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VIVIANITE ON WEICHSELIAN MAMMALIAN BONES FROM ORVELTE (DRENTHE, THE NETHERLANDS)

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In trenches dug for a gas main near Orvelte in the province of Drenthe (The Netherlands), an *in situ* occurrence of fossil mammalian bones was noted in the spring of 1991. In view of the importance of this find, it was soon decided to carry out a large-scale excavation at the site. The collected bones were covered in blue crusts, which at first sight were identified as vivianite, an assignment that was subsequently confirmed. This Fe-phosphate is a common mineral in the Drenthe peat districts. Since the geology of the site was studied in detail, and this vivianite occurrence included euhedric crystals, a description of this find seemed warranted. The results of mineralogical analyses are presented, and previous vivianite records from Drenthe are briefly discussed. The crystal morphology of the Orvelte vivianite is described, and data obtained through X-ray diffraction analysis, X-ray fluorescence spectroscopy and scanning electron microscopy are presented. X-ray diffraction analysis shows that in addition to the monoclinic phase an admixture of an oxidised phase characterises this vivianite record; this observation corresponds with previous records by various authors.

Key words — Vivianite, crystal morphology, X-ray diffraction, X-ray fluorescence spectroscopy, SEM, gyttja, Drenthe, The Netherlands.

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CONTENTS

INTRODUCTION

In May 1991, a number of fossil mammalian bones were encountered near Orvelte (municipality of Westerbork), in trenches for a gas main dug by order of the Gasunie. As soon as the contractor had contacted the archaeologist drs J. Molema on this discovery, a preliminary study confirmed that the bones were assignable to the woolly mammoth [*Mammuthus primigenius* (Blumenbach, 1799)]. In view of the number of skeletal remains and, especially, their *in situ* preservation, it was decided, upon deliberation with the Gasunie and the contractor, to carry out an excavation at the site. This excavation lasted nine days, and upon completion it was surmised that more remains could be present in the immediate vicinity of the site, but, for technical reasons, it proved impossible to extend the excavation area. Subsequent palaeontological studies revealed that the skeletal remains could be ascribed to three (possibly four) individuals of *M. primigenius* and a single individual of the woolly rhinoceros [*Coelodonta antiquitatis* (Blumenbach, 1799)].

The first bones to be discovered by personnel of the contractors were found after a larger pit had been dug at the site for passing the pipeline underneath the Oranje Kanaal (Fig. 1). The finders reported later that, immediately upon excavation, the bones showed a bluish hue, reminiscent of vivianite. This was later substantiated on specimens recovered during the excavation.

In The Netherlands, vivianite is a common mineral, which commonly occurs in earthy and oxidised form, as overgrowth on Holocene mammalian bones. On fossil skeletal remains of Pleistocene age it is less common. The euhedric habitus of this mineral is comparatively rare; the Orvelte vivianite in part comprises more or less transparent crystals.

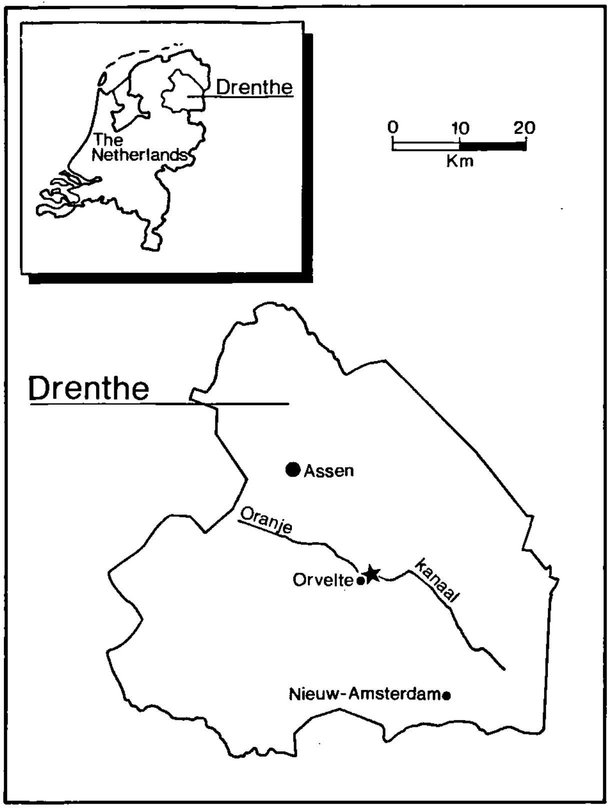

Fig. 1. Locality map showing location of the excavation pit (star).

In view of the importance of this *in situ* find of mammoth and woolly rhinoceros, from the beginning the excavation and subsequent analysis of data collected in the field, were carried out with great care. As a consequence, the geological conditions under which the vivianite formed are well understood. To correspond with this detailed picture it was decided to study this vivianite occurrence using various techniques.

In the present paper a brief discussion of vivianite systematics is presented and previous vivianite records from the province of Drenthe are listed. The Orvelte vivianite has been analysed using optical microscopy, focusing in particular on crystal morphology. Data on crystal structure have been obtained through X-ray diffraction analysis (XRD), X-ray fluorescence spectroscopy (XRF) and scanning electron microscopy (SEM).

VIVIANITE SYSTEMATICS AND PREVIOUS RECORDS FROM DRENTHE

Vivianite ($Fe_3(PO_4)_2.8H_2O$) is assigned to the phosphate group, which, on account of the common occurrence of isotypy and isomorphy (see *e.g.* Nriagu, 1984), is an extremely species-rich class. Phosphates are characterised by the free radical $P0_4$. In Strunz's (1978) classification, vivianite is included in the hydrate phosphates (group VII.C), vivianite series, monoclinic-prismatic.

With the exception of a few species, amongst which are members of the apatite series, phosphates are the product of exogenous, eroding processes. The mechanism behind vivianite genesis, and the Fe oxidation coupled with two sites is still the subject of studies. Zelibor *et al.* (1988) discussed the crystal growth of a synthetic equivalent in redox cells. Vivianite genesis under natural conditions has been described by Rosenqvist (1970), among others.

Essential for vivianite genesis is the supply of iron and phosphate as well as an anaerobic setting, which explains why vivianite occurs so commonly in the Drenthe peat district, and why it has repeatedly been referred to in the literature (Staring, 1833; van Bemmelen, 1895, 1900; Reinders, 1896; van Heuveln, 1956; Jong, 1978; Zuurdeeg, in litt., 1988). It usually occurs as crusts and impregnations. Van Calker (1885) recorded crystals from Nieuw-Amsterdam, found on a mammoth molar, reaching lengths of *c.* 5 mm, but he was unable to carry out goniometric measurements on account of striping and poor development of these crystals. In addition to crystals, also cryptocrystalline crusts of vivianite reportedly occurred on the same molar.

MINERALOGY OF THE ORVELTE VIVIANITE

The vivianite scraped off for further mineralogical analyses was found on a fragmentary tusk, and may be considered representative of the other vivianite occurrences at the same site. All bones recovered have been preserved under similar physical/chemical conditions in the sediment, which holds also true for the degree of recrystallisation of the bone and tooth material itself. The bones were all found in a gyttja deposit (Cappers *et al.*, 1993). Vivianite samples were taken a few weeks after their recovery.

The sample used in the laboratory analyses has been donated to the Drents Museum at Assen (registration number N 95/II-1), the other material is stored in the author's collection (nos 787, 789, 793, 797, 798, 808, 809 and 812-815).

During a preliminary study using optical microscopy, it became clear that the most of the vivianite occurred in crusts and impregnations of cavities in the bones. A smaller percentage consists of euhedric crystals. On the above-mentioned tusk fragments vivianite is found in large quantities (Pl. 1).

The Fe supply originates from the dissolution of ground water, which results in adsorption on the skeletal remains and in their matrix. High Fe concentrations are locally common,. especially along the Drenthe brooks, and it proved worthwhile to exploit it. Booij (1986) presented a historical overview of this iron exploitation, and of the process of Fe circulation within sediments/soils in Drenthe. In the immediate vicinity of the locality described here, a number of shallow boreholes have been sunk to explore soil structure. Sedimentary structures in the Pleistocene strata in the subsurface indicate a former brook valley.

The bone and tooth material on and in which vivianite occurs acted as supplier of P-ions. The substrate of the vivianite studied consists of mainly fossil dentine, the anorganic component of which is comparable to dahlite (= calcium hydroxylapatite ['impure hydroxyapatite' of Legeros & Legeros, 1984]). The extremely complex mineralogy and behaviour of fibres during recrystallisation processes is not discussed further here; the reader is referred to Posner *et al.* (1984) for a discussion.

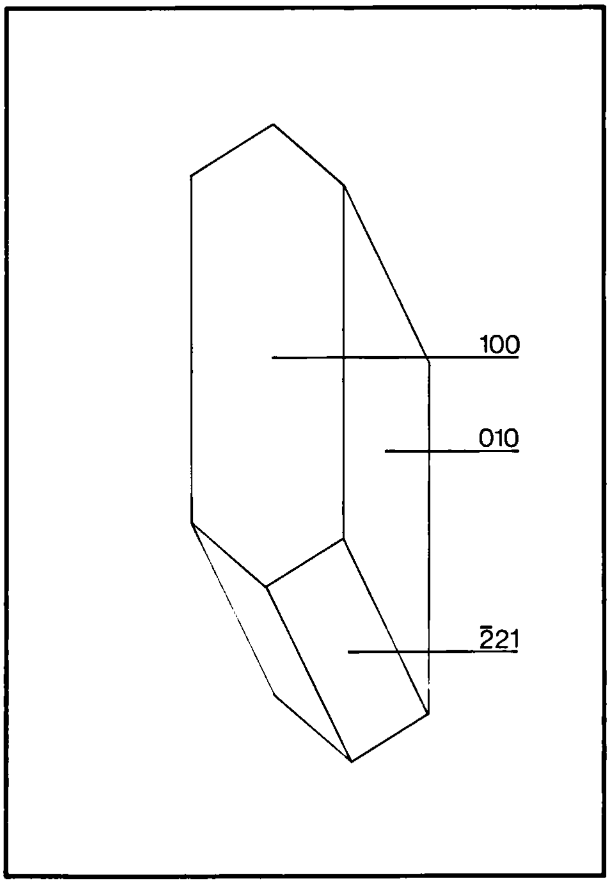

Fig. 2. Idealised crystal shape of part of the Orvelte vivianite.

The Orvelte vivianite consists mainly of crusts, and in thin sections it was seen that the larger part has a cryptocrystalline structure. The coalescence of closely spaced larger crystals has also resulted in crust formation. Occasionally the space in which the crust is found has not filled completely, so that crystal faces are visible (Pl. 1, Fig. 2). The orientation of these crystals differs considerably; attachment to the substrate varies between [100] and [010]. Partly because of this an uninterrupted growth to [001] was possible, and a few crystals are particularly acicular in this direction.

The crystals are delimited by the pinacoids {100}, {010} and the prism {$\bar{2}$21} (Fig. 2), and their shape is therefore simple. The most dominant face in all crystals is {010}, which is also the largest face, occasionally causing flattening of the crystals. This face is often slightly convex.

The tendency of vivianite crystals to coalesce to radially arranged aggregates is also present in the Orvelte occurrence, but well-developed spherical aggregates are not found. The colour of the crystals varies from light green to dark blue, the former being transparent. According to people present during the excavation, the vivianite was blue on removal of the sediment cover. The colour change from white to blue which has often been noted for vivianite was not observed.

In thin sections, cryptocrystalline crusts often are of a cobalt blue colour, which accounts for a decreased transparency. Pleochroism is obvious: X = blue, Y = pale yellowish, Z = bluish green.

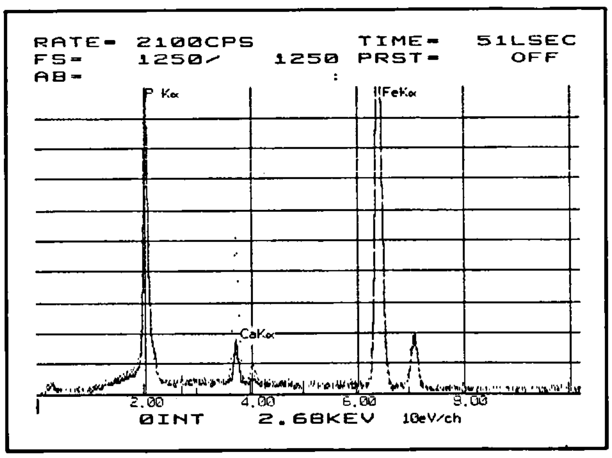

Fig. 3. XRF spectrum of the Orvelte vivianite.

In the transparent crystals inclusions of irregularly shaped pieces of tooth are seen. The source of the Ca detected in the XRF spectrum (Fig. 3) can be related to this fossil dentine which is evenly distributed in the vivianite.

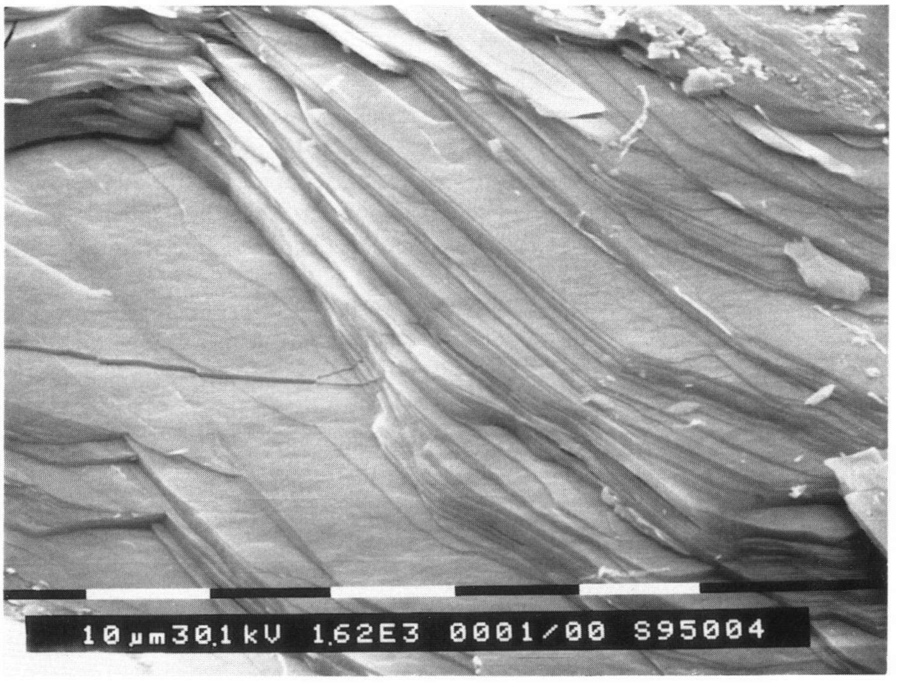

Fig. 4. SEM photomicrograph of Orvelte vivianite, perpendicular to 010 (scale bar equals 10 µm).

X-ray diffraction analysis — Table 1 shows the results of an XRD analysis of the Orvelte vivianite, carried out using a Philips PW 1410, CuKα radiation (25 kV, 40 mA).

Under a microscope a sample as pure as possible was removed of well-crystallised vivianite with a compact structure (Fig. 4). The colour of this sample, which often provides a first indication of the degree of oxidation, is clear blue. From the XRD results it appears that the pattern of reflections does not correspond entirely with ASTM data (American Society for Testing and Materials), chart 30-0662, for vivianite.

A few distinct reflections occur which do not fit the pattern for vivianite. Some of these correspond to, following studies by Sameshima *et al.* (1985) among others, the triclinic metavivianite phase. The comparatively weak 8.7 reflection was demonstrated by Ritz *et al.* (1974) on their metavivianite occurrence from the Big Chief Pegmatite of South Dakota. The largest peak in the diffractogram of the Orvelte vivianite is at 7.05, and is clearly not a reflection which is characteristic of vivianite. Vochten *et al.*'s (1979) vivianite/metavivianite from Retie and Vorst (province of Antwerp, Belgium) shows a reflection at 7.01, which led the authors to conclude that that would indicate the presence of an oxidation product of vivianite. The admixture with a different phase in the Orvelte vivianite may also be assumed on account of the presence of a 3.65 reflection. The vivianite described by Zwaan & Kortenbout van der Sluys (1971) from Haren (province of Noord-Brabant, The Netherlands), and that recorded by Riezebos & Rappol (1987) from Borne (province of Overijssel, The Netherlands) also show such a reflection (3.64). The latter authors did not rule out that their occurrence could represent vivianite/metavivianite. In a detailed study, Sameshima *et al.* (1985) discussed and compared XRD patterns of various vivianites and vivianite/metavivianite admixtures, and referred to results of previous studies. They (p. 82, table 1) assumed the vivianite described by Zwaan & Kortenbout van der Sluys (1971) to represent a vivianite/metavivianite admixture.

CONCLUSIONS

The Orvelte vivianite comprises earthy aggregates as well as well-developed crystals on fossil mammalian bones and tooth material. In view of the palaeontological interest of the recovered remains a detailed study was conducted into the stratigraphy and absolute age of the bones and matrix. The results of C-14 dating of the bone suggest an absolute age of 46.800 +1.500/-1.250 BP and of the gyttja matrix of 44.200 +3.500/-2.400 BP, thus determining a Weichselian age for this deposit.

Vivianite Orvelte		Vivianite ASTM 30-0662	
dÅ	I/I	dÅ	I/I
8.70	11		
8.00	13	7.93	13
7.05	100		
6.80	87	6.73	100
4.90	22	4.90	12
4.50	9	4.55	5
4.32	4	4.34	2
4.09	12	4.08	12
3.80	4	3.84	7
3.65	4		
3.20	10	3.21	16
2.97	17	2.96	8
2.52	10	2.53	8
2.31	10	2.32	7
2.19	10	2.19	5
2.07	14	2.07	4
2.01	4	2.01	2
1.78	10	1.78	3
1.67	10		

Table 1. XRD data for the Orvelte vivianite in comparison with ASTM chart 30-0662. Laboratory conditions are referred to in the text.

Although the ratio Fe^{2+}/Fe^{3+} has not been determined, it may be concluded from the diffractogram that the vivianite consisted partially of an oxidised phase, a few reflections of which closely correspond to those already noted in metavivianite. Sameshima *et al.* (1985) remarked that, in addition to the monoclinic pattern, many "coarsely crystalline 'vivianite'" showed a number of metavivianite reflections. Riezebos & Rappol's (1987) study shows that conventional XRD techniques are not sufficient to obtain a detailed picture of the presence of monoclinic and related phases. The diffractogram does not reveal any carbonate-hydroxy/fluorapatite peaks.

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PLATE 1

Vivianite from Orvelte (municipality of Westerbork, province of Drenthe, The Netherlands):

Fig. 1. Transparant prismatic crystals; Bongaerts Collection, no. 813 (scale bar equals 1 mm).

Fig. 2. Crystal aggregate; Bongaerts Collection, no. 787 (scale bar equals 5 mm).

Fig. 3. Transparant crystals on dentine, also schematically shown in line drawing; Bongaerts Collection, no. 815. Abbreviations: D - dentine, V - vivianite (scale bar equals 1 mm).

Fig. 4. Crystals, perpendicular on 100; Bongaerts Collection, no. 793 (scale bar equals 1 mm).

PLATE 1

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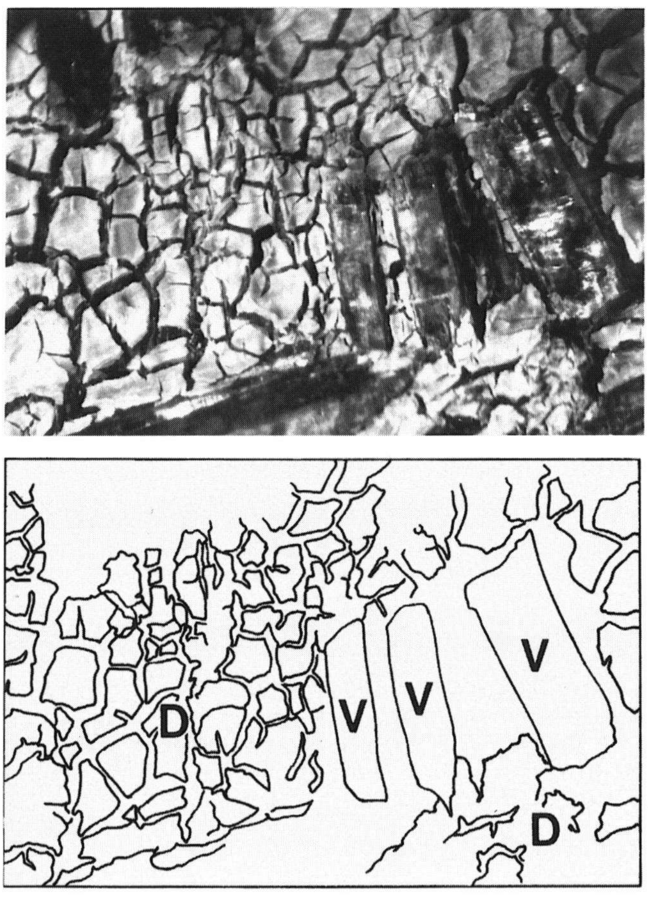

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