Vivianite crystals from Haren, Noord Brabant Province, The Netherlands

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Zwaan, P. C. and G. Kortenbout van der Sluys: Vivianite crystals from Haren, Noord Brabant Province, The Netherlands. – Scripta Geol., 6: 1-7, 6 figs., Leiden, December 1971.

Vivianite crystals, occurring in Holocene fossil bones from *Bos taurus* L., dated at 600 to 300 years B.C., are described. It is the second find of such crystals in The Netherlands which can be observed with the naked eye. One new form $\{\bar{1} 0 1\}$ has been detected. Physical and optical properties are given as well as X-ray powder diffraction data.

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Acknowledgements

The authors are much indebted to Mr. G. J. Verwers of the 'Instituut voor Prehistorie' of Leiden University for presenting the bones and for information on their mode of occurrence. They also acknowledge assistance given by Dr. P. Hartman and Mr. R. O. Felius of the 'Geologisch en Mineralogisch Instituut' of Leiden University, the first for critical reading of the crystallographic part of this article and the second for the goniometer measurements.

Introduction

The occurrence of vivianite in The Netherlands was first mentioned by Van Bemmelen (1896, 1897). He described the mineral as a powdery bluish substance associated with iron carbonate from a moor in Drenthe Province. No physical properties were given, nor crystallographic data. The author added a chemical analysis of impure material.

In another paper (1900) Van Bemmelen described vivianite occurring in peat deposits at Ederveen, Drenthe Province, mentioning crystal aggregates with a blue lustre and small cavities filled with crystals showing a metallic lustre. According to Van Bemmelen these crystals originated from ferro carbonate or iron oxide through interaction with phosphates, the latter being mainly derived from animal remains. In this paper, too, no particular physical or optical data were given.

Subsequently the mineral has been recorded from numerous localities all over the country. It occurs in fossil bones as well as sediments bearing such fossils. A remarkable fact is that these deposits invariably are of a Holocene age, in agreement with Rosenqvist's observations (1970) in Southern Norway. In all these cases vivianite occurred as a powdery bluish material and no crystals could ever be seen with the naked eye.

The material described below consists of numerous distinct elongated prismatic crystals, up to 6 millimeters long and half a millimeter thick, which occur on the inner side of Holocene hollow bones of *Bos taurus* L., probably the remains of a single individual (see figs. 1 and 2).



Fig. 1. Femur of Bos Taurus L. with vivianite crystals



Fig. 2. Mandibula of Bos Taurus L. with vivianite crystals

Occurrence, stratigraphy and age

The bones with vivianite were brought to light by an archaeological excavation carried out by the 'Rijksdienst voor Oudheidkundig Bodemonderzoek' (State Service for Archaeological Investigation in The Netherlands), to the South of the village of Haren – municipality of Megen, Haren and Macharen, Noord Brabant Province – in the Netherlands. The work was directed by Mr. G. J. Verwers, who kindly presented the vivianite-bearing fossils to the 'Rijksmuseum van Geologie en Mineralogie'. They are registered under number RGM 162681. The bones, a mandibula and a femur, belong to domestic cattle (*Bos taurus* L.).

The bones were found in a layer of waste derived from a human settlement and washed down a slope. The waste deposit is situated about 5 feet (1.50 meters) below the present surface. It consists of stringers of fine sand and clay. The waste deposit is overlain by a layer rich in phosphorus and iron and this in turn by a heavy clay and finally, alternating sands and clays. On archaeological grounds the waste deposit is dated at 600 to 300 years B.C. (personal communication by Mr. G. J. Verwers).

Crystallography

A morphological study of a number of the crystals has been carried out by Mr. R. O. Felius, using a two-circle goniometer to measure the forms. It was observed that the majority of the crystals have a columnar habit parallel to [001]. The identified forms of these crystals are:

a	100	v	221
b	010		101
m	110		



The (110) faces appeared to be more developed than the (010) faces, while the latter are larger than the (100) faces. Fig. 3 represents the habit of these crystals.

A minority of the crystals have a platy habit, as they are flattened parallel to $\{010\}$. The identified forms of them are:

a	010	v	221
b	100	r	$\overline{1}11$
m	110	w	201

Fig. 4 represents the appearance of these crystals.

From the data obtained it follows that one new form is present: $\{101\}$.

As mentioned above the crystals occur on the inner side of the hollow bones and form clusters as can be seen in figs. 5 and 6.

Physical and optical properties

The crystals are very dark greenish blue, their lustre is vitreous. Very often distinct cleavage planes parallel to $\{010\}$ can be seen. The specific gravity of some crystal clusters was measured using a hydrostatic balance and both ethylene dibromide and distilled water. One cluster, weighing 74.5 milligrams, has a density of 2.623 (measured in water). Another one, weighing 141.2 milligrams, gave a result of 2.615 (in ethylene dibromide). Both figures seem to be low for vivianite, but each cluster was rising slowly in a heavy liquid – bromoform diluted with toluol –



Fig. 5. A cluster of vivianite crystals $(2 \times)$



Fig. 6. Part of a cluster of vivianite crystals (20×)

in which a small piece of pure quartz just sunk, which means that in any case the vivianite densities are lower than 2.65. The porosity of the clusters, moreover, may have a bearing upon the low values obtained.

The refractive indices were measured by the immersion method. The fresh powder has a white colour but it changes rapidly to blue. The measured values are:

$\mathbf{N}_{\mathbf{z}}$	=	1.631	\pm	0.003
N_y	=	1.603	\pm	0.003
N_{x}	=	1.580	\pm	0.003

In a section perpendicular to one of the optical axes it was seen that +2V is very large, that is almost 90°.

Pleochroism is very strong:

- X = deep blue
- Y = almost colourless
- Z = pale brownish

As to the dispersion it was seen that r < v.

A comparison of these data with those given by Winchell (1959) and Palache, et al. (1951) indicates that the vivianite discussed above has no anomalous properties.

X-ray powder diffraction data

Two powder photographs (Nrs. mm 883 and mm 1683) were made of the vivianite, using Fe-radiation and a camera with a diameter of 114.6 millimeters. They show a pattern in which the three strongest lines are 6.79, 2.97 and 2.71. These patterns appear to be characteristic for vivianite when compared with ASTM-card 3-0070 and data given by De Assunção & Garrido (1953).

In the following table the d-values of all reflections observed are given.

(in Å)	Intensity (estimated)	d (in Å)	Intensity (estimated)
.68	4	2.01	1/2
.99	4	1.964	1/2
.79	10	1.920	2
.91	5	1.892	1
.52	2	1.816	1/2
.33	1/2	1.778	1/2
.08	1	1.736	1/2
.84	4	1.670	3
.64	1/2	1.580	1
.34	1	1.553	1
.20	4	1.520	1/2
.07	3	1.488	1
.97	7	1.468	1/2
.71	6	1.243	1
.64	1/2	1.224	1/2
.52	4	1.173	1
.42	4	1.126	1
.31	2	1.114	1
.23	2	1.035	1/2
.19	1	1.027	1/2
.07	1	0.9970	1/2

X-ray powder diffraction data for vivianite from Haren

References

- Assunção, C. T. de, & J. Garrido, 1953. Tables pour la détermination des minéraux au moyen des rayons X Bull. Mus. Lab. Miner. Géol. Fac. Sci. Lisbonne, 20-21.
- Bemmelen, J. M. van, 1896. Over de samenstelling, het voorkomen en de vorming van Sideroze (witte klien) en van Vivianiet in de onderste darglaag der Hoogveenen van Zuidoost Drenthe – Verh. Kon. Akad. Wetensch., 1, 3: 3-16.
- —, 1897. Sur la composition, les gisements et l'origine de la sidérose et de la vivianite, dans le derri inférieur des hautes tourbières du sud-est de la province de Drenthe – Arch. Néerlandaises Sci. Exactes Nat., Soc. Hollandaise Sci. Harlem, 30: 25-43.
- ----, 1900. Über das Vorkommen, die Zusammensetzung und die Bildung von Eisenanhäufungen in und unter Mooren – Zeitschr. Anorg. Chemie, 22: 313-379.
- Palache, Ch., H. Berman & C. Frondel, 1951. Dana's System of Mineralogy, 2. John Wiley and Sons, Inc., New York.
- Rosenqvist, I. Th., 1970. Formation of vivianite in Holocene clay sediments Lithos, 3: 327-334.
- Winchell, A. N., 1959. Elements of Optical Mineralogy, 2, Descriptions of Minerals John Wiley and Sons, Inc., New York.

Manuscript received 16 July 1971.