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VIVIANITE FROM THE PLEISTOCENE OF THE HORLOFF GRABEN (HESSEN, GERMANY)

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Bongaerts, Hans L. Vivianite from the Pleistocene of the Horloff Graben (Hessen, Germany). — Contr. Tert. Quatern. Geol., 29(1-2): 3-7, 2 figs, 1 pl. Leiden, June 1992.

The structure of nodules containing vivianite [$Fe_3(PO_4)_2.8H_2O$], and crystal aggregates consisting entirely of this mineral is described on the basis of thin sections. The material studied was collected by the author in a lignite quarry at Wölfersheim near Frankfurt am Main (Germany) from a clay lense, *c* 5 m below surface. Here vivianite occurs in the form of crystal aggregates which exhibit a radial structure. In the nodules vivianite is found only as patches on the external surface and in cavities. The degree of oxidation varies widely, which explains the various shades of colours seen. It is quite possible that this vivianite formed during two phases.

Key words — Vivianite, thin sections, Pleistocene, Germany.

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INTRODUCTION

References to authigenic mineral occurrences in Cainozoic clastic sediments of Hessen are numerous in the literature (see *e.g.* Streng, 1890; Dederscheck, 1973; Betz & Schöffmann, 1979). These minerals comprise mainly pyrite/marcasite (cubic/orthorhombic FeS_2, respectively), siderite (trigonal $FeCO_3$), gypsum (monoclinic $CaSO_4.2H_20$) and vivianite (monoclinic $Fe_3(PO_4)_2.8H_20$). Gypsum crystals from a nearby quarry at Zimmersrode have recently been described (Bongaerts & Rutten, 1990). Many of the quarries and pits in the area exposing these sediments are no longer accessible. During a visit (February 1989) to a few of the quarries still in operation, the author extensively sampled a surface area of *c* 10 x 10 m in a lignite quarry.

In previous papers (Streng, 1890; Diehl, 1930; Kirchheimer, 1934; Dederscheck, 1973; Boenigk *et al.*, 1977; Betz & Schöffmann, 1979) describing hydrated iron phosphates from the Horloff Graben, only vivianite has been recorded. A dozen of the nodules and aggregates collected by the author were chemically tested for the presence of Fe and (PO_4); the presence of both ions and of crystal water has been demonstrated for each of these samples. Li, Sr, Na, Ca and Mn could not be detected.

Definitive conclusions can only be drawn once additional chemical and structural data become available. A possible admixture of similar basic iron phosphates and trace elements could then be demonstrated as well. The combination of crystal habit, colour and physical properties strongly suggests that vivianite is involved, which is why the term vivianite has here been used for the entire range of weakly to strongly oxidised iron phosphate.

Vivianite occurs regularly as nodules and aggregates, and has been recorded by Tien (1974), Dobra & Ďuďa (1976), Vochten *et al.* (1979) and Riezebos & Rappol (1987). From the external surfaces of the specimens collected by the author it soon became clear that most of the vivianite seen was strongly oxidised. In order to study the internal structure of the nodules in particular a number of thin sections were made.

GEOGRAPHICAL AND STRATIGRAPHICAL SETTING

The lignite quarry from which the material was collected is located between Wölfersheim and Echzell, *c* 30 km northeast of Frankfurt am Main, and is exploited by the Preussen Elektricitäts AG com-

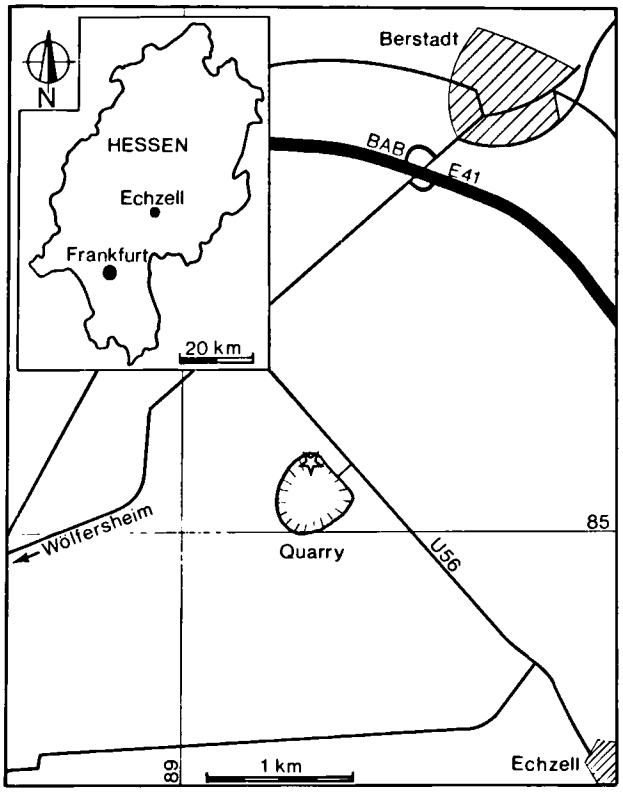

Fig. 1. Simplified map showing location of the lignite quarry from which the vivianite was collected [asterisk] (Gauss-Krüger co-ordinates).

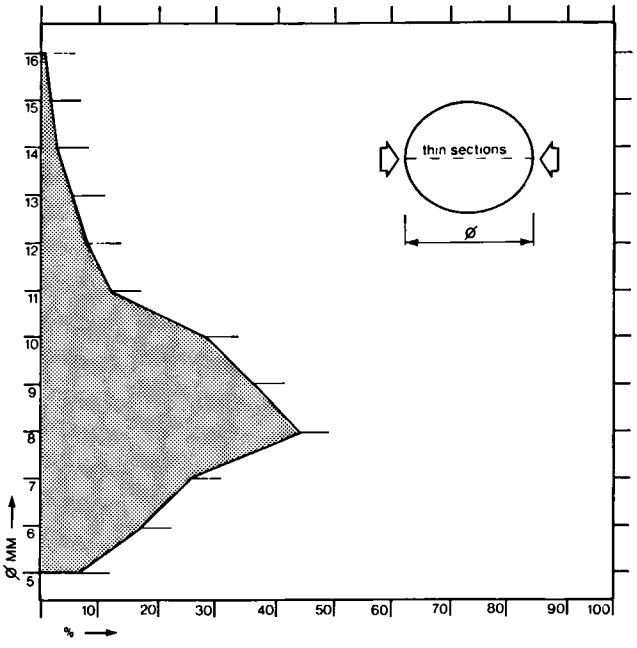

Fig. 2. Graphical representation of the largest diameters of 150 nodules and aggregates. A microscopic analysis for vivianite in the surrounding sediment turned out fruitless. The 5 mm limit therefore represents the smallest dimension.

pany. The area is situated in a structural low (the Horloff Graben), which is some 20 km long and a few hundred metres wide and which extends down to the basaltic basement rock. The quarry directly adjoins the U56 road (the so-called Römerstraße), and is referred to locally and in the literature as 'Grube Römerstraße'. The grid reference to the exact location where the material was collected is as follows: topographical map, sheet TK 25 Hungen, co-ordinates x = 85.500, y = 89.900 (Fig. 1). Here at 5 m below surface is found a sediment of brownish colour, which was described by Boenigk *et al.* (1977) as 'tonig-schluffige Hangendschichten (Vivianitschluff)' and which is most probably of Early Pleistocene (Waalian) age. At the base of this unit is the so-called 'Muddeton' (the last phase of a warmer period); it is overlain by sediments of the 'Elefanten-Lager' (Cromerian Complex).

Mineralogical characteristics

The vivianite collected is found mainly on the external surfaces of nodules and in cavities. Only a small quantity is in the form of crystal aggregates. The habit of the nodules as well as the aggregates is regularly spherical, and a flattening of two opposite sides occurs commonly. In Fig. 2 this dominant form is shown in the upper right-hand corner of the graph. The range of dimensions is also plotted, making use of a total of 150 samples. Spherulites which have coalesced to form larger clusters have not been included into this graph. These clusters reach a maximum length of 45 mm; only few specimens were found. The individual spherulites show on the splitting plane that the constituent crystals are arranged radially. In addition, vivianite has been identified at a short distance from the collection site on fragments of fossil lacustrine bivalves (? *Unio* sp.), as flat, radial aggregates.

As to the nodules and aggregates: their internal structure has been studied in a dozen thin sections (Pl. 1, author's collection). The samples have invariably been cut parallel to their largest diameter (Fig. 2). Subsequently, the thin sections have been mounted on a glass plate using a resin with a refractive index of n = 1.546, and automatically ground to a thickness of 10 µm.

Vivianite aggregates have rather rough surfaces. The individual crystals are grouped radially; they can easily be distinguished from one another by a difference in colour. The crystals extend along [001] and their size along [100] is 0.1 mm on average. Colour intensity is generally low. The crystals are distinctly pleochroic in tones of:

X dark green Y pale yellowish Z dark brown

In the outermost zone the crystals divide into smaller crystals. Amongst these is found a dark brown opaque clayey substance. Apart from this clayey substance there is no additional (detritic) material present in these crystal aggregates.

The nodules consist mainly of cemented quartz grains. The grains are not well rounded; edges and corners are still prominent and have apparently not been subject to (prolonged) fluvial transportation. Sorting is good, and mean grain size of quartz is *c* 0.10-0.15 mm. In each of the nodules studied limonite is the cement; it fills up pores amongst the grains and forms a brownish red coating on these. Particle size, composition and roundness of the matrix are identical to those of the nodules. A stereomicroscopic study of the matrix did not demonstrate the presence of siderite. In the quarry siderite is a prominent constituent of the sediments underlying the source rock of the samples described herein. It may therefore be concluded that the total of Fe on the sample location occurs as iron hydroxides (oxidation of siderite ?) and vivianite. The reader is referred to Postma (1981, 1982, 1983) for an exhaustive discussion of siderite genesis and oxidation processes. In the nearby quarry of Tagebau Wohnbach Fe_2O_3 makes up nearly 10% of the so-called 'Vivianitschluff' (Boenigk *et al.*, 1977).

In the nodules occur many cavities of irregular shape. In a number of nodules vivianite could not be identified, at least not in light microscopy. Vivianite occurring in the other nodules is in the form of crystals and fine-grained masses. The crystals are invariably grouped in bundles, growing from a central point and fanning out by forming subindividuals. Vivianite occurring in fine-grained masses is found on cavity walls in the nodules, but is also present in depressions on the external surface. Its authigenic nature thus appears to be confirmed, which is also evidenced by the external surface appearance of the nodules. There are no traces of abrasion and transportation may thus be ruled out.

Remarkable is the distinct difference in colour between both types of vivianite. The bundles of crystals show dark colours in thin section, ranging from cobalt blue to dark brown, and show an affinity with the aggregates. The fine-grained type of vivianite in the nodules is vivid light blue. Both types co-occur, and where they are in contact, the junction is well marked. During preparation of the thin sections vivianite did not occur in a reduced state, and the characteristic change of colour brought about by oxidation of Fe^{2+} in the crystal lattice was not observed.

It is quite possible that the genesis of both types was not simultaneous. The fine-grained type formed most probably during a later phase, which permits to distinguish two phases:

growth of aggregates, in radial groups and as bundles floating in the matrix

↓

growth of nodules (or parts of these), some enclosing already existing vivianite crystals

↓

crystallisation of vivianite in nodule cavities and external surfaces

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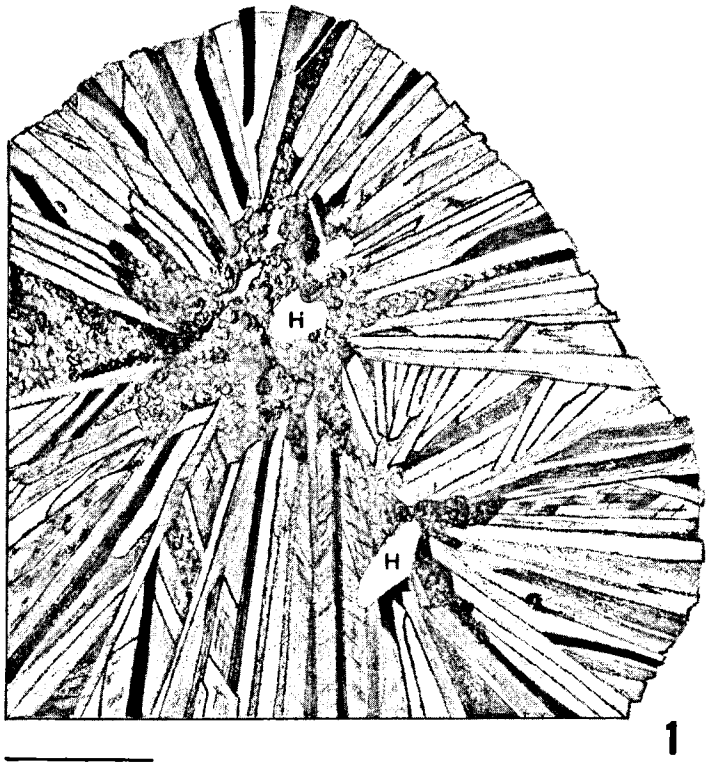
PLATE 1

Fig. 1. Thin section no. 3, H – cavities. Scale bar equals 2 mm.
Fig. 2. Thin section no. 5, V – vivianite, H – cavity, L – limonite, K – clayey substance. Scale bar equals 0.06 mm.
Fig. 3. Thin section no. 10, V – vivianite, S – indurated quartz grains. Scale bar equals 2 mm.
Fig. 4. Thin section no. 2, V – vivianite, H – cavities, K – clayey substance, S – cemented quartz grains. Scale bar equals 2 mm.

PLATE 1



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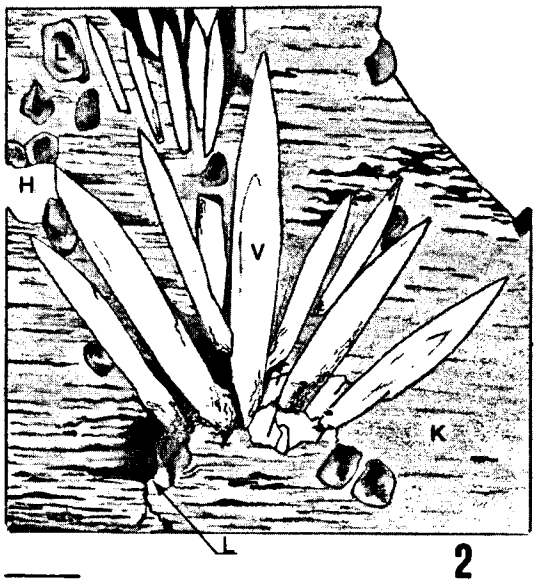

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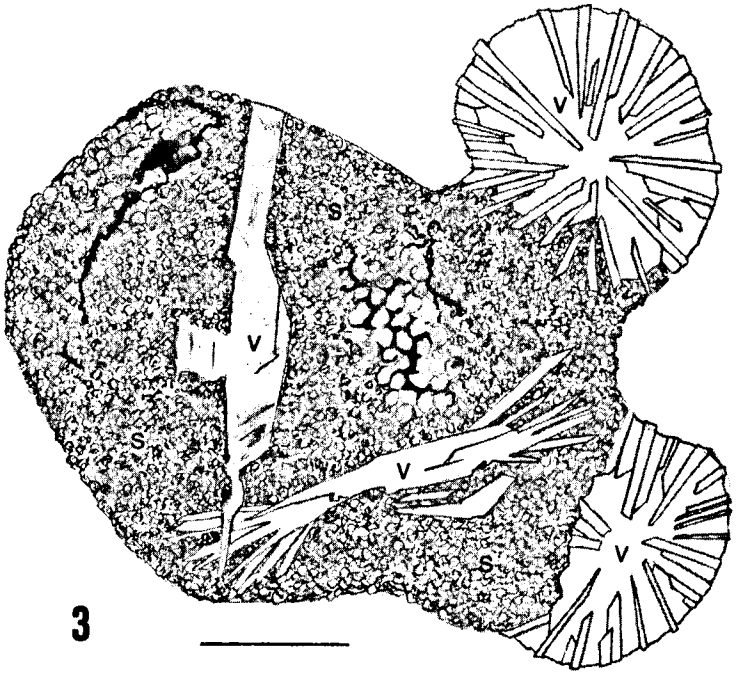

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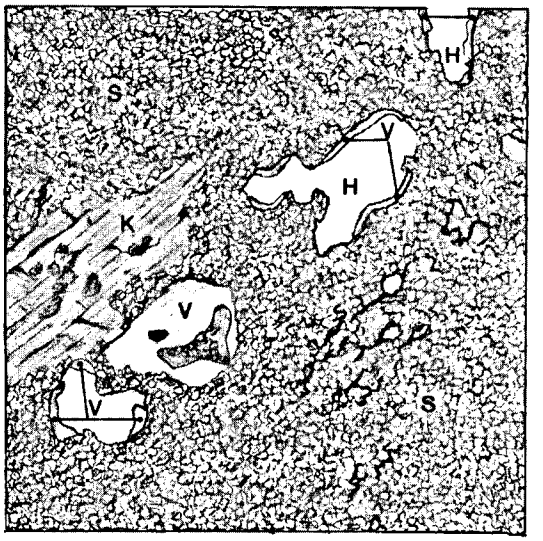

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