Hawleyite and Phosphate Minerals

from bethel church, indiana, including a second occurrence for ferrostrunzite

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INTRODUCTION

Ferrostrunzite, the iron analog of strunzite, was first described by Peacor *et al.* (1983) from sedimentary rocks at Mullica Hill, New Jersey, a phosphate locality discussed by Henderson (1980). They speculated that, although ferrostrunzite is rare at the New Jersey location, it may be common in other places where alleged strunzite occurs in "the absence of manganese-bearing phosphates." We have found ferrostrunzite to be abundant in the weathered black shale at a location in Indiana. In keeping with the prediction of Peacor *et al.* (1983), ferrostrunzite occurs in a host rock that is markedly deficient in manganese, containing less than 200 parts per million (ppm) Mn, versus a crustal average of 950 ppm for this element. The low manganese content for the host rock is particularly striking in view of the high abundances of other heavy metals such as vanadium, molybdenum and zinc in the Excello shale and other shales of its type (Vine and Tourtelot, 1970; Coveney and Martin, 1983).

In addition to ferrostrunzite, several other iron phosphate minerals are present in the shale; for example, leucophosphite, aluminian strengite, phosphosiderite and vivianite (Table 1). All of the phosphate minerals except phosphosiderite and strengite are present as well-formed microcrystals. Most of these are sufficiently abundant to be of interest to collectors and, with the possible exception of vivianite, none have previously been reported from Indiana. In addition to the phosphate minerals, we report here one of the few occurrences of hawleyite at a U.S. locality.*

LOCATION and HISTORY

The Bethel Church fossil dig and phosphate locality lies about 600 meters southeast of the Bethel Church in the Patoka State Fish and Wildlife Area, Pike County, Indiana, within the northwest quarter of Section 3, T3S, R7W, located on the Augusta 7½-minute U.S. Geological Survey quadrangle (Fig. 1). The site consists of a 20- by 40-meter fossil fish dig opened in 1981 in the highwall of an abandoned coal strip mine (Fig. 2). The highwall, dating from the early 1960s, exposes the Excello shale containing both fish fossils (mainly sharks) and phosphate minerals. The shale exposure extends at least 100 m east and west of the fish dig, and other exposures exist in the area, but these have not yet been examined for secondary phosphate minerals. Persons interested in access to the site should contact the Manager, Patoka State Fish and Wildlife Area, Winslow, Indiana.

The secondary phosphate minerals were discovered in July 1983 while several of the authors were sampling for geochemical studies at the Bethel Church Excello shale exposure being worked by Dr. Rainer Zangerl for fish fossils.

*Hawleyite has been reported by Pemberton (1983) from the Crestmore quarry, Riverside County, California. Richard C. Erd (personal communication) has identified it from Mono County, California, and a 1981 list of specimens for sale from Mineralogical Research Company lists hawleyite from Hanover, New Mexico.

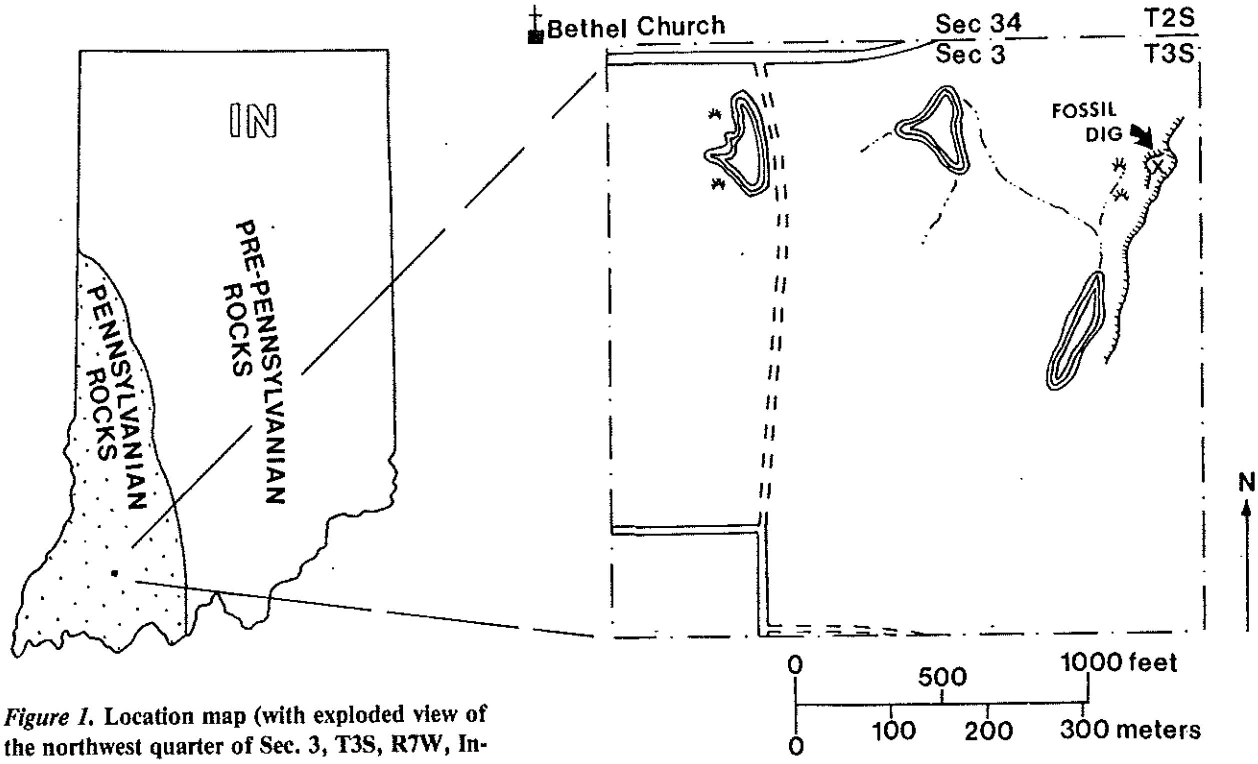

Figure 1. **Location map (with exploded view of the northwest quarter of Sec. 3, T3S, R7W, Indiana).**

GEOLOGY

Named for a town in northeastern Missouri, the Excello shale member of the Petersburg formation (Shaver *et al.*, 1970) is a black shale which crops out over a wide area extending from Indiana to Oklahoma. The Excello is typical of the black shales that occur over coals in Middle Pennsylvanian-age cyclothems, along the eastern edge of the Illinois Basin. Salient characteristics include thinness (less than 1 m), large heavy-metal tenors, and high organic matter content (20–50%). Locally, there are concentrations of fish fossils (especially shark remains) and phosphatic nodules, many of which may have originally been coprolites or gastric residue pellets derived from sharks (Zangerl and Richardson, 1963).

Like the Mecca quarry shale of Zangerl and Richardson (1963), the Excello shale and about 25 other similar Mid-continent Pennsylvanian-age shales characteristically contain various heavy metals. Whole-rock analyses indicate values ranging from hundreds to thousands of parts per million of vanadium, chromium, nickel, zinc, selenium, molybdenum, cadmium, and uranium (Coveney and Martin, 1983). Such metal values are ubiquitous over tens of thousands of square kilometers of outcrop and subsurface occurrences of the shales.

It is generally believed that metalliferous black shales were deposited in shallow Pennsylvanian seas beneath stagnant, oxygen-deficient bottom waters. The heavy metals may have been deposited at the time of sedimentation or possibly were added subsequently by mineralizing solutions. Such relations are currently under investigation by the authors, among others. The interested reader is referred to Coveney and Martin (1983) for more details on possible origins and for a more complete list of references on this aspect.

Pennsylvanian shales of the Midwest are commonly enriched in phosphate. For example, P_2O_5 contents of 1–3% are typical for the Pennsylvanian-age Hushpuckney shale of Kansas City. The Pennsylvanian shales of the eastern edge of the Illinois Basin, such as the Excello shale of Bethel Church, and the Mecca Quarry shale of Indiana, normally contain lesser quantities of phosphorus, however. Ordinarily, the Indiana shales carry less than 1% P_2O_5, but sporadic concentrations exceeding 5% phosphate are found, mostly as nodules. Such is the case for Bethel Church where clusters of phosphate nodules and their secondary products are concentrated at the east end of the shale exposure.

The Excello contains 6.5–10.5% iron. This is higher than most black shales which average about 2% Fe (Vine and Tourtelot, 1970). The Excello contains only minor amounts of manganese. Grades of manganese for Pennsylvanian-age black shales typically fall in the range of only 50–200 ppm on a whole rock basis, well below the crustal average of 950 ppm for this element. As manganese is an essential element for the formation of strunzite, it is not surprising that ferrostrunzite, instead, occurs in the Excello shale.

MINERALS

The following descriptions cover only those minerals which are likely to be of interest to mineral collectors. (Other phosphate minerals, for example Al-free strengite and fluorapatite, occur only as microscopic grains.) All minerals have been identified from X-ray powder diffraction photographs (114.6-mm Debye-Scherrer camera, Ni-filtered, CuKα radiation), supplemented by electron microprobe analysis and other techniques where appropriate. All specimens described are housed in the Museum of Geosciences, University of Missouri – Kansas City (UMKC). Excepting hawleyite (CdS), all minerals described are iron phosphates, most of which have not previously been described as occurring in Indiana. However, many of the phosphates have previously been reported from weathering profiles and sedimentary settings. For example, leucophosphite, first described as forming from the action of bird guano on serpentinite in Australia, has been found as colorful crystals in metalliferous shale from Nevada (Zientek *et al.*, 1979). Nevertheless, crystalline examples of the minerals reported here are most typically collected from pegmatite occurrences, rather than from sedimentary host rocks. Just as in pegmatite occurrences, the Indiana phosphates originated through alteration of primary phosphate material, probably as a result of natural weathering processes. However, because the phosphate locality is in the headwall of a long-abandoned strip mine, it is possible that some of the minerals were formed subsequent to excavation.

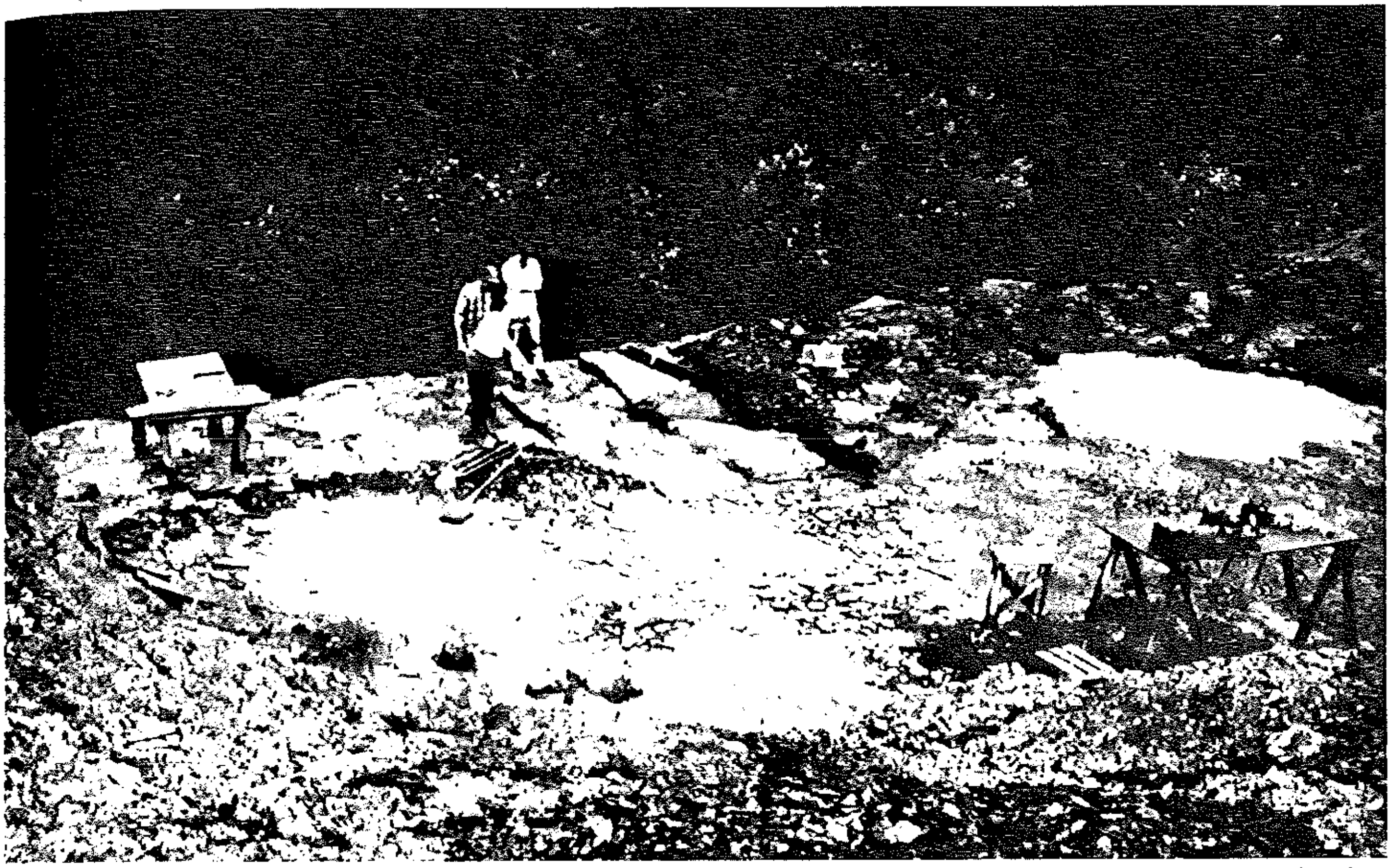

Figure 2. Bethel Church phosphate location. (Rainer Zangerl pointing out Excello shale outcrop to authors Allen and Blankenship.)

Figure 3. Dark green beraunite crust surrounding a white ball of phosphosiderite and overgrown partly with orange ferrostrunzite (lower right). From the crust of the diadochite nodule. The phosphosiderite ball is about 0.5 mm in diameter. UMKC specimen.

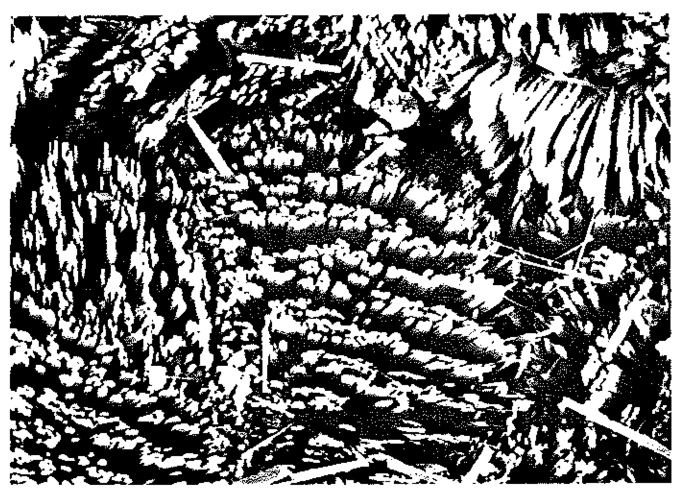

Figure 4. Beraunite needles with crust of diadochite nodule. (SEM photo; width of view is 300 μm.)

Beraunite $Fe^{+2}Fe_5^{+3}(PO_4)_4(OH)_5 \cdot 4H_2O$

Beraunite occurs as clusters of 2–3 mm long capillary hairs, on the rim of the one diadochite nodule found loose on the mine dump (Fig. 3). In some cases the beraunite needles are arranged in sprays resembling corn rows (Fig. 4).

Diadochite $Fe_2^{+3}(PO_4)(SO_4)(OH) \cdot 5H_2O$

Diadochite occurs as (~ 100 μm) microcrystals and seems to be quite rare, as it was found on the waste dump as only a single nodule measuring approximately 6 cm across (Fig. 5). Despite its

Figure 5. **Fragment of 6-cm diadochite nodule, Bethel Church phosphate location, Museum of Geosciences, University of Missouri – Kansas City (UMKC) specimen. Dark balls of leucophosphite are approximately 1 mm in diameter. Angular chunk to upper right consists of diadochite. White rind is phosphosiderite. Light gray balls and crust are ferrostrunzite. Darker gray crust is beraunite. Photo by Jon Dunn.**

rarity, the diadochite is of special interest because it is coated by a thin (~ 3 mm) rind containing some of the finest specimens of ferrostrunzite and leucophosphite and because it contains the only beraunite and phosphosiderite found at the locality.

Ferrostrunzite $Fe^{+2}Fe_2^{+3}(PO_4)_2(OH)_2 \cdot 6H_2O$

Ferrostrunzite occurs principally as tufts of colorless to straw-yellow, radiating, capillary crystals lying along bedding planes and, to a lesser extent, along joints in the shale (Fig. 6). In this occurrence it is commonly associated with euhedral vivianite crystals or aluminian strengite (Fig. 7) or with both minerals. Characteristically, the individual ferrostrunzite crysals in the shale are about 50–200 μm in length and about 5–10 μm thick. The mineral is sufficiently abundant in this occurrence that we found about 100 specimens in two hours of collecting.

Excellent examples of ferrostrunzite also occur in the single diadochite nodule, in which the mineral forms well-developed capillary fibers (Fig. 8) ranging in color from the typical straw-yellow of strunzite-group species to white, bright orange or brown. In some cases, the ferrostrunzite needles show evidence of corrosion on their tips (Fig. 9).

A cell refinement based on monochromatized CuKα X-ray diffractometry of Indiana ferrostrunzite yields the following parameters: a = 10.173(5)Å; b = 9.783(5)Å; c = 7.395(11)Å; α = 88°44′; β = 97°36′; γ = 117°36′; V = 645.9(9)Å^3.

Ferrostrunzite has an ideal formula of $Fe(Fe)_2(PO_4)_2(OH)_2 \cdot 6H_2O$. The chemical formula for Indiana ferrostrunzite is close to $Fe_{.95}Fe_{1.9}Mn_{.005}(PO_4)_2(OH)_2 \cdot 6H_2O$. For our specimens, we have determined the combined water and hydroxyl content to be approximately 27.5% (by measurements of the weight losses accompanying incremental heating of two samples over the range 50–200° C).

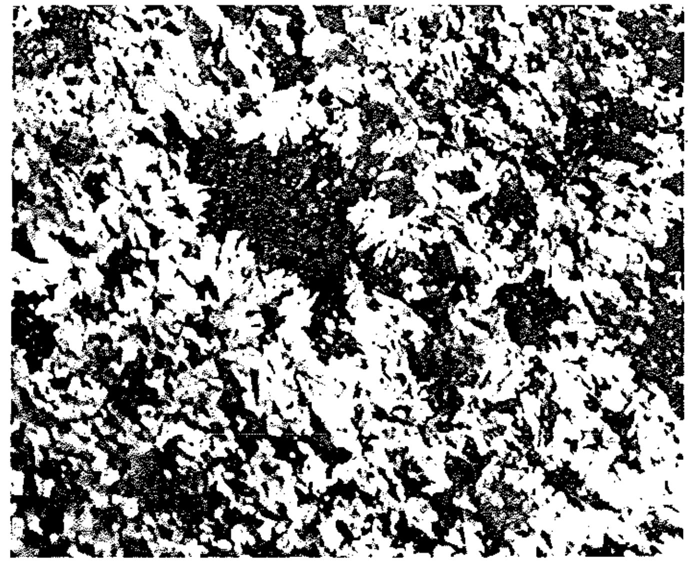

Figure 6. **Tufts of ferrostrunzite crystals to 0.4 mm on shale bedding plane. UMKC specimen. Photo by Jon Dunn.**

Figure 7. **Ferrostrunzite with aluminian strengite on shale. (SEM photo; width of view is 46 μm.)**

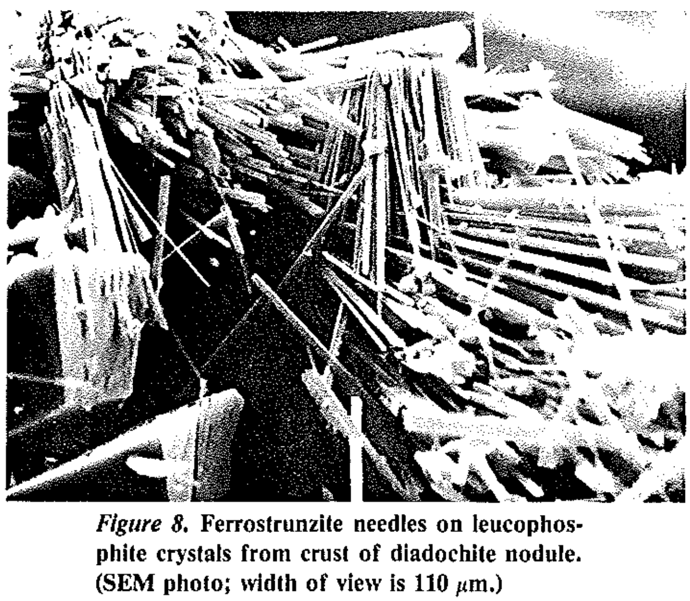

Figure 8. **Ferrostrunzite needles on leucophosphite crystals from crust of diadochite nodule. (SEM photo; width of view is 110 μm.)**

This value is within 1% of the water and hydroxyl content predicted from the ideal formula for ferrostrunzite (28.4%). The remaining constituents (43.17% combined FeO and Fe_2O_3, 29.91%

Figure 9. **Corroded ferrostrunzite crystals from crust of diadochite nodule. (SEM photo; width of view is 36 μm.)**

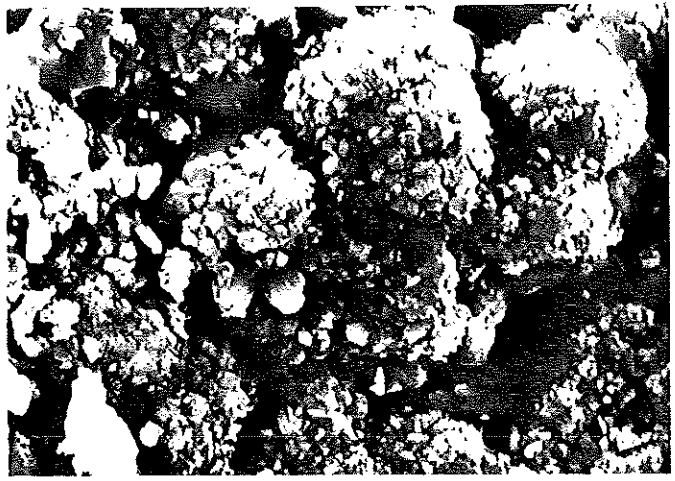

Figure 10. **Hawleyite clumps. (SEM photo; width of view is 26 μm.)**

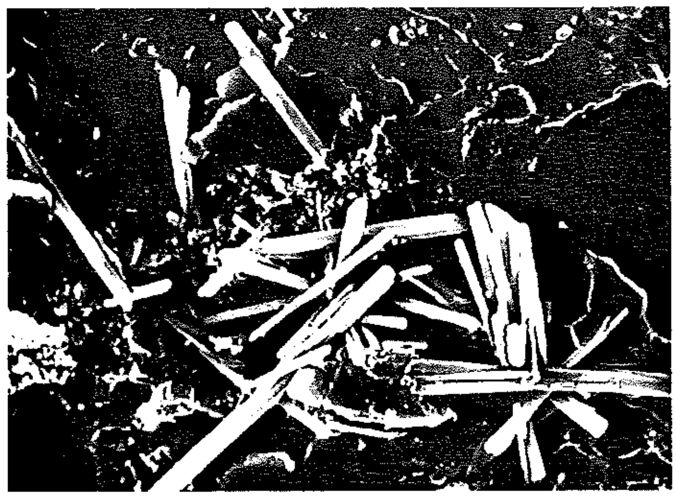

Figure 11. **Barite crystals with hawleyite clumps on coaly plant fragment from Excello shale. (SEM photo; width of view is 31 μm.)**

P_2O_5, and 0.06% MnO) were determined by electron microprobe analysis with almandine, Ba-chlorapatite, and rhodochrosite as standards for Fe, P, and Mn (operating voltage of 15 KV; a sample current of 15 nanoamperes, measured on brass). The ratio of Fe^{+3} to Fe^{+2} is assumed to be 2:1 in accordance with the ideal formula.

Debye-Scherrer X-ray powder patterns for Indiana ferrostrunzite compare well with that of the New Jersey ferrostrunzite (Peacor *et al.*, 1983). It should be noted, though, that several lines appearing in diffractometer tracings of the Indiana ferrostrunzite were not reported for the New Jersey material, e.g., 8.62Å (25), 8.46Å (15), and 3.20Å (30). (All of these extra lines, however, can be indexed with the calculated powder pattern generated from our cell-refinement data.) It also should be mentioned that the pattern for Indiana ferrostrunzite radically differs from that of the strunzite-like mineral reported from Belgium by Van Tassel (1966). Of more serious concern, however, is the fact that the powder patterns for Indiana ferrostrunzite match as well with Frondel's (1957) Hagendorf strunzite pattern as it does for the New Jersey pattern. We have resolved this ambiguity by electron microprobe analysis and X-ray fluorescence analysis for iron and manganese. The results, indicating a preponderance of iron, clearly point to ferrostrunzite as the identity of the Indiana mineral. Generalizing from our experience, we can only conclude that a chemical test to supplement X-ray data would ordinarily be necessary to distinguish between strunzite and ferrostrunzite.

Hawleyite CdS

Hawleyite, the isometric dimorph of greenockite, which was first described from an occurrence in the Yukon, is found along joints and in association with fossil plant remains within the Excello shale at Bethel Church. A bright orange to yellow pulverulent material, it provides a striking contrast to the jet black shale in which it occurs. A particularly fine example consists of yellow-orange hawleyite splotches on the surface of a flattened plant stem measuring 20 cm by 1.5 meters. The hawleyite from this occurrence consists of rounded, irregular clumps of anhedral crystals (Fig. 10). Some hawleyite is associated with white barite (Fig. 11) and traces of sphalerite. Although hawleyite is present in comparatively unweathered shale, it too may be a product of the early stages of weathering.

At the original occurrence, Traill and Boyle (1955) found hawleyite forming as a result of the action of acid ground waters on primary sulfide minerals. These workers suggested that, "Much material previously identified as greenockite by casual hand specimen examination may prove to be hawleyite when identified by X-ray diffraction." Subsequently Jedwab and Van Tassel (1978) found that many samples from Belgium, labeled as greenockite, are actually hawleyite. Hence hawleyite may be far more widespread than generally supposed. Probably this situation would be altered if more U.S. samples of CdS were investigated by X-ray techniques. However, there is a possibility that hawleyite *is* comparatively rare in the United States. This is because the most important domestic ores containing Zn and the allied element, Cd, are hosted by carbonate rocks that would tend to neutralize the acid solutions needed to form hawleyite.

Leucophosphite $KFe_2^{+3}(PO_4)_2(OH)_2 \cdot 2H_2O$

Leucophosphite occurs chiefly as very lustrous, greenish brown, equidimensional crystals in thin veinlets cross-cutting fluorapatite nodules in the black shale. The finest examples at the Bethel Church dig, however, occur in the crust of the diadochite nodule which contains tiny balls consisting of adamantine, nearly opaque, green-brown, wedge-shaped crystals (Fig. 12). In some cases, leucophosphite balls occur embedded in diadochite (Fig. 13).

Phosphosiderite $Fe^{+3}PO_4 \cdot 2H_2O$

Phosphosiderite (metastrengite), probably the least interesting (to collectors) of the secondary phosphate minerals from Bethel Church, occurs mainly as white chalky material (Fig. 5) in the crust

Figure 12. **Leucophosphite ball from diadochite nodule. (SEM photo; width of view is 1100 μm.)**

Figure 13. **Leucophosphite balls (0.5 mm) embedded in diadochite. White ball in cavity is phosphosiderite; the adjacent light gray ball, composed of radiating crystals, is ferrostrunzite. UMKC specimen. Photo by Jon Dunn.**

of the diadochite nodule. In some cases it occurs as 0.5–1 mm white balls embedded in diadochite (Fig. 13) or surrounded by crusts of other iron phosphates (Fig. 3).

Strengite (aluminian) $(Fe^{+3},Al)PO_4 \cdot 2H_2O$

Aluminian strengite (*barrandite*) occurs as microscopic, light gray, 20–50 μm ellipsoids on the bedding planes of the shale and associated with ferrostrunzite. Scanning electron microscopy reveals that the microscopic clusters of strengite consist of rows of radiating crystals (Fig. 7).

Vivianite $Fe_3^{+2}(PO_4)_2 \cdot 8H_2O$

It was the flashy, bright, 1–2 mm crystals of vivianite occurring on black shale that first drew our attention to the phosphate minerals of Bethel Church. This mineral is the most common of the secondary phosphates at the locality. The mineral occurs as stubby prisms, as radiating aggregates, and, to a lesser extent, as blue powdery material. Most of Bethel Church vivianite crystals are clearly secondary, occurring chiefly as fresh prisms and rosettes (Fig. 14) scattered along the surfaces of open joints and dilated bedding planes. Some of the powdery material and a few crystals of vivianite occur in cavities within phosphate nodules and may be diagenetic in origin, similar to the vivianite at the Mullica Hill, New Jersey, occurrence described by Henderson (1980). Although the Indiana vivianite scarcely rivals the spectacular material from Virginia, there are some good microspecimens present and attractive, small cabinet-sized examples can be found.

Figure 14. **Vivianite rosettes to 5 mm on shale bedding plane. UMKC specimen.**

DISCUSSION

The secondary iron phosphates in the shale at the Bethel Church locality were formed by the action of meteoric waters. Most likely the weathering processes involved acid waters that leached iron, aluminum and, to a lesser extent, potassium from the shale matrix to react, in turn, with fluorapatite nodules or dissolved phosphate, thus forming the principal secondary phosphate minerals (vivianite, ferrostrunzite, aluminian strengite, and leucophosphite). Clearly the abundances of fluorapatite nodules and iron in the shales are critical factors for the formation of the minerals found. No less critical to the occurrence is the paucity of manganese which explains the overwhelming predominance of iron phosphates and the absence of any secondary manganese minerals such as strunzite.

The origin of the peculiar nodule containing diadochite and several other crystalline phosphate minerals is unclear owing to the small quantity of sample material and because the one nodule found occurred loose in the mine dump. It is possible, however, that this nodule formed as a pyrite or marcasite concretion which reacted with dissolved phosphate during weathering to precipitate ferroan sulfate-phosphate. The crust, surrounding the diadochite and containing ferrostrunzite, beraunite, phosphosiderite and leucophosphite, may have formed at a later stage or as a result of a diffusion gradient that resulted in a dominance of phosphate ions along the exterior margin of the nodule, during the initial weathering.

Iron phosphate minerals are abundant in the Excello shale at Bethel Church. We find it curious that no secondary phosphates containing the other heavy metals known to occur in the shales have been found at the Bethel Church location. For example, one might expect to find hopeite ($Zn_3(PO_4)_2 \cdot 4H_2O$) or other zinc phosphate mineral species. Possibly the absence of such minerals is related to a relative immobility of heavy metals other than iron in the weathering zone of such locations.

Table 1. **Phosphate minerals occurring at the Bethel Church location, Pike County, Indiana.**

Name	*Chemical Formula*	*Occurrence*
Beraunite	$Fe^{+2}Fe_5^{+3}(PO_4)_4(OH)_5 \cdot 4H_2O$	In crust on diadochite nodule
Diadochite	$Fe_2^{+3}(PO_4)(SO_4)(OH) \cdot 5H_2O$	As loose 6-cm diameter nodule found on mine dump
Ferro-strunzite	$Fe^{+2}Fe_2^{+3}(PO_4)_2(OH)_2 \cdot 6H_2O$	As radiating fibers on bedding planes, fluorapatite nodules and joints in black shale and in crust of diadochite nodule
Fluor-apatite	$Ca_5(PO_4)_3F$	As micro-crystalline nodules and in fossil fish fragments in black shale
Leuco-phosphite	$KFe_2^{+3}(OH)(PO_4)_2 \cdot 2H_2O$	In fluorapatite nodules and in crust on diadochite nodule
Phospho-siderite	$Fe^{+3}PO_4 \cdot 2H_2O$	As white crust on diadochite nodule
Strengite (aluminian)	$(Fe^{+3},Al)PO_4 \cdot 2H_2O$	With ferrostrunzite on bedding planes in black shale
Vivianite	$Fe_3^{+2}(PO_4)_2 \cdot 8H_2O$	Along bedding planes, joints and in fluorapatite nodules in black shale

Questions remain about just how widespread the secondary phosphate mineralization is. It could be merely local. It is worth noting, however, that the discovery of the unusual phosphate minerals of the Bethel Church location was largely an accidental by-product of geochemical and paleontologic studies of the shales. Prospects seem favorable for locating other, and possibly better, phosphate mineral collecting localities in southern Indiana. Moreover, it is conceivable that more prolific locations exist elsewhere in the outcrop belt of the Midcontinent Pennsylvanian-age black shales that occur in a region extending from Pennsylvania to Kansas and from Iowa to southern Missouri and Oklahoma. Although these occurrences exist outside the normal haunts of mineral collectors, it is possible that other ferrostrunzite locations are waiting to be found in the Midcontinent by the patient collector.

SUMMARY

The Bethel Church phosphate locality contains ferrostrunzite, vivianite, aluminian strengite and leucophosphite in abundance and lesser amounts of beraunite, diadochite and phosphosiderite. This is the second occurrence yet described for ferrostrunzite and the first Indiana occurrence for most of the other iron phosphate minerals. All of these minerals occur as secondary species in moderately to heavily weathered black shale beds in the Excello member of the (Middle Pennsylvanian) Petersburg formation. Also present is hawleyite, very few occurrences of which are known in the U.S. The extent of the occurrence is uncertain. It may be confined to the 300-m outcrop containing the Bethel Church fossil fish dig. However, numerous unexamined outcrops of Excello shale and similar Pennsylvanian black shales occur elsewhere within the same abandoned mine and in the surrounding region and may well contain similar phosphate minerals.

ACKNOWLEDGMENTS

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