acta
geologica
polonica

Vol. 28, No. 2 Warszawa 1978

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Vivianite from the Middle Jurassic fossiliferous concretions of Łuków, Polish Lowland

ABSTRACT: Vivianite occurring in fossiliferous concretions dispersed in the Middle Jurassic clays exposed at Łuków (Polish Lowland), and forming rosette-shaped, coarse-crystalline aggregates up to several centimeters in diameter, partly filling the secretion fractures, as it is evidenced by the X-ray powder patterns, *DTA*, chemical and spectral emission analyses, and measurements of refractive indices, displays composition close to theoretical with very low content of Fe^{3+} ion. The mode of the occurrence of vivianite within septarian-fractured concretions testify its early diagenetic origin.

INTRODUCTION

Vivianite is a common and widespread supergene mineral in Poland, that forms earthy, blue dusts and aggregates in peats and in bog--iron ores (Zieleniewski 1945). It was also recorded (Traube 1888) from the oxidation zone of pegmatitic veins in the Sudetes, exposed at Modliszów near Świdnica, at Michałkowa near Wałbrzych, and in mica schists at Olszyna near Lubań, as well as in the Silesia region at Dziemierz near Racibórz and at Tarnowskie Góry. The investigated occurrence size of vivianite has hitherto been unknown in literature.

This study of vivianite was undertaken as an investigation project kept by the *Scientific Circle of Undergraduate Students in Geology (KMG)*, University of Warsaw.

Acknowledgements. The authors are greatly indebted to Dr. A. Kozłowski for his kind advice and help during their work and preparation of the manuscript.

MODE OF THE OCCURRENCE

At Łuków, in the Polish Lowland (120 km ESE from Warsaw), an erratic mass of the Middle Jurassic clays laid down within the bottom moraine of the Middle Polish (Riss) glaciation is commonly known (cf.

Jahn 1949). The clays bear a world-famous, numerous and perfectly preserved Callovian fauna, above all ammonites, excellently monographed by Makowski (1952, 1962).

Callovian clays forming this erratic mass, cropping out in a series of clay-pits of the brickyard Łapiguz at Łuków, are homogenous, black colored and they bear mica flakes. Numerous concretions, variable in size, shape and mineral composition, are irregularly scattered throughout the whole mass of the clays. The most frequent calcite concretions are a few up to 30 cm in diameter; their shape being variable but most commonly spherical. Larger concretions are usually replete with diversified fauna, the large female ammonites including (*cf.* Makowski 1952, 1962). Rarer than the calcite concretions, one may find loafy spherosiderites and small, several centimeters long, irregular concretions consisting of almost pure pyrite.

Calcite concretions often display septarian structure with well visible veinlets of yellow-whitish calcite, the surfaces of which are covered by fine crystals of pyrite. The latter mineral commonly forms heavy encrustations on the shells of mollusks, essentially cephalopods (nautiloids, ammonites, phragmocones of belemnites). In some cracks cemented with calcite, in a relatively small number of concretions studied, the aggregates of vivianite are recognizable (Text-fig. 1 and Pl. 1, Figs 1—3).

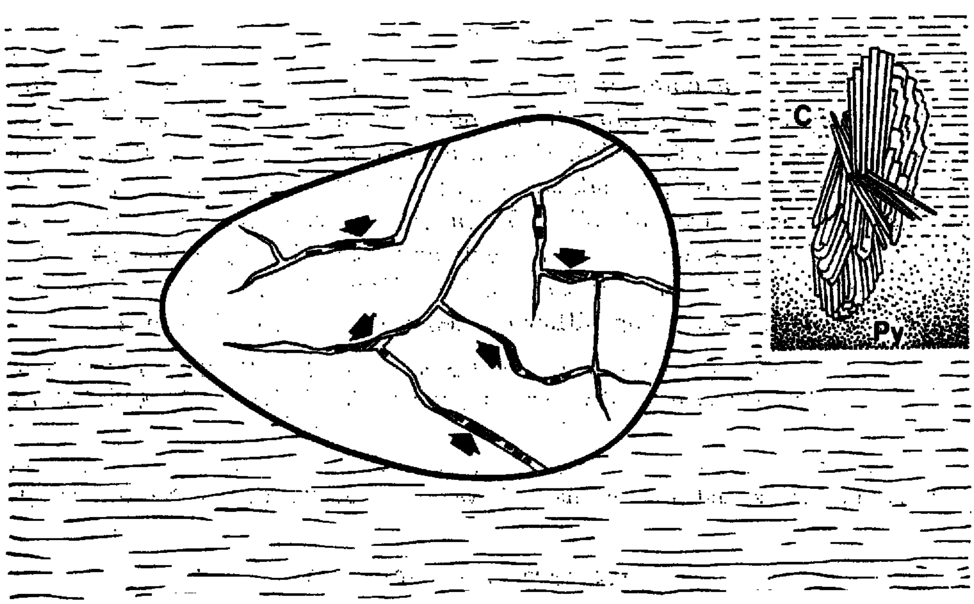
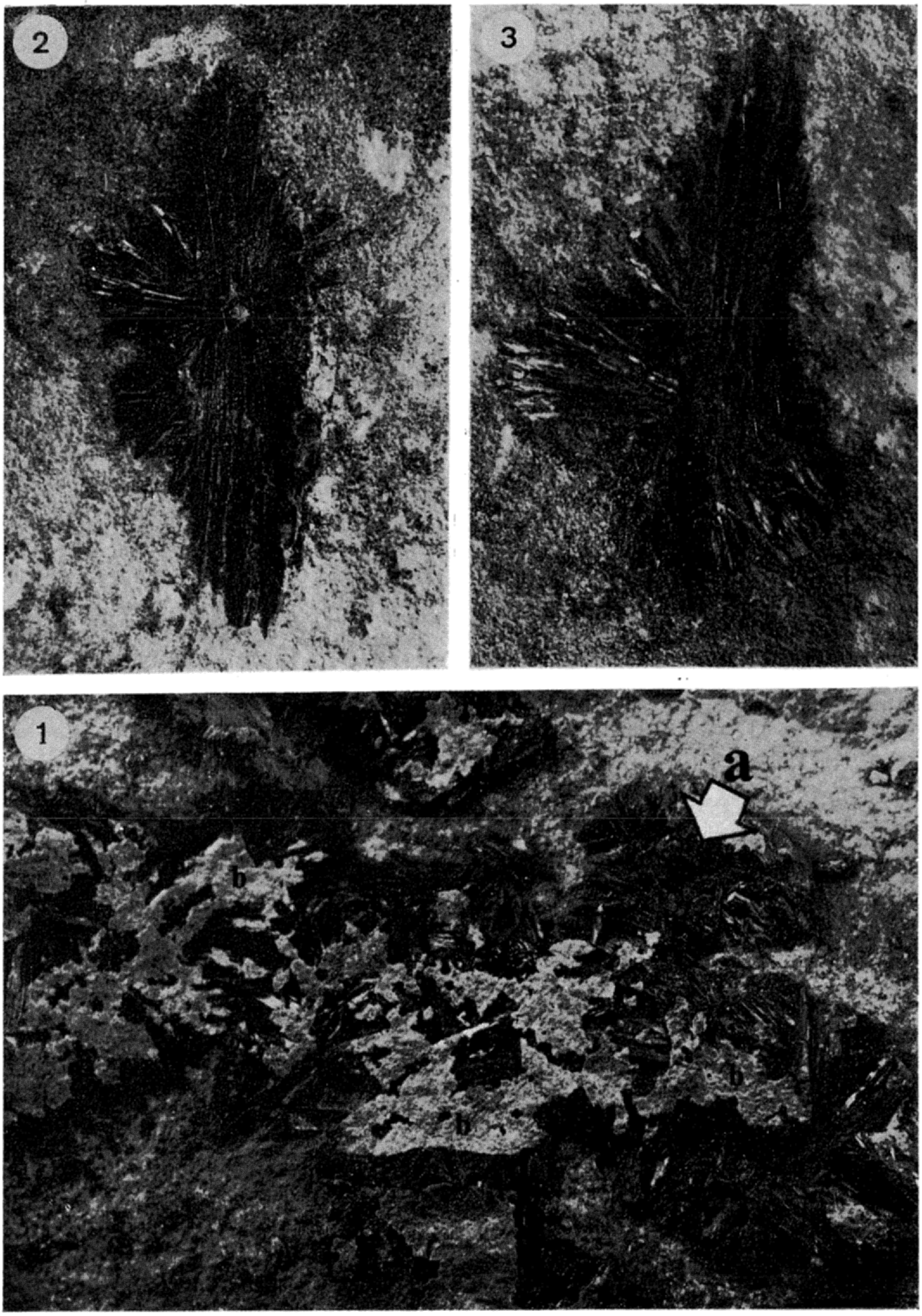


Fig. 1. Calcite concretion bearing vivianite (arrowed) and pyrite (marked as black rectangles), occurring in the Callovian clays; and single rosette of vivianite on the calcite (*C*) surface of septarian fracture, partly covered with fine-grained pyrite (*Py*)



1 — Surface of the secretion fracture in calcite concretion (*cf*. Text-fig. 1) with crowded aggregates of fine vivianite crystals *(a)*, partly covered with fragments of the opposite wall of the fracture *(b)*; × 4.

2—3 — Single, rosette aggregates of slaty crystals of vivianite from another surface of the secretion fracture; × 4.

Table 1

X-ray powder pattern of minerals forming vivianite-bearing concretions at Łuków

d/n, Å	Intensity I/I_0	Minerals
7.92	9	illite
7.08	5	chamosite(?)
4.99	4	illite
4.25	9	illite
3.84	10	calcite
3.34	40	illite
3.02	100	calcite
2.828	2	illite
2.487	16	calcite
2.278	21	calcite
2.088	2	calcite
1.989	2	illite
1.870	16	calcite

Table 2

Chemical composition of vivianite from Łuków

Component	weight %
Fe_2O_3	0.81
FeO	42.19
MnO	trace
MgO	trace
CaO	0,3
P_2O_5	28.01
H_2O	28.63
Insoluble in HNO_3	0.24
Total	100.21

Table 3

Comparison of X-ray powder pattern of vivianite from Łuków with the data presented by Vasilev & *al.* (1974)

Vivianite from Łuków		Data after Vasilev & al. 1974	
d/n, Å	I/I_0	d/n, Å	I/I_0
7.94	21	8	27
6.71	100	6.80	100
4.90	21	4.81	40
4.53	12	4.50	13
4.05	12	4.09	13
3.84	21	3.84	40
3.62	9	3.65	5
3.34	44[a]	3.35	3
3.19	14	3.20	53
2.97	23	2.97	67
2.70	12	2.71	67
2.53	9	2.52	33
2.43	10	2.42	40

[a]) coincidence with calcite

The X-ray powder studies (Table 1) indicate that the vivianite-bearing concretions consist, taking into account the carbonates, only of calcite, that however contains a significant admixture of illite. Neither siderite nor any other iron minerals were found by the X-ray method, besides of a problematic presence of chamosite. The above recognition is confirmed by the *DTA* curves (Fig. 2*A*) with distinct endothermic effect at 120°C typical of illite, and strong endothermic effect with maximum at 940°C testifying the presence of calcite.

Vivianite individuals crystallized in fractures of concretions and this resulted in their flat, slaty habit (*cf.* Pl. 1, Fig. 1). They usually form elongated, wedge-shaped laths up to 7 mm long, arranged in cha-

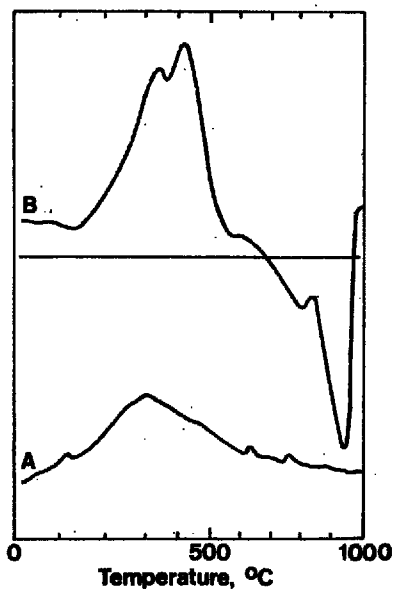


Fig. 2

DTA curves of vivianite *(A)* and host concretion *(B)* from Łuków

racteristic rosette-shaped aggregates to 1.5 cm in diameter, and 2—3 mm thick (*cf.* Pl. 1, Figs 2—3). The vivianite aggregates occur individually or with fine crystals of pyrite (*cf.* Text-fig. 1).

ANALYTICAL DATA

The studied vivianite is macroscopically dark-green with yellowish tint. Streak is deep blue. Thin cleavage chips are almost colorless. Crystals have glassy lustre.

Refractive indices determined by the immersion method equal as follows:

$n_{\alpha} = 1.5780$; $n_{\beta} = 1.6023$; $n_{\gamma} = 1.6290$

Pleochroic colors appear in agreement with scheme: α = blue, γ and β = light yellow-brown. Low refractive indices are indicatives of low content of Fe^{3+}, as the process of oxidation of Fe^{2+} to Fe^{3+} in vivianite (*cf.* Zieleniewski 1945) is accompanied by an increase of the refractive indices. Ordinary vivianites from peats and bog deposits (*cf.* Zieleniewski 1945) have refractive indices: n_α = 1.580—1.612; n_β = 1.602—1.636; n_γ = 1.630—1.656.

Density of the investigated vivianite, determined at 18°C by the picnometer method, equals 2.670 g/cm³.

Chemical analyses (Table 2) confirms a low content of Fe^{3+} recognized by the optical studies. Chemical composition of the analysed vivianite agrees well with the theoretical molecule and iron is replaced only by trace amount of Ca^{2+}, Mg^{2+} and Mn^{2+}. The spectral emission analysis proved the absence of other elements. As it is resulting from the chemical analysis, the crystallochemical formula of the studied vivianite may be expressed as follows:

$$(Fe^{2+}_{2.94}\,Fe^{3+}_{0.02}\,Ca_{0.03})\,[PO_4]_2\cdot 8H_2O$$

Spacing of the studied vivianite, obtained with the use of *CuKα* radiation (Table 3) are very similar to the values given by Vasilev & *al.* (1974).

The *IR* spectrum absorption (Fig. 3) was taken in ranges 400—3800 cm⁻¹. It consists of bands 575, 820, 1055 cm⁻¹ typical of PO_4^{-3} and bands 1640, 3430⁻¹ due to crystallochemically linked water.

The *DTA* proved (Fig. 2B) that the studied vivianite begins to lose water at temperature 40°C; dehydration process is the most intensive at temperature 120

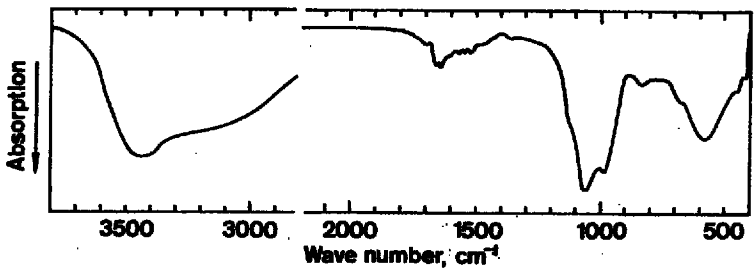


Fig. 3. *IR* absorption curve of vivianite from Łuków (*KBr* pellet technique, *UR-20* spectrophotometer)

to 140°C. The final point of dehydration is difficult for ascertaining because at higher temperature the oxidation of Fe^{2+} coincides with the end of dehydration. Presumably, total water is removed only at 600°C, and resulting in alteration of the crystal lattice of the mineral. The observed dehydration of vivianite differs from the loss of water in the bog vivianites, that finishes at 200°C, and it is similar to the dehydration of coarse-grained vivianite from Ibex Mine, USA (*cf.* Zieleniewski 1945).

ORIGIN OF THE INVESTIGATED VIVIANITE

The calcite concretions from Łuków bearing the studied vivianite are syngenetic or early diagenetic, as it is proved by often observed their squashing, and formation of secondary septarian veinlets, as well as by the presence of delicate shells of ammonites excellently preserved in many concretions.

The studied vivianite is the secondary mineral in relation to the host concretions, and it has been formed during their cracking at the earliest diagenesis of clayey material within the Middle Jurassic sedimentary sequence. The reducing conditions, apparent from a significant concentration of pyrite, and the abundant organic matter, supplying moreover the phosphate ions, were favorable for the origin of vivianite. The presence of Fe^{2+} ions and organogenic phosphate ions in circulating waters caused crystallization of vivianite in fractures of the septarian-cracked concretions. The occurrence of vivianite together with pyrite in the septarian fractures that are healed towards the surface of the concretions proves that it cannot be a supergene mineral related to the weathering processes within the erratic mass of the Callovian clays deposited by the Middle Polish (Riss) icesheet in the bottom moraine at Łuków.

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WYSTĘPOWANIE WIWIANITU W KONKRECJACH ŁUKOWSKICH

(Streszczenie)

Przedmiotem pracy jest analiza wiwianitu znalezionego w powszechnie znanych konkrecjach występujących w obrębie kry iłów kelowejskich w Łukowie.

Wiwianit wykształcony jest tutaj w postaci ciemnozielonych, grubokrystalicznych tabliczek i rozetkowych skupień (*patrz* fig. 1 oraz pl. 1, fig. 1—3) rozwiniętych na septariowych spękaniach niektórych konkrecji.

Wyniki badań laboratoryjnych, w tym analizy rentgenowskiej, spektrofotometrii w podczerwieni, analizy termicznej i składu chemicznego (*patrz* fig. 2—3 oraz tab. 1—3) oraz pomiary optyczne wskazują na dużą czystość badanego minerału i niski stopień utlenienia żelaza.

Sposób występowania badanego wiwianitu w obrębie konkrecji wskazuje na jego wczesnodiagenetyczne pochodzenie, podczas gdy same konkrecje mają charakter utworów syngenetycznych, powstałych w obrębie świeżo złożonego kompleksu iłów kelowejskich.