnah Creek was identified in 2008 about 30 m upstream from the vivianite locality. Investigation revealed that the organic-rich layer, which occurred beneath the loess (Fig. 4), included fossil logs, leaves, nuts, seeds, and insect remains. A similar accumulation of organic remains in clay, including some mastodon bones, was discovered in the 1970s a few km downstream along Nonconnah Creek (Brister et al., 1981). The site had been exposed and scoured by the creek at high water and no vivianite was observed on any materials from the site (pers. comm., R. Brister, 2012). Radiocarbon dating of some of the organics at the mastodon site indicated ages in the 17,000 to 20,000 y range. In the absence of any known dumps or landfills in the study area, the most likely local source of phosphate for the formation of vivianite is the organic-rich horizon just upstream from the gravel bar containing vivianite.

Recent Observations of Vivianite in the Creek and Indications about the Origin of the Vivianite—On several occasions during late 2009 and early 2010, we were able to confirm that the crystals of vivianite found in Nonconnah Creek were appearing in one section of the creek, and in a relatively short period of time. Several observations point to vivianite crystals being moved into position or precipitating on the point bar during the hours the creek covered the gravel bar following a rain. First, it was observed on days before a heavy rain that very little vivianite remained on the gravel bar after mineral collectors had been there. Following the rain, plus the time that it took for storm water to drain into the creek, there was a period of less than 8 hr before the water level fell exposing the gravel bar, with many vivianite crystals now present on the bar. Of particular interest is the fact that some of the crystals were not even attached to rocks, but were lying loose in the sand. Second, many of the specimens were attached to a variety of pebbles from small to large, and some were attached between several pebbles or sand grains, in effect cementing them together. All of this indicates that they had not been transported any significant distance but had formed in the creek bed or banks at or near this location.

On the basis of our observations of the cut bank location just upstream from the vivianite containing point bar, a model for local vivianite

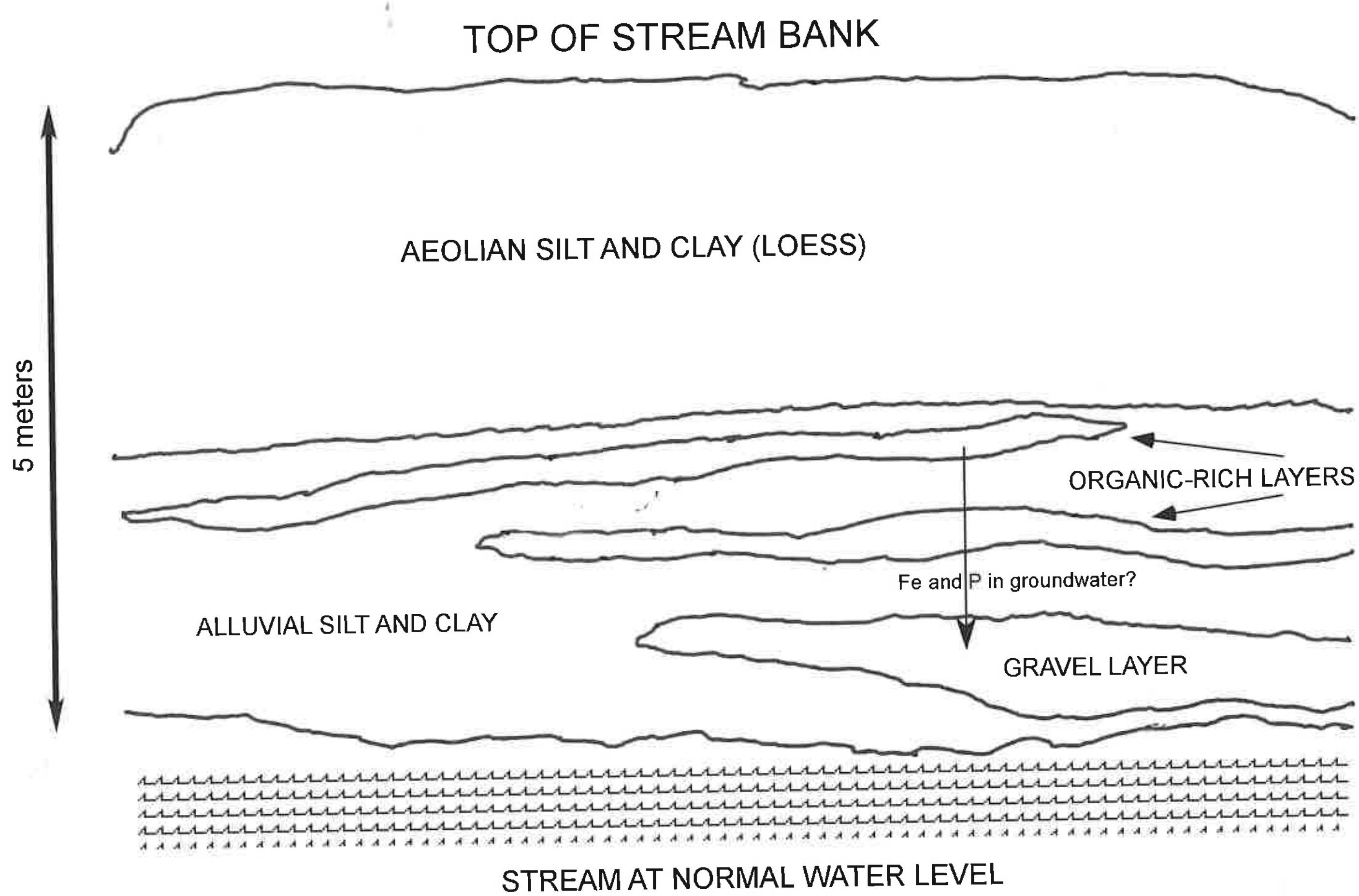

Fig. 4. Line drawing of the cut bank immediately upstream from the vivianite-containing point bar on Nonconnah Creek (summer 2008). The horizontal scale is approximately the same as the vertical scale.

formation can be stated as follows. The phosphate $(PO_4)^{-3}$ ions are probably derived from the organic-rich clay layer below the loess. The Fe^{+2} ions are abundantly present in the reduced waters of the unconfined aquifer. The siliceous gravel below the organic-rich clay layer provides a suitable crystalline substrate for phosphate precipitation. It must be noted that only a few vivianite samples have been found at the cut bank location; however, this location seems the most likely point at which the creek at high water could have excavated the mineral. But we wondered, what else, if anything, may have contributed to vivianite formation?

Biologically Mediated Vivianite Formation?—After a high water event has passed and left the creek bed partially uncovered, a blood-red biofilm sometimes leaks out of the gravel layer near the base of the cut bank wall. As it runs into the creek water, it creates bacterial/algal colonies that are rusty-red in color. This phenomenon begs the question of a possible connection between the bio-film, the bacterial cultures, and vivianite crystal formation.

It is interesting to note that there is an abundance of recent research that describes examples of mineral formation associated with biological reactions. Some laboratory experiments have indicated that μm-size vivianite crystals can be grown in a few weeks with the introduction of microbes into a solution containing poorly crystalline hydrous ferric oxide and phosphate anions (Glasauer et al., 2003). An important implication of this research is that biogeochemical reactions may be more significant in producing some minerals in the sedimentary environment than usually recognized.

As noted earlier, blue/purple cryptocrystalline encrustations also believed to be vivianite have been found on the creek cut bank clays and on gravel of the point bar. At the cut bank location (Fig. 4), below the organic-rich layer, cryptocrystalline encrustations appear after some high water events, much like the bio-film mentioned above. Because of the timing and proximity, it is tempting to draw a connection between the encrustations and the bio-films. Published laboratory experiments like the one referred to above suggest that tiny crystals like those of the blue/purple encrustations might be grown in a bio-film in the short time frame available after high water events. It also seems possible that the growth of the mm to cm size vivianite crystals, inferred to have precipitated in the gravel now exposed on the creek bank below the organic layer, could have been facilitated by bacterial processes over a longer time period. However, since the larger individual crystals have not been found precipitated on anthropogenic materials, it is possible that they were formed within the unexposed sediments of the creek wall some hundreds or thousands of years ago.

Anthropogenic phosphate has been implicated in the formation of algal blooms in water bodies and the ensuing reduction of dissolved oxygen that causes the die off of other plants and animals. Our observations in Nonconnah Creek, and laboratory experiments described in the scientific literature, suggest that some bacterial processes can lead to fixation of phosphate as the mineral vivianite. This mechanism possibly could have a place in bioremediation efforts to control algal blooms and maintain water quality. This problem at the interface of biology, chemistry, and geology is a promising topic for further investigation, both in the laboratory and *in situ* in the field.

Post-script—As of June 2010, ever-changing Nonconnah Creek had further eroded its cut bank just upstream from the point bar where vivianite has been localized. The extent of exposure of organic-rich remains varies as the creek erodes the bank. Vivianite specimens are presently less abundant on the point bar. It is possible that recent high water events are simply reorganizing the gravel on and in the point bar and bringing a few earlier deposited vivianite crystals to the surface from time to time rather than forming new crystals.

Conclusions

In the first known occurrence in western Tennessee, macroscopic crystals of the iron phosphate mineral vivianite were discovered in some abundance on a gravel point bar along Nonconnah Creek, Shelby County, Tennessee. Mineral identity was verified by a combination of XRD and EDAX analyses. Based on various lines of evidence including the minimal water wear exhibited by the crystals, the vivianite appears to have originated in the immediate vicinity of the point bar. Microcrystalline encrustations on the sediments of the creek banks at this location also appear to be vivianite. A local formation model is proposed for the macroscopic vivianite crystals in which phosphate may have been derived from weakly fossilized organic-rich deposits that occur in the sub-loess alluvium along the creek. A possible bacterial mediated origin of the microscopic vivianite encrustations is discussed.

Our findings have answered many of our initial questions, but prompted new questions that will require further interdisciplinary research. Future work should include new measurements of phosphate concentration in Nonconnah Creek water and sediments in the vicinity of the vivianite-bearing point bar. Identification of the bacteria present in the bio-films observed and microscopic evidence for biomineralization are also desirable.

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