

A blue encrustation found on skeletal remains of Americans missing in action in Vietnam

Robert W. Mann^{a,*}, Melanie E. Feather^b, Charles S. Tumosa^b, Thomas D. Holland^a, Kim N. Schneider^a

^a*Physical Anthropologists, U.S. Army Central Identification Laboratory, 310 Worcester Ave., Hickam AFB, HI 96853-5530, USA*

^b*Conservation Scientist and Senior Research Chemist, respectively, Conservation Analytical Laboratory, Smithsonian Institution, CAL-MSC, Washington, DC 20560, USA*

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Abstract

A blue encrustation was found on the repatriated remains of three U.S. Servicemen listed as missing in action (MIA) from Vietnam after 28 years. The identification and origin of the blue material was determined. Scanning electron microscopy with energy dispersive analysis and powder X-ray diffraction identified the material as the mineral vivianite, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$. Vivianite has been found often associated with fossilized bone and teeth, but this example is unusual in that it is only the second published forensic example of vivianite growing from human bone after such a short period of time. The presence of vivianite provides information leading to a more complete and accurate understanding of the taphonomic process associated with American MIA remains. © 1998 Elsevier Science Ireland Ltd. All rights reserved.

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1. Introduction

In an effort to resolve the fate of men and women lost during the Vietnam War, the U.S. Army Central Identification Laboratory, Hawaii (CILHI), is responsible for the worldwide search, recovery, and identification of service members and civilians listed as missing in action (MIA). This goal is achieved in two principal ways. First, the CILHI

*Corresponding author.

deploys personnel worldwide to conduct archaeological site recoveries of downed aircraft and graves and second, the alleged remains of U.S. servicemen are received from official repatriations of those governments involved (for example, the Lao People's Democratic Republic). The remains discussed in this paper were received from the Socialist Republic of Vietnam in March of 1992.

2. Background

When remains are received at the CILHI, an initial triage of the biological material and any personal effects and clothing are conducted. The staff of forensic anthropologists, forensic dentists, and casualty data analysts examine the accession, and each specialist independently provides an analysis.

In the present case, personal effects, dental remains with individually unique restorations, and authentic identification media (i.e. identity cards) provided an association to an event that involved three American and one Vietnamese servicemen.

In 1963, a B-26B aircraft was on an air cover mission over South Vietnam. After completing its mission, the aircraft was relieved by another aircraft and the plane was last seen turning north towards Danang air base. The trip back to the air base should have taken only 30 minutes, and when the aircraft failed to arrive within the hour, an immediate communication and airfield check was conducted without success. All further search efforts failed to locate either the aircraft or its crew. Hindering the search was the fact that the return route of the aircraft was over rugged jungle-covered mountains.

Remains associated with the B-26B were received by U.S. officials in Hanoi from provincial officials who stated that they had been recently recovered (27.5 years after the incident). However, the state of preservation of both the human remains and associated personal effects, including a paper survival manual, suggested that these items had been stored or curated for years before being brought to the attention of Socialist Republic of Vietnam officials (paper won't survive very long in the hot and humid jungle).

Simple storage, for example in someone's home, of MIA remains sometimes occurs as a result of such activities as digging wells, cultivating crops, and home construction. When Vietnamese citizens, for example, find remains they may immediately rebury them, hold/store them for various reasons, turn them over to Vietnamese officials (humanitarianism), or attempt to sell them to unsuspecting citizens or tourists. There is a pervasive myth (and cottage industry of bone dealers) across much of Southeast Asia that the U.S. government pays anyone for handing over American MIA remains. On the contrary, although recovery efforts are time consuming and costly, the U.S. government does not pay citizens for remains. If they did it would be inundated with unscrupulous remains dealers and the humanitarianism would be replaced with greed and deceit.

Curation, on the other hand, is usually thought of as synonymous with "warehousing," an organized, governmentally-sanctioned practice intended to coerce and deceive. Distinguishing between the two, therefore, is an important factor and a prime consideration of the CILHI scientists when examining MIA remains.

There have been other accessions received at the CILHI via official repatriation that

have displayed a wide variety of postmortem conditions and alterations, some of which are believed to have been purposeful [1]. The CILHI has received remains which have shown postmortem burning, cuts and scrape marks, some bones have been written on while others were suspected to have been coated with unknown substances (paint) or had various materials applied. The purpose of the present study, therefore, was to determine whether a blue discoloration was an intentional marking of the bones or the result of natural taphonomic processes.

3. Case report

The commingled remains of a minimum of four individuals were received at the CILHI. The accession included long bones, cranial and hip portions, foot bones, and a few rib fragments. The long bone shafts display irregular surface abrasion of their outer surfaces. On one femur, a peacock-blue colored “rim” of material can be observed encircling an island of non-abraded bone as shown in Fig. 1. A similar blue colored material is also present on portions of the skull and bones of the arms, legs, and one foot. The substance is unevenly distributed in clusters or speckles and appears to be present only where the smooth dense outer surface of the bones has eroded.

While one cannot deduce the postmortem conditions to which these bones were exposed, it is known that the aircraft crashed and that the remains were received from a

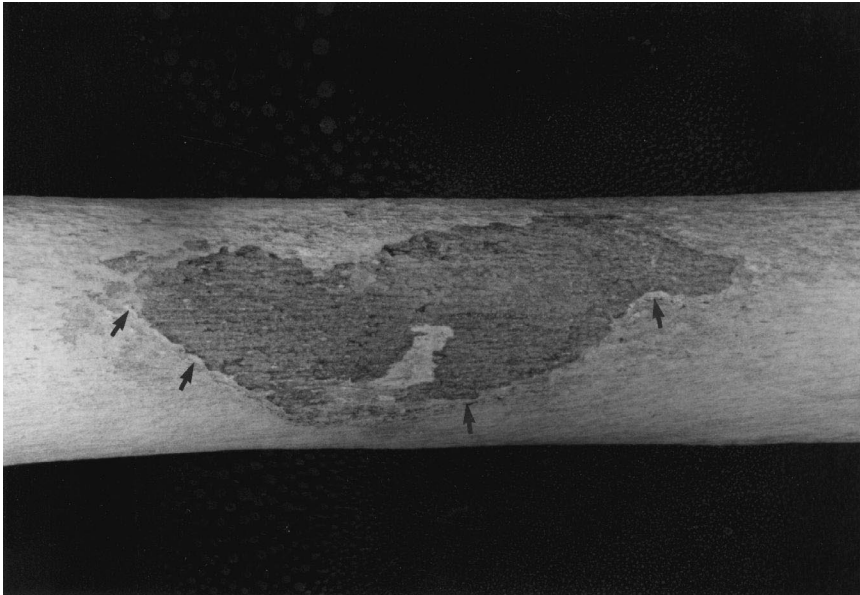


Fig. 1. Photograph showing location of the blue encrustation present on one of the bones. On this specimen vivianite encircles (arrows) an island of non-abraded outer cortex.

province in Vietnam characterized by generally acidic soil conditions. Acidic soils destroy bone much more quickly than alkaline soils.

4. Analytical methods

Examination with the scanning electron microscope (SEM) showed several small particles of a blue material (with shades ranging from light to dark blue) as well as cream colored particles which were placed onto a graphite SEM stub with a carbon conductive sheet used as the conductive adhesive. The sample stub was then coated with a thin layer of evaporated carbon to increase conductivity under the electron beam. The scanning electron microscope utilized for this study was a JEOL JXA-840A with a Tracor Northern TN-5502 energy dispersive X-ray analysis system (EDA) and a Microtrace detector.

Imaging was done at 10 kV and 25 mm working distance. Secondary electron photomicrographs were taken to show the morphology of the blue crystals.

Qualitative EDA was performed on several spots of the blue particles to determine the major and minor elements present. The detector can identify elements with an atomic number greater than ten. Acquisition of spectra was done at 20 kV and 39 mm working distance for 120 seconds.

Standardless semi-quantitative (SSQ) analysis was also performed to determine the atomic ratios of the major elements.

A small piece of the blue material (with shades of light and dark blue) was mounted onto the tip of a glass fiber with a rubber cement/toluene mixture and examined by X-ray diffraction (XRD). The XRD spindle was placed into a 114.6 mm radius Gandolfi camera and run on a Philips PW-1720 generator with Ni-filtered CuK_α radiation and a tube voltage of 45 kV and a current of 45 mA for thirteen hours. Kodak DEF-392 Direct Exposure Film was used to record the XRD pattern.

The film pattern was then indexed for d -values and relative intensities of the lines. A search was then conducted to find known compounds with matching values, using the Materials Data, Inc., "MicroID" search/match XRD computer program. The results of the SEM/EDA were used to assist in the search.

5. Results

Scanning electron microscopy showed that the bone encrustation is made up of small ($\sim 10 \mu\text{m}$ long) bladed crystals (Fig. 2). EDA on both the light and dark blue areas of the particles and the one cream-colored area produced the same results; major amounts of iron and phosphorous, minor calcium, and occasional traces of manganese (Fig. 3). Some, if not most, of the calcium is probably from adhering bone material (usually hydroxylapatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$).

All of the lines of the XRD powder pattern can be accounted for by the iron phosphate hydrate mineral, vivianite. Both d -values and the relative intensities of the lines of the pattern correspond to standard patterns of synthetic vivianite [2,3] and to

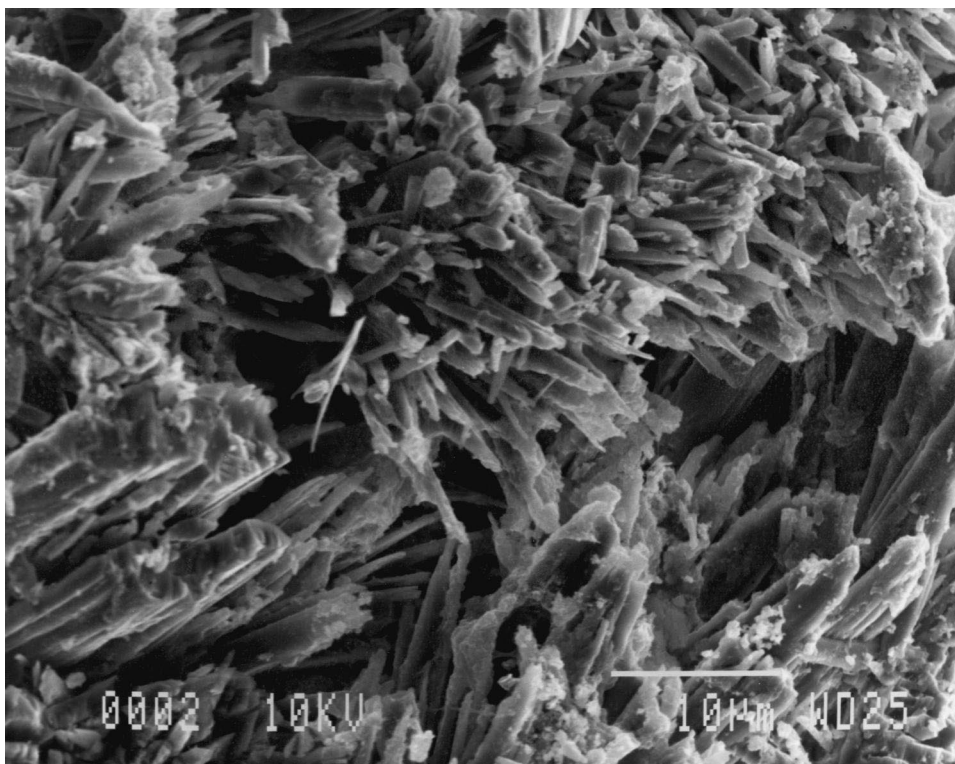


Fig. 2. SEM secondary electron photomicrograph of the blue encrustation in the form of small bladed crystals. Scale bar is 10 μm .

naturally occurring vivianite samples [4,5]. Hydroxylapatite (from the bone) was not observed.

An average of the SSQ analyses for iron and phosphorous from seven of the EDA spectra produced an average atomic ratio for Fe/P of 1.4, as compared to 1.5 calculated for vivianite.

6. Discussion

Vivianite is a monoclinic mineral with the chemical formula $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$. The ratio of atoms of iron to phosphorous for the mineral vivianite is 1.5, for the specimens tested this ratio was found to be 1.4. Minor amounts of manganese, magnesium, and calcium may substitute for the iron and manganese and calcium were found to be present in the samples. Vivianite crystals are usually prismatic and can be found in encrusting masses with a divergent bladed structure. It occurs relatively well-crystallized as a secondary mineral [6]. The samples from the bone fit this description (Fig. 2).

Vivianite is colorless and transparent when fresh and unaltered, but becomes pale blue

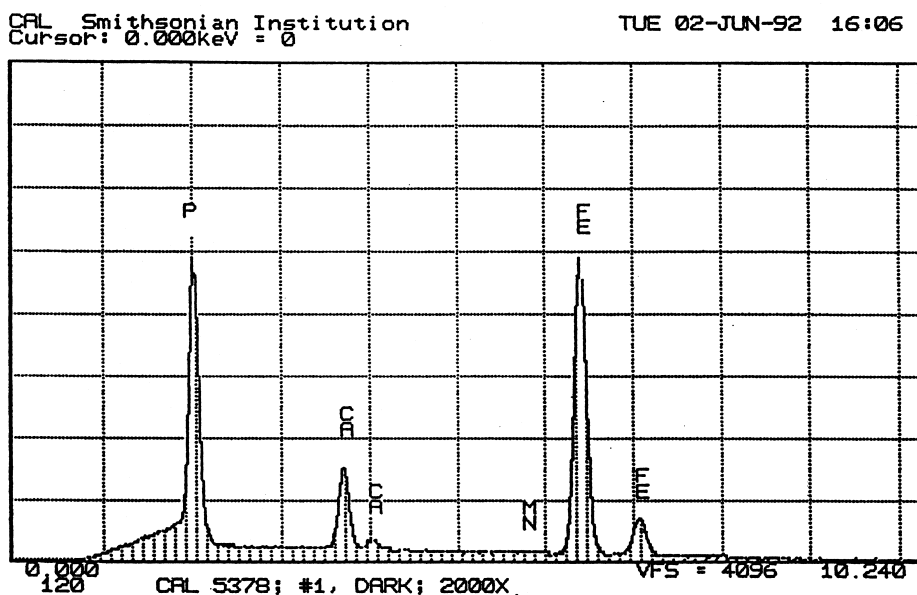


Fig. 3. EDA spectrum of blue encrustation on bone. P=phosphorous; Ca=calcium; Mn=manganese; Fe=iron.

on oxidation of the ferrous iron to ferric iron and then darkens to indigo blue with continuing oxidation. This change of ferrous to ferric iron can occur over a wide range without any apparent change in the crystal structure, with only the aforementioned changes in color [6]. The one sample piece examined showing both cream-colored and dark blue areas, with the same EDA spectra, represents an area where some of the vivianite was oxidized (the dark blue), while the cream-colored area had less oxidation, presumably because of facing inward before removal for analysis.

Vivianite can be found in sedimentary deposits where it is often associated with bone, decayed wood, and other organic remains. It is found as a reaction product of the hydroxylapatite of bone with iron-containing solutions [7]. The resulting blue coloring is often mistaken for turquoise [6].

The vivianite found on these bones is about twenty-eight years old. The forensic literature records only one occurrence of vivianite on human bone within such a short period of time. This find involved human remains discovered in a lake in Germany in 1964 [7]. The remains were found with a heavy iron sheet attached (most likely as a weight) and were estimated by clothing style to have been in the lake for about 30–50 years. The favorable conditions found in the lake (deep, cold water) allowed the iron sheet to slowly corrode, giving off Fe^{+2} ions that combined with the phosphate from the bones, forming vivianite. Upon exposure to air, the whitish vivianite rapidly turned dark blue.

Vivianite was associated with human teeth and jaws recovered from individuals who drowned when the Swedish flag ship *Wasa* capsized and sunk in the Harbor of Stockholm in August 1628 [8]. These remains contained small particles of vivianite in

the pulp chambers of some of the teeth and on some of the mandibles, depending upon their location in the ship. Those teeth and jaw bones that contained vivianite changed to a blue color in air and were always found near an iron object, such as a cannon ball or bolt.

Vivianite is often associated with fossil bone and teeth. One such example is a series of mammoth tusks collected in the arctic zone of Siberia [9]. These tusks had their surfaces colored by phosphates, including vivianite.

A recent research study involving fish bones in Lake Erie sediment and water showed that rapid formation of vivianite on young bones is possible when the correct conditions are present [10]. In this case, the incongruent dissolution of the fish bone apatite allowed the secondary formation of vivianite.

While this article was in review, two of the authors found trace to moderate amounts of vivianite on the skeletal remains of two more American MIAs from Vietnam. Both were occupants on an F-4 Phantom jet that crashed into a shallow stream in South Vietnam in 1970. In 1995, 25 years after the incident, U.S. recovery teams excavated the F-4 crash site and recovered more than 80 bone fragments and hundreds of pieces of pliable soft tissue (a rare finding in the humid jungles of Vietnam). The remains were recovered at a depth of about 2 meters in waterlogged soft clay saturated with jet fuel. The water and jet fuel created either an anaerobic or diminished oxygen environment that not only preserved the bones, but the soft tissue as well (including footprints). Only after the remains dried in the laboratory was the dark blue vivianite visible on some of the long bones. Without having done the previous vivianite research on the bones from the B-26B crash site, this substance would have been noticed by CILHI scientists, but unidentified.

7. Conclusion

With reducing and acidic conditions (such as in anaerobic, waterlogged soil or in deep water) [11], and an iron source (such as from the soil or from a metal object nearby), the mineral vivianite can form naturally as bone deteriorates.

If human remains are found under such conditions, and a blue encrustation (or white turning blue upon exposure to air) is found on the bones, the mineral vivianite may be the cause of the blue coloration. In the B-26B case just described, the bones in acidic soil associated with iron-containing clay or metal from the aircraft were found to exhibit a blue color by the formation of the iron phosphate mineral, vivianite. Although the presence of vivianite on these remains does not fill in all of the postmortem details, it does provide scientists with a better understanding of human taphonomy and evidence for distinguishing naturally from culturally modified bone.

The significance of finding vivianite on bones and teeth for forensic anthropologists and pathologists is that its presence can provide corroborative evidence relating to the elapsed time since death and soil conditions to which the remains were exposed. Distinguishing vivianite, a naturally occurring mineral, from paint and other surface applications indicating human-altered bone such as was found on human skulls in the

possession of American serial killer Jeffrey Dahmer, might also be of forensic significance in some cases.

This report represents only the second example in the forensic literature where vivianite has been identified from a post deposition process [7]. Subsequent to this identification the authors (MEF, CST) have noted three other occurrences of vivianite associated with historical burials. The presence of vivianite in these and other remains provides information leading to a more complete and accurate understanding of the taphonomic process associated with human and non-human remains.

References

- [1] P.S. Sledzik, S. Ousley, Analysis of six Vietnamese trophy skulls, *Journal of Forensic Sciences* 36(2) (1991) 520–530.
- [2] Joint Committee on Powder Diffraction Data–International Centre for Diffraction Data. Powder Diffraction File, Set 3, No. 70, 1953.
- [3] Joint Committee on Powder Diffraction Data–International Centre for Diffraction Data. Powder Diffraction File, Set 30, No. 662, 1980.
- [4] T. Sameshima, G.S. Henderson, P.M. Black, K.A. Rodgers, X-ray diffraction studies of vivianite, metavivianite, and barinite, *Mineralogical Magazine* 49(Part 1) (1985) 81–85.
- [5] F.N. Blanchard, S.A. Abernathy, X-ray powder diffraction data for the phosphate minerals: vauxite, metavauxite, vivianite, Mn-heterosite, scorzalite, and lazulite, *Florida Scientist* 43(4) (1980) 257–265.
- [6] C. Palache, H. Berman, C. Frondel, *The System of Mineralogy of James Dwight Dana and Edward Salisbury Dana*, 7th ed., Vol. II, John Wiley and Sons, New York, 1951.
- [7] S. Berg, H. Suchenwirth, K.L. Weiner, Über ein rezentes vivianit-vorkommen im walchensee/obb, *Naturwissenschaften* 54(8) (1967) 199–200.
- [8] G. Johanson, Iron from cannon balls in teeth and jaws, *OSSA* 3–4 (1976) 183–187.
- [9] N.K. Vereshchagin, A.N. Tikhonov, 1987, Investigation of mammoth tusks from the permafrost of the Siberian north-east, *Zoologicheskii Zhurnal* 66(4) 632–634 (in Russian).
- [10] J.O. Nriagu, Rapid decomposition of fish bones in Lake Erie sediments, *Hydrobiologia* 106(3) (1983) 217–222.
- [11] M.A. Courty, P. Goldberg, R. Macphail, *Soils and Micromorphology in Archaeology*, Cambridge University Press, Cambridge, 1989.