The Significance of Vivianite in Archaeological Settings

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Vivianite is a bluish mineral sometimes encountered in archaeological deposits. It is notable for its tendency to change color from white or grayish to blue on exposure to air. Vivianite requires specific conditions for its formation—sources of iron, phosphate, and water, as well as low levels of oxygen and sulfide. Microbial activity is also thought to play a part in vivianite formation. The majority of archaeological texts do not discuss vivianite to any great degree, preventing a more detailed interpretation of site conditions and features. Vivianite was found in 25 exhumed burials from the North Brisbane Burial Ground, Queensland, Australia. Research indicated that bone or tissue samples for DNA analysis are best taken from areas distant from vivianite encrustations and that presence of vivianite has implications for artifact conservation. Vivianite at the North Brisbane Burial Grounds helped protect some skeletal and dental elements, preserved the impressions of metal coffin lacing, and also corroborated the oral history of temporary waterlogging and acted as a measure of pollution levels across the site. © 2006 Wiley Periodicals, Inc.

INTRODUCTION

Vivianite is a mineral noted for its tendency to change color from white or grayish to blue on exposure to air. It is sometimes encountered in archaeological deposits, particularly those associated with human remains and ancient industries, where its presence is considered noteworthy but incidental to the interpretation of the site. By understanding the chemical and microorganism requirements for the archaeological formation of vivianite, additional information can be obtained about the postdepositional history of the site, as well as explaining intrasite variations in artifact preservation. The importance of vivianite to understanding these issues is demonstrated by recent excavations conducted at Lang Park, Brisbane, Queensland, Australia (Figure 1).

Between August 2001 and May 2002, the University of Queensland Archaeological Services Unit conducted a salvage excavation of 19th-century burials disturbed during a football stadium redevelopment project (Prangnell and Rains, 2001; Rains and Prangnell, 2002). These graves formed part of the North Brisbane Burial Grounds,
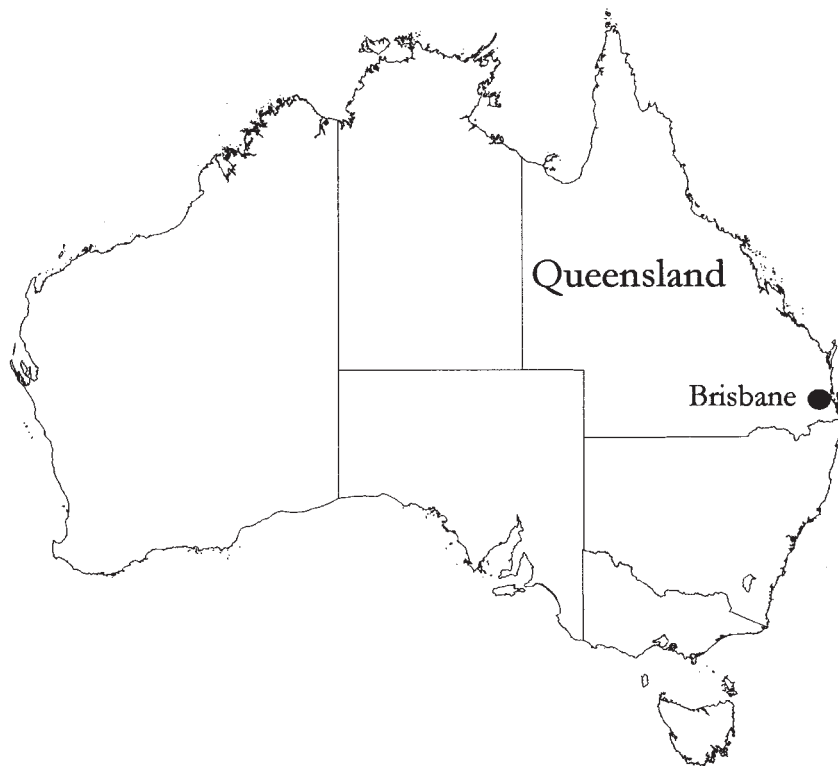
Figure 1. Location of Brisbane within Australia.

the principal cemeteries for Brisbane between 1843 and 1875. The Burial Ground was divided into separate Anglican, Presbyterian, Roman Catholic, Jewish, Wesleyan, Baptist, and Congregationalist sections and an Aboriginal section located within the Anglican cemetery. The cemeteries were located on south- and west-facing slopes, dissected by numerous channels that drained into a low-lying swamp that eventually fed into the Brisbane River (Figure 2).

Following closure of the cemeteries, there were 40 to 50 bodies exhumed and relocated (Fisher, 1994, p. 52). The cemeteries continued to be maintained by their denominational trustees until 1914 when the area was converted to parkland (Prangnell and Rains, 2001, p. 21). To achieve this, 99 remains and 148 memorials were relocated, 4300 mounds were leveled, and grave hollows filled. From the 1920s, the parkland became a major garbage and nightsoil dump for Brisbane city (Prangnell and Rains, 2001, p. 33). Most of the garbage and nightsoil was deposited at the northern end of the parkland covering the Roman Catholic and Jewish cemeteries, such that during the salvage excavations up to 13 m of overburden was removed to access the Roman Catholic graves.
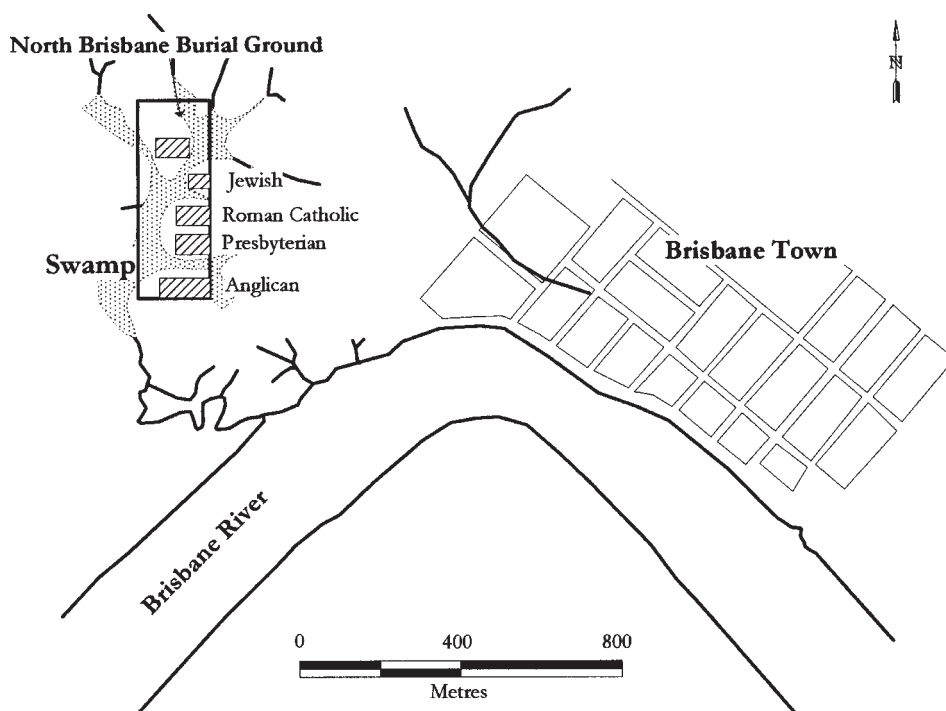
Figure 2. Location of North Brisbane Burial Ground showing creeks and swamp (based on Wade, 1844).

The salvage team excavated 397 graves (Prangnell and Rains, 2002; Haslam et al., 2003) from the Anglican, Presbyterian, and Roman Catholic cemeteries. Twenty-five of these graves contained a mineral that turned blue on exposure to air. Fifteen of the graves (60%) containing the blue mineral were in the low-lying Roman Catholic part of the cemetery, eight were in the Presbyterian, and one in the Anglican cemetery, and it was suspected that the mineral was vivianite because it occurred in close association with bone.

Most archaeological texts give scant information concerning the occurrence of vivianite and its archaeological importance (e.g., Shackley, 1975, p. 80; Courty et al., 1989, p. 180; Goldberg et al., 2001, p. 261). Therefore, in this article we seek to remedy the dearth of information in the literature regarding vivianite in archaeological settings, to outline the conditions required for vivianite formation, and to demonstrate the implications of finding vivianite within archaeological contexts.

MINERALOGY OF VIVIANITE

Vivianite was named in 1817 after J.G. Vivian, an English mineralogist who first found the mineral in its crystalline form in Cornwall, England (Brauns, 1912). Up

Table I. Comparison of vivianite and liroconite.

Property	Vivianite[a]	Liroconite[b]
Chemical formula	$Fe_3(PO_4)_2 \cdot 8H_2O$	$18CuO \cdot 4Al_2O_3 \cdot 5As_2O_5 \cdot 55H_2O$
Color	White or light gray, changing to blue or bluish-green on exposure to air	Blue to green
Crystals	Monoclinic Long prismatic to tabular	Monoclinic
Lustre	Vitreous Mother-of-Pearl luster on cleavage faces	Vitreous to resinous
Cleavage	Complete	Indistinct
Fracture	Bladed, fibrous, soft	Uneven
Hardness (Mohs Scale)	1·5–2	2–2·5
Streak	Colorless, white, light blue, indigo, brownish, depending on degree of oxidation	Blue to green
Specific gravity	2.6–2.7	2.88–2.98
Solubility	Readily soluble in hydrochloric and nitric acids	Soluble in nitric acid
Other	Thin crystals are flexible Vivianite is radioopaque on X-ray	

[a]Data derived from Read (1970), Johanson (1976), and Schumann (1992).
[b]Data derived from Smith (1953).

until this point, vivianite had been referred to as "inorganic Prussian blue" in the scientific literature (Nriagu, 1972) and colloquially as "blue iron earth" or "blue ironstone" (Clark, 1993). Vivianite closely resembles the vivid blue or blue green crystal formations of the arsenic mineral liroconite (Table I). It is, therefore, important archaeologically to distinguish between vivianite and the presence of arsenic resulting from embalming practices (Borstel and Niquette, 2000, p. 3). One archaeological example of bones stained blue as the result of remineralization of rodent bones with calcite containing copper impurities has also been reported (Robles et al., 2002).

Vivianite is a hydrated iron phosphate mineral with the chemical formula $Fe_3(PO_4)_2 \cdot 8\,H_2O$ (Gaines et al., 1997). It occurs as either an amorphous mass or may crystallize as small encrustations or radiations of monoclinic crystals. Thin crystals are flexible (Read, 1970). A related mineral, paravivianite, has the chemical formula $(Fe, Mn, Mg, Ca)_3(PO_4)_2 \cdot 8\,H_2O$ and occurs in similar forms to vivianite proper (Teodorovich, 1961). The mineral structure of vivianite consists of $FeO_2 \cdot 4\,H_2O$ octahedra and $Fe_2O_6(OH)_4$ octahedra linked together in uneven layers with PO_4 tetrahedra connected between the layers via weak H_2O–H_2O hydroxyl bonds (Dixon and Weed, 1989).

When fresh and unoxidized, vivianite is colorless or faintly whitish or grayish in color (Teodorovich, 1961). As vivianite progressively oxidizes through exposure to air, Fe^{2+} in the crystal structure is isomorphically replaced by Fe^{3+}. The valency is com-

pensated for by the replacement of H_2O by OH (Dixon and Weed, 1989), and the monoclinic crystal structure remains the same (Teodorovich, 1961).

This process of oxidation is accompanied by a color change from the colorless or faintly white or gray hues of the unoxidized form to distinctive bluish and greenish colors that become progressively darker as oxidation progresses. Teodorovich (1961), in an extensive study of the oxidation of vivianite, concluded that the pure unoxidized form of the mineral is most rightly called *vivianite*, while its colorful oxidation products should more rightly be known as *kerchenite*, named and first identified from the iron deposits of the Kerch Peninsula in the Ukraine. There are three subtypes of kerchenite, α, β, and γ, each with increasing proportions of Fe^{3+} in the crystal structure (Teodorovich, 1961). With further oxidation, kerchenite is transformed to bosphorite and oxykerchenite, minerals varying in color from brown to yellow to red-brown (Teodorovich, 1961). Further environmental degradation of these minerals yields amorphous ferric phosphate and strengite (Nriagu, 1972) (Figure 3).

There is a common belief that the oxidation of vivianite is accelerated by exposure to light (Roberts et al., 1990). While oxidation of vivianite on exposure to the atmosphere has been extensively studied (Teodorovich, 1961; Nriagu, 1972), the action of light on the mineral has not received similar attention. To date, it appears that the mechanism of photo-oxidation or the wavelengths involved are not fully understood.

OCCURRENCES OF VIVIANITE

Vivianite is a reasonably common and complex breakdown product of the interaction of phosphate, iron, and water in the natural environment. It is encountered across a number of scientific disciplines (Table II). Vivianite has been identified in various archaeological contexts from as early as the mid-1800s (e.g., "An Anglo-Saxon Cemetery," 1866); however, no attempt at synthesizing the information relating to the archaeological importance of vivianite has previously been attempted. Typically, archaeological examples of vivianite occur in association with human remains, human and animal waste deposits, industrial waste deposits, and areas rich in iron.

Secondary Deposits on, or in, Human Remains

During the 1960s excavation of human remains from the wreck of the *Wasa* off Stockholm, some skeletal elements (in particular some mandibles) were noted to rapidly change color from white to dark blue upon contact with air, suggesting the presence of vivianite (Johanson, 1976). Of particular interest were blue needle-shaped deposits within the pulp chambers of teeth. X-ray diffraction analysis found these needles to consist of 95% vivianite. Johanson (1976) notes that the bones which changed color and the teeth containing vivianite were always found near iron objects, such as cannon balls or bolts. It was postulated that these objects were the source of the iron for vivianite formation and that proteins or amino-polysaccharides in the bones and pulp acted as sites for iron binding.
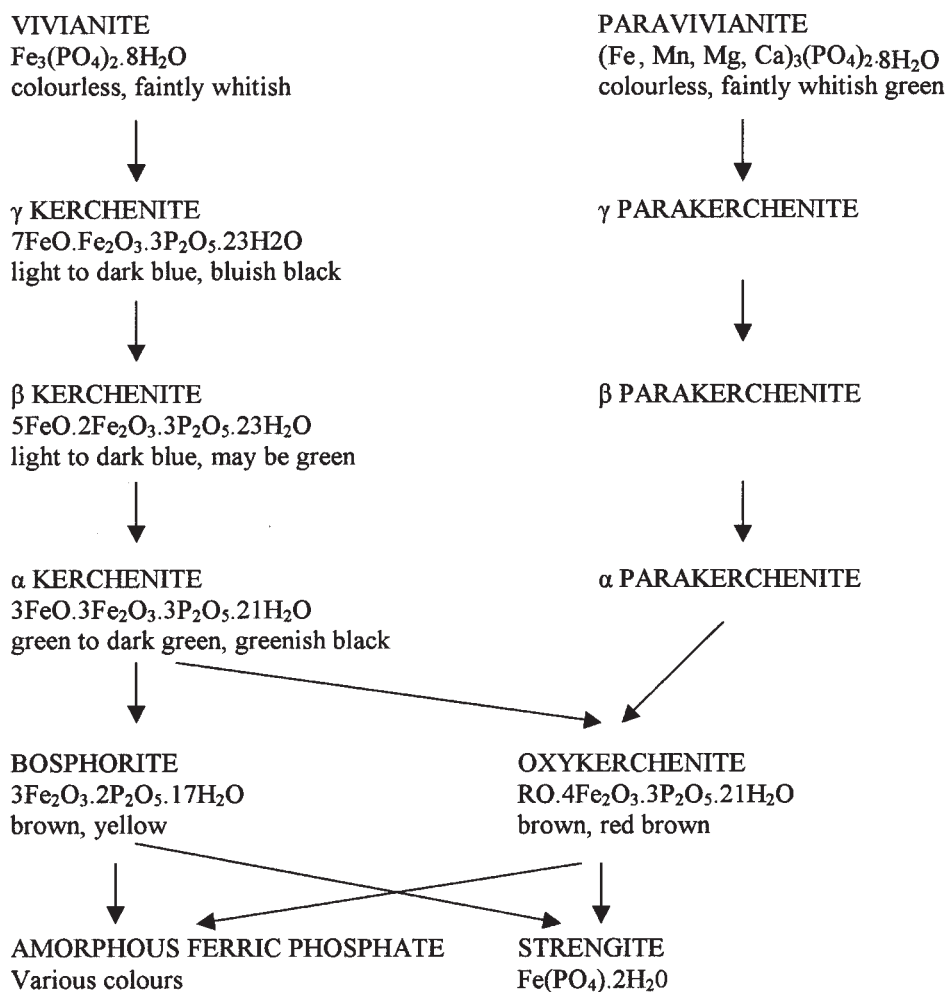
VIVIANITE
$Fe_3(PO_4)_2.8H_2O$
colourless, faintly whitish

PARAVIVIANITE
$(Fe, Mn, Mg, Ca)_3(PO_4)_2.8H_2O$
colourless, faintly whitish green

γ **KERCHENITE**
$7FeO.Fe_2O_3.3P_2O_5.23H2O$
light to dark blue, bluish black

γ **PARAKERCHENITE**

β **KERCHENITE**
$5FeO.2Fe_2O_3.3P_2O_5.23H_2O$
light to dark blue, may be green

β **PARAKERCHENITE**

α **KERCHENITE**
$3FeO.3Fe_2O_3.3P_2O_5.21H_2O$
green to dark green, greenish black

α **PARAKERCHENITE**

BOSPHORITE
$3Fe_2O_3.2P_2O_5.17H_2O$
brown, yellow

OXYKERCHENITE
$RO.4Fe_2O_3.3P_2O_5.21H_2O$
brown, red brown

AMORPHOUS FERRIC PHOSPHATE
Various colours

STRENGITE
$Fe(PO_4).2H_20$

Figure 3. The oxidation process of vivianite and paravivianite (after Teodorovich, 1961 and Nriagu, 1972).

Pabst and Hofer (1998) studied deposits within the lung tissue and on the surface of the skin of the Tyrolean Iceman discovered in 1991. Electron energy loss and electron diffraction analyses identified aggregates of small columnar crystals within the Iceman's lung tissue as oxidized vivianite. Because these crystals were not found within anthracotic areas of the lungs (i.e., they had not been inhaled), it was concluded that they formed in the tissue post mortem. In places where the Iceman's skin was in contact with the underlying rock, an iron-containing para/ortho-gneiss, blue "pustules" of vivianite were found on the skin surface (Pabst and Hofer, 1998, pp. 10–11). In this case, the source of the iron for

Table II. General occurrences of vivianite.

Field of study	Occurrence	References
Archaeology	As secondary deposits in the teeth and bones of dead bodies in close proximity to a source of iron and buried in waterlogged conditions	Berg et al., 1967; Johanson, 1976; Piepenbrink 1989
	As encrustations on the surface of bones of soldiers killed in action and buried in waterlogged tropical soils	Mann et al., 1998
	As crystal growths in the interior of late-19th-century cast iron coffin burials subjected to groundwater infiltration	Owsley and Compton, 1997
	As a protective coating on some ancient iron tools	Farrer et al., 1953; Booth et al., 1962
	As layers at the edges and in the infill of pits dug for industrial activities, such as flax retting, metalworking, and hide tanning during medieval times	Biek, 1993; Fechner and Kleiner, 1997
	As residues on bone tools	Francis, 2002
	In ancient Chinese ceramic glazes to achieve the blue-green celadon finish that imitated jade	Guthrie, 1990, p. 79
Engineering	As a weathering product on iron reinforcement bars and ties embedded in stone in some historic buildings	Fort Gonzalez et al., 2004
	As a protective coating on mild steel	Volkland et al., 2001
Geology	In the weathering layers of iron, copper, and tin ore deposits	Gaines et al., 1997
	As a weathering product of iron-manganese minerals in pegmatites	Nriagu, 1972
	In bogs in association with clay and peat	Postma, 1977; Read, 1970
Hydrology	In sediments on the floor of lakes where there is a highly reducing environment at depth	Ferrini and Flood, 2001; Nriagu, 1983
	In river sediments in close proximity to sewage treatment outlets	Hearn et al., 1983
Palaeontology	As encrustations on the surface of some fossil bones	Guthrie, 1990; Read, 1970
Soil Science	In soil profiles surrounding leaking septic tanks	Ptacek, 1998; Robertson et al., 1998
	In deposits downslope from the sites of ancient cess pits	Macphail, 1991
	In deposits downslope from the sites of modern dairies	Harris et al., 1994
	As a breakdown product of phosphate fertilizers	Dixon and Weed, 1989
Zoology	As nodular encrustations in the intestines of some horses, tapirs, and zebra	Hassel et al., 2001; Murphy et al., 1997; Schiffman, 1998

the vivianite is suggested as the iron-containing gneiss underlying the body, while the phosphate is thought to have derived either from the manure of animals using the rock hollow as a shelter from the elements, or from the Iceman's own tissue (Pabst and Hofer, 1998, pp. 10–11).

During an archaeological salvage operation in Laurel, Maryland, a cast iron coffin containing the body of railway engineer John White, who was interred in 1861, was exhumed and the body was examined (Owsley and Compton, 1997). The body was in a good state of preservation and surrounded with large quantities of vivianite and arsenic crystals, the latter derived from embalming powders liberally sprinkled around the body. Some time prior to exhumation, the coffin's glass faceplate had broken, allowing the infiltration of acidic groundwater that reacted with the cast iron of the coffin. This liberated Fe^{2+} and Fe^{3+} ions that combined with phosphate ions from the body's tissues, eventually forming vivianite crystals in the space between the body and the interior sides of the coffin.

Pits Associated with Ancient Industry

During their research into the archaeological interpretation of pits and other dug structures, Fechner and Kleiner (1997) noted that many archaeological sites in Belgium showed greenish precipitations in or along dug structures, especially in sites dated from Roman times onwards. Fechner and Kleiner (1997) used scanning electron microscopy and X-ray diffraction to investigate vivianite occurrences at two ancient industrial sites in Belgium. The first site at Tournai/Esplechin, close to the Belgian–French border, showed vivianite formation at the base of a pit dug for flax retting in the medieval period. Vivianite formation, in this case, was probably fostered by the presence of organic material, waterlogging, and poor oxygenation.

The second site in the center of Brussels itself dates from the 13th century and featured "spectacular accumulations" of vivianite and other iron-containing minerals at the base of a large concave pit lined with a 5-cm layer of organic material including bark fragments. It is believed that this pit originally functioned as a tanning pit, and then was later filled with refuse from butchery (bone pieces) and shoemaking. Fechner and Kleiner (1997) suggest that the presence and distribution of vivianite and other secondary minerals at the site can be used to chart the successive pollution of this wetland area of ancient Brussels.

Similarly, at the mediaeval Cistercian industrial complex of metal workshops and watermills at Bordesley Abbey, Worcestershire, vivianite was found on water-logged bone (Lovett, 1993, p. 231) and on iron fragments (Biek, 1993, p. 201). Bordesley Abbey operated between the late 12th century and the late 14th century; it has evidence of some of the earliest water-powered metalworking in Britain as well as evidence of an established local textile, leather, and ceramic industry (Astill, 1993).

Cess Deposits

Macphail (1991) records that the dumping of domestic waste (cess) and burned herbivore manure during the late Roman period at Deansway, Worcester, and the subsequent construction of a street through the dump, created deposits of vivianite where solutions derived from the dumped waste drained downslope.

Weathering Product on Iron Reinforcements Embedded in Stone in Historic Buildings

During an investigation into the fractured stone architrave elements in the Royal Palace of Madrid built in the 18th century, Fort Gonzalez et al. (2004) discovered that the original metalworking process had produced microfissures in the iron ties embedded in the stone, and that this served to increase the likelihood of corrosion. In addition, there were streaks of slag containing vivianite and titanomagnetite within the iron, and these bands provided a focal point for the further weathering of the iron. The pivotal weathering agents, in this case, were atmospheric oxygen and infiltrating acidic rainwater. Owing to the mineralogy of the metal, the final weathering products, in this case, were the minerals lepidocrocite and goethite, which, due to their crystal structure, caused an 83% increase in the volume of the iron ties. This, in turn, exerted a pressure of 196 MPa on the stone, leading to fissuring and, in some cases, disintegration.

Preservation Layer on Some Metal Tools

Farrer et al. (1953) investigated iron nails and knives that ranged in age from early Roman to the medieval period, found in an excellent state of preservation on a site at Hungate, York. Soil at the site was waterlogged and anaerobic, and the authors expected that any iron artifacts would have corroded away due to the action of sulfate-reducing bacteria that favor such soil conditions. As part of their metabolism, these bacteria may generate hydrogen sulfide that can corrode metal objects, producing metal-sulfide complexes (Hamilton, 1985). Indeed, the sulfate-reducing bacteria *Desulphovibrio desulphuricans* was found to be present in the soil at Hungate but in an inactive state.

Many of the iron objects had blue patches on their surface, and X-ray diffraction showed these patches to be composed of vivianite (in the proportion of 50% ferrous and 50% ferric iron) with traces of tannate. It was supposed that animal refuse, and, in particular, a large number of dog bones found at the site, provided the phosphate necessary for vivianite formation on the surface of the iron implements.

The authors noted that the site had an unusually high content of tannates, derived from peat layers in the soil, a great quantity of hazel and birch brushwood, and compressed leaves and grass. Deposits of tanned leather scraps also served to locally increase the tannate level of the soil. Farrer et al. (1953) postulated that the tannate inhibited the activity of the sulfate-reducing bacteria at the site, thus preventing the initial corrosion of the iron objects. Laboratory experiments with *D. desulphuricans* taken from the site showed the bacteria to be active in the absence of tannates but the addition of tannic acid at a concentration of 0.001% greatly reduced this activity. Concentrations of tannic acid equal to or greater than 0.01% completely arrested the growth of *D. desulphuricans* (Farrer et al., 1953, p. 83).

It was concluded that the exceptional preservation of the iron objects at Hungate was because of two factors:

- The formation of a vivianite coating on the surface of the iron objects that served to protect and insulate them from the surrounding environment

- High levels of tannate in the soil, which inhibited the corrosive activity of sulfur-reducing bacteria

Following on from this discovery, Booth et al. (1962) investigated vivianite coverings on exceptionally well-preserved nails from the early 16th century excavated at St. Neots, Huntingdonshire. Again, heavy anaerobic soils were expected to have been highly corrosive to the buried iron nails, as in the case at Hungate. X-ray diffraction analysis showed that the coating on the nails was composed solely of vivianite, with no detectable quantities of iron oxides or iron sulfides. This led Booth et al. (1962) to conclude that the vivianite coating had formed very soon after the burial of the nails, thus preventing any appreciable corrosion, even in the presence of some sulfide-reducing bacteria in the soil.

REQUIREMENTS FOR VIVIANITE FORMATION

Reported archaeological occurrences of vivianite consistently show that a combination of three conditions is necessary for vivianite formation in the archaeological record:

- Waterlogged or submerged soil with poor oxygenation (e.g., Farrer et al., 1953; Johanson, 1976; Fechner and Kleiner, 1997)
- Presence of a phosphate source, such as human and animal bones and tissues (e.g., Farrer et al., 1953; Johanson, 1976; Owsley and Compton, 1997) or effluent and manure (e.g., Macphail, 1991; Pabst and Hofer, 1998)
- Presence of an iron source, such as manufactured objects (e.g., Farrer et al., 1953; Johanson, 1976; Biek, 1993; Owsley and Compton, 1997; Maritan and Mazzoli, 2004) or iron-containing soils or bedrock (e.g., Pabst and Hofer, 1998)

Nriagu (1972) conducted geochemical experiments to ascertain the stability of vivianite crystals under varying conditions of pH, Eh (redox potential), phosphate concentration, and sulfide concentration. These tests determined that in the system $Fe_3(PO_4)_2$-H_3PO_4-H_2O-H_2S at pH 7, vivianite exists in the low Eh range (–0.2 to –0.4) and at high to very high phosphate concentrations (log $aHPO_4^{2-}$ of 0 to –5) (Nriagu, 1972, p. 466). However, when H_2S was removed from the system, vivianite was found to be stable in a broader range of Eh spanning low to medium values (–0.07 to –0.36) and also stable in a broader range of phosphate concentrations from high to medium values (log $aHPO_4^{2-}$ of 0 to –6) (Nriagu, 1972, p. 467). The pH field of vivianite stability was determined to fall between pH 6 and 8.5.

From these results, Nriagu (1972) concluded that vivianite formation is unlikely to proceed where significant sulfide exists in the environment unless the concentration of phosphate is exceptionally high compared to normal geological conditions. This is borne out by the observations of Postma (1977), who determined that high levels of dissolved sulfide in bog waters inhibited the formation of iron carbonate minerals (such as siderite) and iron phosphate minerals (such as vivianite).

Organic plant matter in association with vivianite is a feature of some archaeological sites (Farrer et al., 1953; Fechner and Kleiner, 1997), and it may be that this mate-

rial releases sufficient tannins into the environment to inhibit the growth of sulfate-reducing bacteria that would otherwise increase the prevailing sulfide concentration and significantly decrease the stability of vivianite, as demonstrated by Nriagu (1972).

THE ROLE OF MICROORGANISMS IN VIVIANITE FORMATION

Organisms That Promote Vivianite Formation

Zachara et al. (1998) linked dissimilatory metal-reducing bacteria (DMRB), microorganisms that reduce metal oxides in anoxic conditions, with the formation of vivianite. In the case of iron, the substrate used by these microorganisms is an amorphous Fe^{2+} Fe^{3+} hydroxide known as "green rust" (Hansen and Poulsen, 1999).

In poorly oxygenated soils, some microorganisms degrade phosphate-containing minerals and organic matter, while in others the DMRB place themselves in direct contact with green rust deposits. The process of iron reduction is directly enzymatically linked to the electron transfer chain in the metal-reducing bacteria and is mediated by anthraquinine-2,6-disulfonate (AQDS), which functions as an electron shuttle between the bacteria and green rust (Zachara et al., 1998). AQDS contains a quinone group that is known to be present in humic substances, and it is suggested by Zachara et al. (1998) that *both* amorphous iron oxides and humus are required for efficient reduction of iron and survival of dissimilatory metal-reducing bacteria.

In laboratory experiments conducted with the DMRB *Shewanella putrefaciens*, incubated with amorphous iron oxide in the presence of AQDS, Zachara et al. (1998, p. 1431) found that vivianite precipitated from the suspension within 11 days. These researchers were unable to establish, however, whether DMRB organisms act to nucleate or direct the precipitation of vivianite.

Hansen and Poulsen (1999) studied the interaction between green rusts and phosphate in soils that leads to the subsequent crystallization of vivianite. They make the connection between soil microorganisms that break down phosphate minerals and organic matter, thus releasing phosphate into the soil solution, and the adsorption of these phosphates onto the green rust to form an iron hydroxide phosphate, which gradually transforms into well-crystallized vivianite. Hansen and Poulsen (1999) note that green rusts fall into the pyroaurite class of layered double metal hydroxides, and that the phosphate in soil solution is bonded electrostatically between the iron hydroxide layers, forming a greenish-colored amorphous Fe^{2+} Fe^{3+} hydroxide phosphate. In laboratory experiments, this amorphous iron hydroxide phosphate gradually crystallized into stable vivianite within 40 days (Hansen and Poulsen, 1999, p. 316).

In a modern industrial application, Volkland et al. (2001) have recently used the bacteria *Rhodococcus* sp. and *Pseudomonas putida* to induce a surface reaction on mild steel to produce a protective coating of vivianite. This vivianite coating was shown to decrease the corrosion weight loss in mild steel by up to five times the loss of unprotected steel.

In summary, in an anaerobic, waterlogged soil environment, microorganisms play an important role in the release of iron and phosphate into the soil profile, thus providing the raw materials for vivianite formation.

Organisms That Prevent Vivianite Formation

As discussed above, the presence of active sulfate-reducing bacteria in the soil may increase sulfide levels to the extent that vivianite is prevented from forming (Nriagu, 1972; Postma, 1977). A notable example of these bacteria, although not the only one, is *Desulphovibrio desulphuricans* (Farrer et al., 1953). The activity of these microorganisms will also significantly increase the corrosion of buried metal artifacts.

IMPORTANCE OF VIVIANITE IN THE ARCHAEOLOGICAL SETTING

Over the years, archaeologists have sought to interpret the presence of vivianite in a number of different ways.

Relative Dating

In 1933, there was debate among the archaeological community in the United Kingdom as to whether the presence of vivianite could be taken as an indicator of the age of a site, and that it might be possible to use the presence of vivianite as a relative dating tool (Anonymous, 1933). This was postulated on the basis that many archaeologists had not encountered vivianite on sites dated after A.D. 1650. However, it was pointed out by others that vivianite had formed at a waste-dumping site at Brighton within the space of 50 years, and it was speculated that the mineral may form in as little as 5 years. Thus, the concept of vivianite as a relative dating material was abandoned.

In the modern forensic setting, the presence of vivianite on bones is generally taken to represent a burial period of between 15 and 20 years (e.g., Haglund and Sorg, 1997, p. 266). However, Wright et al. (2005) observed vivianite on the remains of victims of the Srebrenica massacre after they had been buried in a mass grave for only 3 years. Geochemical laboratory experiments have shown vivianite forming in lacustrine sediment samples within 21 days (Nriagu, 1983), and experiments involving DMRBs incubated with amorphous iron oxide found that vivianite precipitated from suspension within 11 days (Zachara et al., 1998, p. 1431).

Soil Condition Indicator

Nriagu's (1972) geochemical experiments indicate that in locations where sulfide exists in trace amounts, vivianite is stable in conditions of low to medium Eh (–0.07 to –0.36), high to medium phosphate concentrations (log $aHPO_4^{2-}$ of 0 to –6), and pH between 6 and 8.5. In areas where sulfide levels are higher, vivianite will only form where phosphate concentrations are extremely high, such as deep within a cess deposit or at the very surface of bones.

Pollution Index

As vivianite has been found at archaeological sites in association with cess and manure deposits (Piepenbrink, 1989; Macphail, 1991) and is also found in the efflu-

ent plumes emanating from buried septic tanks (Ptacek, 1998; Robertson et al., 1998), the discovery of this mineral at an archaeological site may lend weight to the interpretation of some features as being dumps for human and/or animal manures.

Alternatively, Fechner and Kleiner (1977) have noted the presence of vivianite in pits dug originally for industrial purposes, such as flax retting and leather tanning and which have subsequently been infilled by refuse from other industries, indicating a progressive pollution of the land by successive occupiers.

Weathering Product on Iron Structural Elements in Some Historic Buildings

It is important to note that the presence of vivianite impurities in iron ties used to reinforce stonework in historic buildings increases the likelihood of further weathering of the stone, particularly when exposed to rainwater, and especially acid rain (Fort Gonzalez et al., 2004). Therefore, the detection of vivianite during a structural inspection should not be taken as a benign or insignificant finding, particularly when the structure is exposed to air and susceptible to the infiltration of rainwater.

Preservation Layer on Iron Tools

In contrast to the above example where vivianite on iron fixtures is exposed to atmospheric oxygen and water of neutral or acidic pH, the work of both Farrer et al. (1953) and Booth et al. (1962) demonstrates that the preservation of buried iron objects may be exceptionally good at sites where the soil is anaerobic and wet and contains both sources of phosphate that favor vivianite formation and sources of tannate that inhibit the corrosive activity of sulfate-reducing bacteria.

Damage to the Purine Moieties of DNA

Berger et al. (1993) included crystalline vivianite in a study to determine the radical oxidation capability of various iron-containing minerals and two asbestos minerals in an attempt to further clarify the genotoxicity of these minerals and the implications for miners and manufacturers. The authors postulated that iron oxo radicals (and also to some extent iron hydroxyl radicals) arising from the interaction of Fe^{2+} ions with molecular oxygen at the mineral's surface are able to abstract a hydrogen atom from the C(8) position of both guanine and adenine residues within DNA.

When exposed to calf thymus DNA, vivianite was determined to be among the most reactive of the iron minerals tested and was able to hydroxylate the guanine moiety of the DNA at the C(8) position. This hydroxylation reaction was found to be more efficient than the indirect effects of gamma radiation on DNA (Berger et al., 1993, pp. 44–45).

The research described above concentrated largely on the guanine moiety. However, further studies involving the exposure of purine 2[1]-deoxyribonucleosides to crystalline vivianite showed that this mineral was able to hydroxylate both 2[1]-deoxyadenosine and 2[1]-deoxyguanine at the C(8) site, although vivianite demonstrated a preference to hydroxylate guanine over adenine (Berger et al., 1993, p. 43). It is likely that

the iron-rich minerals studied produce other oxidation products of both purine and pyrimidine bases in DNA and these may be detected with further research.

Additional molecular archaeological research is required into the effects of vivianite; however, the research conducted by Berger et al. (1993) would seem to indicate that DNA in human bones or tissues in direct contact with vivianite crystals might be damaged by this contact. Therefore, at present, it may be more appropriate to take DNA samples from those parts of the remains not affected by vivianite growth.

NORTH BRISBANE BURIAL GROUNDS CASE STUDY

At the North Brisbane Burial Grounds salvage excavation site, vivianite was found primarily in, on, or near bones and teeth, although some vivianite formed along the edges of pits dug for graves. Therefore, most of the vivianite was formed *in situ*, and only some formed by iron and phosphate-rich solutions migrating along the boundary between the soil infilling the grave pit and the soil surrounding the pit.

In the northern low-lying part of the North Brisbane Burial Grounds (particularly within the Roman Catholic cemetery), all of the conditions for vivianite formation appear to have been met.

Waterlogged or Submerged Soil and Poor Oxygenation

Historical records show that even while the cemetery was in operation, the soil was periodically submerged or waterlogged. For example, in 1870, a petition was submitted to the Colonial Secretary stating that in the wet weather, many of the graves were entirely submerged (Fisher, 1994, p. 41). On May 14, 1875, the *Brisbane Courier* newspaper reported that the swamp adjacent to the cemetery frequently overflowed several of the denominations' burial grounds. During the archaeological salvage excavation in 2001, evidence of past periods of waterlogging was noted in the soil laminations, and some graves were still waterlogged while being excavated. Poor soil oxygenation would have occurred during the periodic (and, in some places, permanent) waterlogging of the cemetery soil.

Presence of a Phosphate Source

As the vivianite at North Brisbane Burial Grounds was found, for the most part, in close proximity to, or encrusting, human bones, the primary source of phosphate is considered the soft tissues and the bones themselves. However, some vivianite also occurred at the edge of the pits dug for the coffin burials, and this may indicate a certain mobility of vivianite-forming solutions. Many burials were also placed in close proximity to bedrock, where phosphate-rich solutions percolating down through the soil profile could be expected to gather. Other sources of phosphate particular to the North Brisbane Burial Grounds site were, therefore, considered.

From the early 1920s, the former cemetery was used as a rubbish dump, which, according to residents living nearby at the time, "stank to high heaven" and was populated by "rats as big as cats" (Haymann, 1994, p. 42). Under these circumstances,

the volume of domestic waste, as well as the remains of vermin, may well have acted as additional sources of phosphate for vivianite formation.

Perhaps more importantly, however, was the sustained dumping of human effluent at North Brisbane Burial Grounds, which in its fresh semiliquid form, could have percolated easily and quickly downward through the soil profile. By the 1930s, the North Brisbane Burial Grounds were being used for the disposal of up to 37,000 pans of nightsoil and sawdust per week (Prangnell and Rains, 2001:33; Rains and Prangnell, 2002).

Presence of an Iron Source

In almost every exhumed burial, corroded iron coffin handles and nails were discovered, and these could be considered the immediate sources of iron for vivianite formation. However, solutions containing iron may well have leached down from the overlying layers of domestic refuse. In 1928, sewage workers found that the refuse fill over the Catholic cemetery was already 1.8 m deep and contained "rags, bags, scrap iron, tins, bottles, etc." (reported in the *Brisbane Courier* on February 4, 1928). Piepenbrink (1989) has also suggested that bilirubin in human and animal feces may be a viable iron source for vivianite formation. The North Brisbane Burial Grounds site was filled with nightsoil refuse throughout the 1920s and 1930s (Rains and Prangnell, 2002).

Low Sulfide Levels

As described earlier, Farrer et al. (1953), excavating at Hungate, York, determined that tannates in the soil inhibit the activity of sulfate-reducing bacteria to the extent that vivianite formation is possible. At the North Brisbane Burial Grounds site, it is suggested that tannates were liberated, at least locally, from the pine boards used for coffin construction, as well as the leather clothing items in which some individuals would have been buried. In addition, tannates may have made their way downwards from overlying refuse deposits in which sawdust (mixed with nightsoil) was dumped in great quantities during the 1930s.

Extension of the pH Stability Range for Vivianite

Laboratory experiments conducted by Nriagu (1972:467) found that in the absence of sulfide, the stability of vivianite falls within the pH range of 6 and 8.5, and when sulfide is present, vivianite is stable at pH 7. Field measurements of pH at the North Brisbane Burial Grounds excavation determined that the soil in the gravesites containing vivianite had a pH of 5.5. This extends the pH stability range of vivianite in archaeological settings to at least between pH 5.5 and 8.5.

CONCLUSION

Far from being an incidental finding, the presence of vivianite has the potential to enrich the interpretation of archaeological deposits. Vivianite is a mineral that changes color from white to blue or blue-green on exposure to air. It occurs in archae-

ological deposits that are rich in iron, phosphate, and water, low in oxygen and sulfides, and is stable within a pH range of 5.5 to 8.5.

The presence of vivianite in the archaeological record indicates that:

- Waterlogging, either intermittent or permanent, will be a feature of the site's history. At the North Brisbane Burial Grounds, the presence of vivianite helped to corroborate the oral history and newspaper accounts of periodic inundation of the site.
- The horizons in which vivianite is found will be poorly oxygenated, and, therefore, may contain artifacts and remains that would have decomposed under more oxygen-rich soil conditions. This did not prove to be the case at the North Brisbane Burial Grounds, as the combined effects of the considerable weight of the overburden, the corrosive nature of the landfill contents, the acidity of the shallow bedrock, and the inadequate nature of contemporary burial practices far exceed the preservation benefits of poor oxygenation and vivianite formation.
- A source of phosphate will be present nearby or upslope. This may include animal remains, human remains, leather, human effluent, animal manure, waste from past industrial processing of organic materials, or phosphate fertilizer applied to the topsoil by modern farmers. Further investigation is then warranted to determine the phosphate source. The human remains were the most likely phosphate source at the North Brisbane Burial Grounds; however, as the vivianite was located in those areas underlying the deepest accumulation of human, domestic, and industrial waste, phosphate-rich leachate cannot be discounted as a phosphate source.
- A source of iron will be present nearby or upslope. This may include manufactured iron or steel objects, or iron-rich bedrock. The reliance of the early Brisbane population on cast iron coffin ornaments and furniture greatly increased the availability of iron in the sediments for vivianite production.
- The distribution pattern of the vivianite is important. As noted above, vivianite may form *in situ* in close proximity to phosphate and iron sources, or vivianite may form along the boundary of dug structures where iron and phosphate-rich solutions have migrated over time. Therefore, careful study of vivianite distribution may aid in mapping the location of dug structures, or burials where no actual bone remains. For example, in Burial 256 in the Roman Catholic cemetery, vivianite-forming solutions migrating along the boundary of the dug grave interacted with metal coffin lacing, producing a vivianite deposit that preserved the form and pattern of the lacing within the clay sediment.
- Soil sulfide levels will be low enough to allow vivianite to be stable. This may favor the preservation of metal objects that would otherwise be corroded by the sulfuric acid produced by sulfate-reducing bacteria.

Two recommendations arise from this study of vivianite:

- Bone or tissue samples for DNA analysis should be taken from those areas that are most distant from any vivianite encrustations to minimize the risk of sampling damaged DNA.

- For purposes of conservation, where vivianite is found on iron reinforcements within stone elements of an excavated or existing historical structure, it may be necessary to carefully remove the vivianite, or at least protect it from exposure to atmospheric oxygen and rainwater, to prevent further weathering of the mineral and subsequent expansion of the iron and destruction of the stone.

The presence of vivianite within 25 of the burials at the North Brisbane Burial Grounds unexpectedly enriched the possible interpretation and understanding of the site. It helped corroborate historical data, preserve coffin lacing and some human remains, and acted as a pollution index for sections of the site. Vivianite in the archaeological record must therefore be considered as far more than an incidental finding.

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