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A SIDERITE-VIVIANITE OCCURRENCE FROM LATE PLEISTOCENE DEPOSITS NEAR WESSEM, PROVINCE OF LIMBURG (THE NETHERLANDS)

by

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An occurrence of siderite and vivianite is reported from a quartzite rock found in fluviatile Pleistocene deposits exploited by dredging near Wessem, province of Limburg, The Netherlands. The find recorded here consists of siderite, vivianite, quartz (including intensely corroded crystals) and chlorite; their morphological characteristics are described. As far as can be ascertained, the vivianite crystals are the first to be reported from central Limburg. Earlier records of this mineral from the area (especially from Pleistocene strata in the Central Graben) are invariably related to Pleistocene mammalian remains. The authigenic origin of the vivianite crystals is evidenced.

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Contents —

SAMENVATTING

Een voorkomen van sideriet-vivianiet in laat-pleistocene afzettingen bij Wessem, provincie Limburg (Nederland).

In dit artikel wordt een voorkomen van sideriet en vivianiet gemeld, aangetroffen in een kwartsiet afkomstig uit fluviatiele Pleistocene afzettingen. Deze afzettingen worden ontgonnen en verwerkt

door Holland Split Wessem B.V., nabij Wessem, provincie Limburg. Gezien het feit dat deze afzettingen onder water worden ontgonnen door opzuiging is de exacte geografische en stratigrafische herkomst van de vondst onbekend.

De hier besproken vondst bestaat uit sideriet, vivianiet, kwarts (waaronder intensief gecorrodeerde kristallen) en chloriet; de morfologische eigenschappen worden beschreven. Voor zover kon worden vastgesteld zijn de hier beschreven vivianietkristallen de eerste die worden gemeld uit centraal Limburg. Vroegere vermeldingen van dit mineraal uit deze streek (speciaal uit Pleistocene afzettingen in de Centrale Slenk) zijn zonder uitzondering gerelateerd aan Pleistocene zoogdierresten. De authigene herkomst van de vivianietkristallen wordt aangetoond.

INTRODUCTION

In March 1984, Mr S.J. Kuypers, non-professional palaeontologist at Ittervoort (The Netherlands), came across a large rock of quartzite on a gravel dump near Wessem, province of Limburg (The Netherlands). On this erratic boulder, and as it turned out later, also inside it, numerous small crystals were found, amongst which those of vivianite are particularly noteworthy. When this find was reported to the author, the rock had unfortunately already been strongly fragmented by collectors. Several samples appeared to have found their way to private collections.

Subsequently, attempts were made to contact the collectors, who, in the course of this study, kindly provided the author with their material. After a preliminary note (Bongaerts, 1984), it now seems advisable to describe this interesting find in some detail. The minerals and their morphological characteristics have been analysed mainly through optical microscopy; in addition, some of the identifications have been carried out at the University of Amsterdam (Fysisch Geografisch en Bodemkundig Laboratorium).

GEOGRAPHIC AND GEOLOGIC SETTING

The rock under discussion was discovered on the storage site of the Holland Split Wessem B.V. company, where unprocessed as well as fractured gravels that are mainly used for foundations in road works, are dumped. The surroundings are locally known as 'Op het Hobus 1', while the exact location on the topographical map 1 : 25,000 of The Netherlands, sheet 58D Roermond, is at coordinates 190.170/352.930 (Fig. 1). The dredging works that are needed to obtain the gravels are, however, carried out in an area of approximately 15 kilometres around this location, so that the exact provenance of the rock cannot be determined. Consequently, the find cannot be assigned any stratigraphic age either: the location is situated on a rather isolated spot. The upper portion of the gravels occurring in the area is referred to the Kreftenheye Formation (fluviatile deposits, locally overlain by younger Pleistocene strata; Doppert *et al.*, 1975). These are surrounded by deposits of the Betuwe Formation (fluviatile strata; Doppert *et al.*, 1975). Chronostratigraphically, the base of the Kreftenheye Formation is roughly taken at the start of the Eemian (Zandstra, 1978), whereas the top is correlated with the transition Weichselian/Holocene. In a complete section, the Kreftenheye Formation is overlain by the Betuwe Formation. Both units were laid down by river systems (especially Rhine and Meuse), with the latter being responsible for the deposition of the larger part of the strata that were being exploited at the time of the discovery of the rock under discussion.

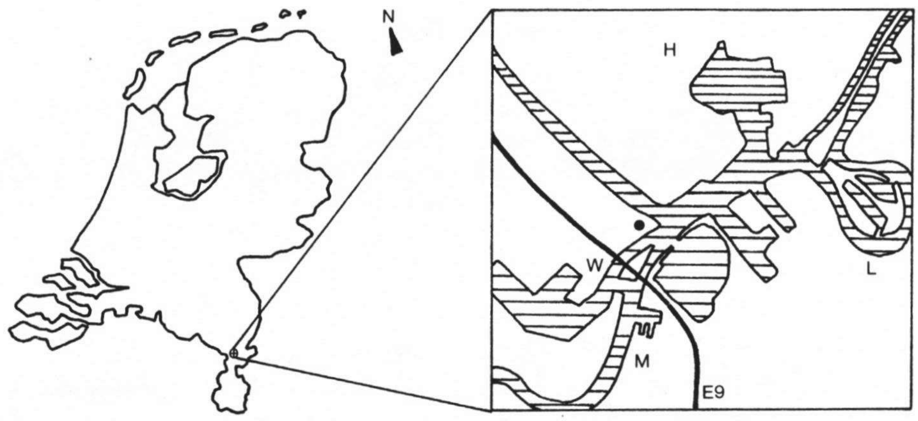

Fig. 1. Locality map showing the location of the storage site (dot) of the Holland Split Wessem B.V. H = Herten, L = Linne, M = Maasbracht, W = Wessem.

Lithologically, the association of large rock fragments comparable in size with the block discussed below unequivocally points to a Meuse assemblage as these comprise mainly quartz (in large quantities), siliceous silt, silicified limestones, Palaeozoic limestones and sandstones, and flint (especially the poorly rounded types).

MATERIAL

The material studied is kept in the following collections:

- J.L. Bongaerts, Posterholt. Registration nos 732-1 to 732-12, 1044, 1168.
- J. Kuypers, Ittervoort. Unregistered fragments.
- S.J. Kuypers, Ittervoort. Specimens marked Y by the author.
- R. van Neer, Sittard. Registration nos 812-821, 823 and some fragments marked A to X by the author.
- J. Parren, Ittervoort. A single fragment.
- W. Rutten, Posterholt. Registration nos 662-1 and 662-2.

MATRIX

Before describing the separate minerals, some data on the matrix are here given. It consists of a quartzite with numerous quartz veins, displaying a distinctly schistose structure in some of the samples examined. Unfortunately, the original size of the rock and the degree of abrasion cannot be determined with the fragments before me. Possibly it was a poorly rounded quartzite with an overall length of *c.* 600 mm. Grain size is approximately 75 µm. A clear film is seen on surfaces broken or split along the (pseudo-)stratification, possibly consisting of a mineral of the glimmer group (muscovite ?). Quartz and biotite are the main constituents (Figs 2a-d). Despite the fact that in some samples pyrite crystals have sporadically been observed, this greenish-grey quartzite does not show any characteristics that allow it to be classified as a pyrite quartzite, although pyrite content and distribution may vary considerably. This latter type of quartzite is commonly found in gravel deposits

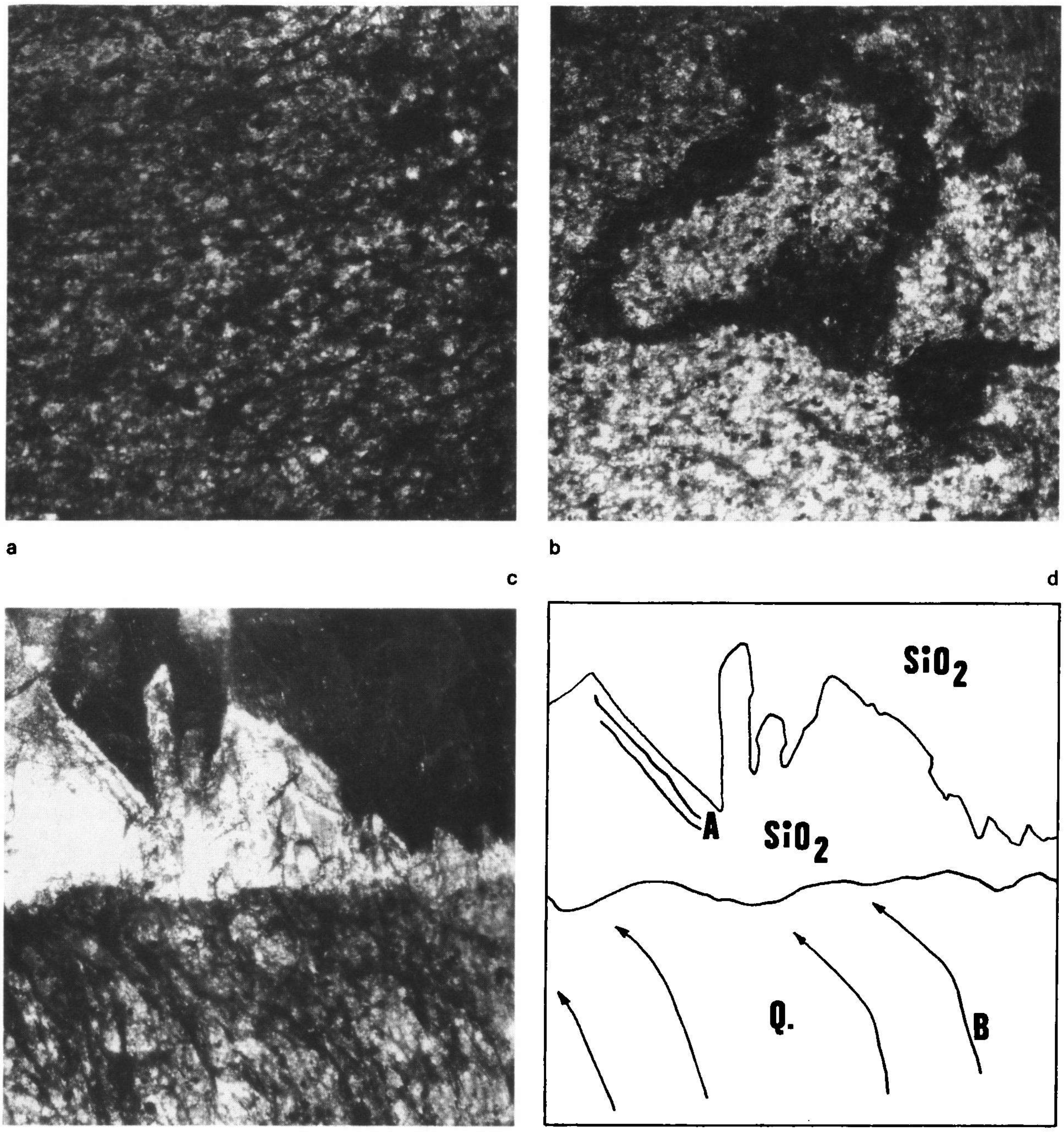

Fig. 2. Thin sections of the matrix, X-nic., lin. magnification × 10 (Bongaerts collection).
a. quartzitic structure; registration no 1171.
b. limonite stains; registration no 1169.
c-d. contact of quartz and matrix (Q), with some recognisable growth stages (A) and orientation of the quartzite (arrow, B); registration no 1168.

in the area, but is darker in colour and lacks a clearly schistose structure. Van Straaten (1946) described some types of quartzite from fluviatile strata in southern Limburg, thereby remarking that almost all phyllites from the Meuse sediments may be quartzitic, so that there can be no clear-cut distinction between these rock types.

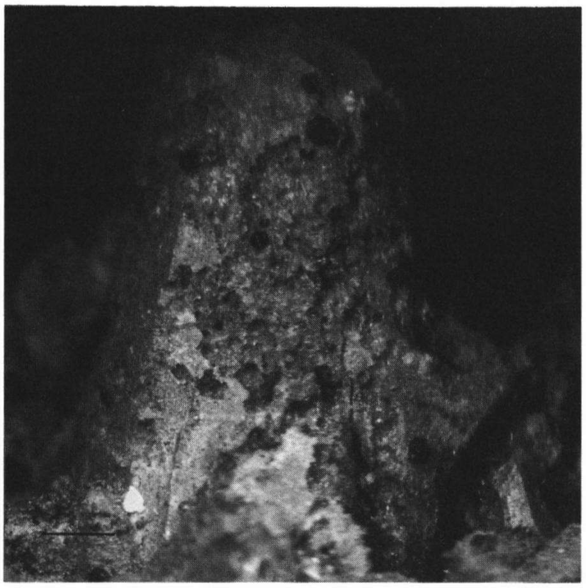

Fig. 3. Strongly corroded quartz crystal with some spherical siderite aggregates. Bar length is 1 mm. Specimen Y in coll. S.J. Kuypers.

DESCRIPTION OF THE MINERALS

Siderite, $Fe(CO_3)$ trig.

A common mineral in this rock has been analysed through X-ray diffraction and identified as siderite. On nearly every sample examined it is present. Parageneses of siderite and vivianite (see below) have often been recorded in the literature (see *e.g.* van Heuveln, 1956; Anthony, 1977; Postma, 1977). Their co-occurrence is undoubtedly due to identical physiochemical conditions that prevail during their genesis (Postma, 1982). The siderite consists of spherical aggregates with a mean diameter of 0.2-0.5 mm. The growth density varies considerably: several samples show extremely many siderite spheres, to such an extent that they are connected and form a crust in which the once separated aggregates can be vaguely discerned. The siderite is found attached directly to the matrix and occasionally on quartz crystals (Fig. 3). It is also found on some vivianite crystals and forms the basis for the growth of these as well.

When fresh, siderite is usually whitish-yellowish to yellowish-brown, but upon oxidation (Rösler, 1984) it turns dark brown to black, and it is this colour that is found in the present samples.

Quartz, SiO_2 trig.

Quartz is present in the form of a. infill of numerous veins in the matrix, and b. euhedric crystals in some samples.

a - The brecciated matrix which is mainly composed of quartz grains, is veined by transparent white quartz. The thickness of the veins varies considerably: from a few millimetres to *c.* 50 mm. Brownish-yellowish stains that are the result of limonite inclusion are common. These stains are not arranged

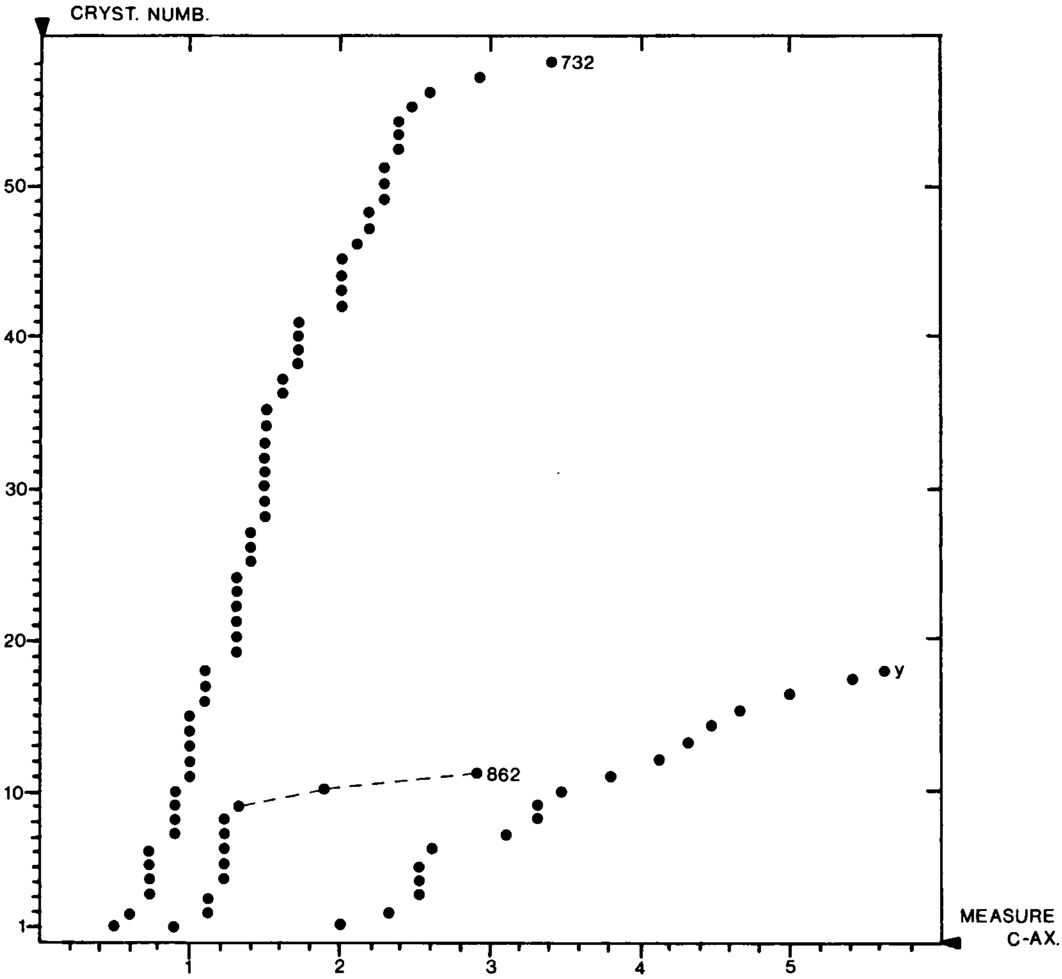

Fig. 4. Lengths parallel to the C-axis of vivianite crystals in sample 732 compared with those in sample 862 (both in Bongaerts collection). The lengths of the quartz crystals in sample Y (S.J. Kuypers coll.) are also indicated. All measurements in mm.

regularly, but form patches. A fibrous structure which is tectonically induced, is clearly seen in specimen 732-11 in the author's collection. Thin sections show this structure to be present also in the thinnest quartz veins. The angle between these fibres and the contact with the matrix is always 90°.

b - Euhedric quartz crystals are found in those places where there was enough room for the crystals to grow. This is clearly seen in specimen Y of the S.J. Kuypers collection, which is a quartz rock without matrix. On this quartz vein of *c.* 50 mm thickness, a crust of some millimetres thickness of chlorite scales can be noted. On these, crystals have formed which are concentrated in two spots. The opposite side of this quartz rock was part of the original outer side of the quartzite from which it was collected. This is readily apparent from the quartz crystals all sides of which are well rounded. These crystals are considerably larger than those found inside the boulder. Their length parallel to the C-axis is 25-30 mm; in Fig. 4 the lesser length of the crystals found inside the rock is shown. The quartz shows rather many fluid inclusions and air-filled fractures which cause an opaque whitish colour (Rösler, 1984).

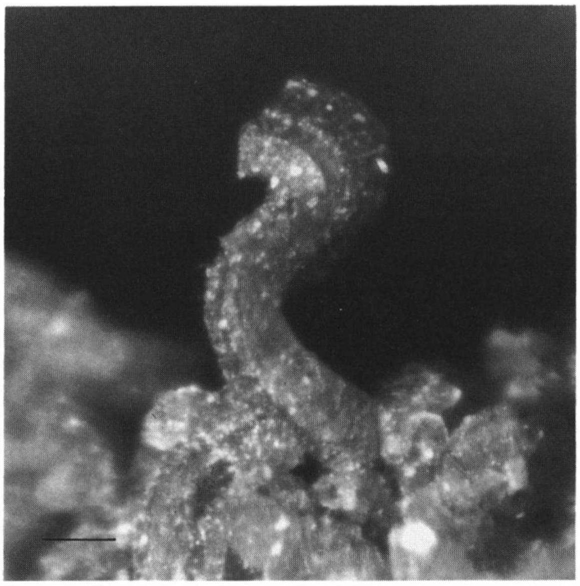

Fig. 5. Aggregate of chlorite. Bar length is 1 mm. Bongaerts collection no 816

The quartz base is invariably across $10\bar{1}0$; only a single crystal has grown in such a way that both $10\bar{1}1$ and $01\bar{1}1$ have developed on the +C and -C axes. Other faces are missing, while the morphology is simple, as is the case in most crystals of this type. Both rhomboeders $10\bar{1}1$ and $01\bar{1}1$ are identical; the increase in size of $10\bar{1}$ at the expense of $01\bar{1}1$ which is often found in quartz crystals, is missing here. Partly because of this, the prism $10\bar{1}0$ does not show the characteristic striation.

Most remarkably, many of the crystals found inside the boulder are strongly corroded. This corrosion reveals itself as dull surfaces and deep pits (Fig. 3), and is in some samples so intensive that the original shape of the crystals has been completely lost. Some of these U-shaped pits are filled with spherical siderite aggregates. This type of corrosion strongly resembles the one described by van der Waals (1967, tentative diagram of the forms of corrosion and growth, B: pitting hollow, holes and tooth-shaped protuberance). What caused this corrosion is not clear; normally, quartz is very resistant to this type of corrosion.

Chlorite, general chemical composition: $A_{5-6}Z_4O_{10}(OH)_8$, A = Al, Fe^{+2}, Fe^{+3}, Li, Mg, Mn^{+2}, Ni and Z = Al, B, Fe^{+2}, Si (Fleischer, 1988).

Another mineral, here tentatively identified as belonging to the chlorite group, is also present in large quantities in two samples: specimen 816 and the fragment marked Y. On the former, the chlorite has developed best. Because of its chemical and morphologic properties it may be compared favourably with chloritoid. Chlorite is a very common mineral in fluviatile deposits in southern Limburg, and the main constituent of chlorite phyllite (van Straaten, 1946).

The chlorite found here is green in colour and occurs on the quartzite as well as on the quartz crystals. Morphologically, it consists of small scales of irregular shape, arranged according to 001, with the number of scales, and therefore the length of the aggregates, varying considerably. All aggregates show a strong curvature (Fig. 5).

Vivianite, $Fe_3(PO_4)_2.8H_2O$ mon.

Without doubt, the most interesting mineral encountered is vivianite. Upon visual examination it soon became clear that vivianite was the most likely candidate, especially so as the other associated minerals pointed in that direction. The colour change so typical of vivianite (see *e.g.* Postma, 1982; Hearn *et al.*, 1983) has at least been noted once (van Neer, pers. comm.).

Morphologically and chemically similar minerals are the tricline phase of $Fe_3(PO_4)_2.8H_2O$ metavivianite (Ritz *et al.*, 1974) and the magnesium-analogue, baričite (Sturman & Mandarino, 1976). Seeing that the vivianite has developed as euhedric crystals, it can be excluded on morphological grounds that it represents metavivianite.

Some samples have been analysed through X-ray diffraction, and the results suggest that vivianite is indeed present, although the possibility that baričite is involved cannot be wholly dismissed (earthy vivianites can hardly be distinguished from baričite by means of XRD, Henderson *et al.*, 1984). However, the mineral association found in the boulder, suggests that it is indeed vivianite (P. A. Riezebosch, pers. comm.). The occurrence of vivianite is mainly confined to Quaternary, mostly Holocene, sediments (Riezebosch & Rappol, 1987), and is often related to organic matter (Rosenqvist, 1970). In The Netherlands is has commonly been reported as earthy grains and nodules (see *e.g.* van Bemmelen, 1895), but only rarely as crystals. An early report (van Calker, 1885) concerns vivianite crystals found on a molar of the elephant *Mammuthus (Mammuthus) primigenius* (Blumenbach, 1799). As far as I can ascertain, the Wessem find here described is the first record of crystals from central Limburg. When registering the large collections of Quaternary mammalian remains in the museum of the Heemkundevereniging Roerstreek at St. Odiliënberg, a mandibula fragment of *Bos taurus* Linné, 1758 was found to contain vivianite crystals (Bongaerts, 1988). Some data of this find are incorporated in Fig. 4.

The Wessem sample consists of crystals only; crusts and other superficial structures are absent. The crystals show a pleochroism which varies from deep blue to greenish blue. The length of the crystals parallel to the C-axis is fairly constant and varies between 1 and 2.5 mm; Fig. 4 shows the lengths of 58 crystals (specimens 732) measured, which are held to be representative of the dimensions of the crystals found on the other samples. The lengths of the A- ad B-axes are approximately 0.2-0.4 mm in all crystals. The crystal habitus is similar to the one described by Zwaan & Kortenbout van der Sluys (1971) for vivianite crystals from Haren. It has subsequently been pointed out that this Haren find might be a mixture of vivianite and metavivianite ('tricline phase', see Sameshima *et al.*, 1985).

In a few deformed crystals all faces across the C-axis and 010 are absent. The very good cleavage along 010 is clearly visible in many crystals. In addition to many free crystals numerous aggregates are present, the crystals of which radiate from a central point (Fig. 6); amorphous aggregates are also found (Fig. 7).

In some places, the matrix on which the vivianite is found is covered with a thin, yellowish-brown to reddish-brown crust; this is probably limonite. Occasionally vivianite is found directly attached to the quartzite or to the quartz. Most interesting is the fact that some crystals occur on the original outer side of the boulder. Seeing that the hardness of this mineral is very low (maximum 2), it seems more than likely that the vivianite has formed after definite sedimentation of the rock (Hearn *et al.*, 1983).

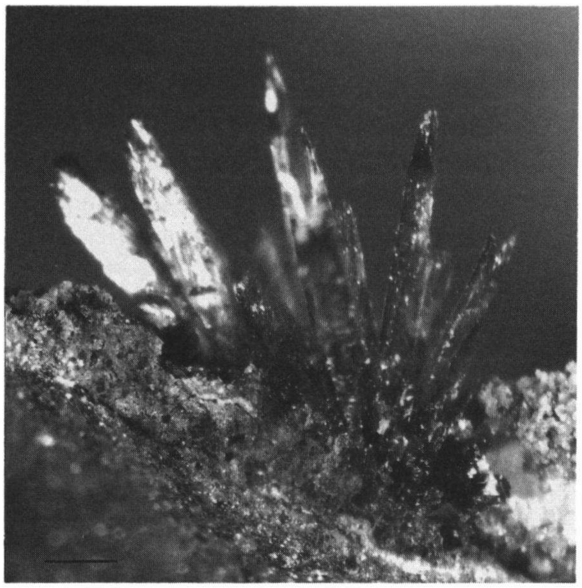

Fig. 6. Vivianite crystals. Bar length is 0.2 mm. Bongaerts collection no 820.

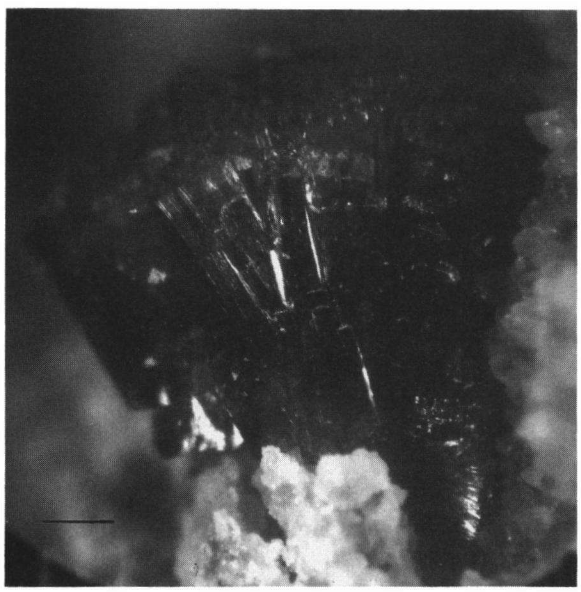

Fig. 7. Vivianite crystals. Bar length is 0.2 mm. Bongaerts collection no 818.

DISCUSSION

The find here described is especially interesting as it is a vivianite occurrence associated with the largest fraction of fluviatile deposits (Dücker, 1948; Clarke, 1950; Cailleux, 1954), in contrast to occurrences from central Limburg that are restricted to fossil or Holocene mammalian bones. In addition, the vivianite consists of euhedric crystals, which have so far not yet been reported from comparable sediments.

The authigenic origin of at least the vivianite is indicated by the presence of undamaged, unrounded crystals on the outer side of the rock. The quartz crystals here described probably originated at an early stage, possibly during the filling with SiO_2 of the cracks in the matrix. The occurrence of siderite on the corroded portions of the quartz crystals clearly points to a later genesis of this mineral. Inclusions of siderite in quartz have not been observed. The phase of the chemical corrosion can therefore be placed between the quartz and the siderite/vivianite geneses. The vivianite is evenly distributed over all samples studied, whereas the siderite is rare except for the above mentioned concentrations.

It seems desirable to register all available mammalian remains from central Limburg housed in private and museum collections in the near future. More than likely, the total known vivianite finds would increase considerably in this way, which is of course directly related to the fact that through extensive dredging works the thick sand and gravel beds have been exploited in this area over the years. Naturally, the most serious disadvantage of such finds is that data on their exact geographic and stratigraphic provenance can never be given.

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