

Vochtenite, (Fe²⁺,Mg)Fe³⁺[UO₂/PO₄]₄(OH) · 12–13 H₂O, a new uranyl phosphate mineral from Wheal Basset, Redruth, Cornwall, England

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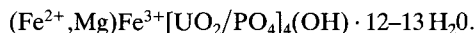
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Abstract

Vochtenite, a new mineral from the Basset Mine, southeast of Camborne in Cornwall, England, is a ferrous–ferric magnesium-bearing hydroxy uranyl phosphate mineral. It is monoclinic with $a = 12.606$, $b = 19.990$, $c = 9.990$ Å, $\beta = 102.31^\circ$, $Z = 3$; the ideal formula is:



The strongest lines in the X-ray powder diffraction pattern are: 9.998(100)(020), 4.999(30)(040), 4.892(45)(002), 3.475(70)(311), 3.333(50)(060), 3.087(40)(232), 2.205(40)(244) and 2.111(45)(344, 471). Vochtenite is brown in colour with a bronzy lustre and is non-fluorescent. Mohs hardness is 2.5 and the density (calc.) = 3.663 g/cm³. There is a prominent (010) cleavage. Vochtenite is optical biaxial negative, $2V$ (calc.) = 89(3)°; its dispersion is indiscernible. Refractive indices are $\alpha = 1.575(2)$, $\beta = 1.589(2)$, $\gamma = 1.603(2)$, and the pleochroism is very weak. Orientation $X(\alpha) \parallel b$ is perpendicular to (010) and $Z(\gamma) \wedge c$ is small. The mineral occurs as subparallel (0.5–1.0 mm) crystal aggregates with a pseudo-quadratic outline. The mineral is named vochtenite after Prof. Dr. Ing. R. F. C. Vochten of the State University of Antwerpen, Belgium.

KEYWORDS: vochtenite, new mineral, uranyl phosphate group, Wheal Basset, Cornwall, England.

Introduction

THE Basset Mine is located between Carn Brea and Carnmenellis near Carnkie, southeast of Camborne, and southwest of Redruth in Cornwall. The mineralization occurs at the contact of the post-Carboniferous Carnmenellis granite intrusion and the Devonian sandstones and consists mainly of the copper and tin minerals, chalcopyrite CuFeS₂, chalcocite Cu₂S, cassiterite SnO₂, with the accessory minerals arsenopyrite FeAs pyrite FeS₂, wolframite (Fe,Mn)WO₄, and minor quantities of bassetite Fe(UO₂/PO₄) · 8H₂O (Palmer and Neaverson, 1987).

An olive-green and transparent mineral identified as bassetite, and having a density of 3.40 g/

cm³, is the only primary uranyl phosphate mineral from this locality. In addition, an accessory brown-yellow mineral occurs, with a significantly lower density of 3.08 g/cm³, that has been identified as oxidized bassetite (George, 1949). It was shown by Vochten *et al.* (1984) that the density of synthetic bassetite diminishes gradually from 3.68 to 3.06 g/cm³ for fully oxidized bassetite.

Another accessory and characteristic mineral, opaque in thick crystal fragments with a typical bronzy lustre, is the new mineral from this locality described in this paper.

The new mineral, belonging to the group of uranyl phosphates, is a ferrous–ferric magnesia-bearing hydroxy-uranyl phosphate, for which the

physical and crystallographic properties are significantly different from bassetite or oxidized bassetite. The new mineral is named vochtenite in honour to Prof. Dr. Ing. R. F. C. Vochten of the State University at Antwerpen, Belgium, who discovered the mineral and published numerous papers on the field of uranium mineralogy.

The mineral and its name have been approved by the Commission on New Minerals and Mineral Names, IMA, in April 1988. Type-material is deposited in the mineral collection of the Smithsonian Institution (National Museum of Natural History) at Washington DC (Reg. file No. 362974).

Physical and optical properties

Vochtenite occurs as crystal aggregates with a pseudo-quadratic outline, consisting of relatively small subparallel crystals (0.5–1.0 mm) and displaying irregular fractures. The mineral is brown in colour, opaque in thick crystal fragments, and shows a typical bronzy lustre. The streak is pale brown, the hardness is about 2.5 on Moh's scale, and the tenacity is not strong. A prominent {010} cleavage is visible. The mineral is soluble in 1:1 HCl at room temperature. Vochtenite is biaxial negative, with $\alpha = 1.575(2)$, $\beta = 1.589(2)$, $\gamma = 1.603(2)$ determined at 589 nm and $2V$ is calculated as $89(3)^\circ$. Pleochroism is very weak and difficult to determine. The mineral is non fluorescent.

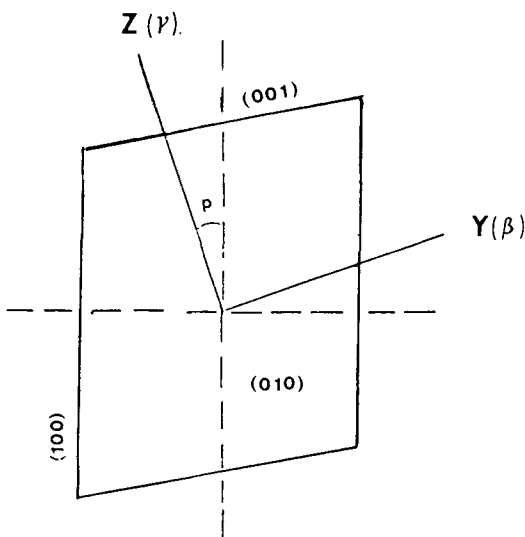


Fig. 1. Optical orientation of vochtenite.

The optical orientation is $Y(\beta)$ and $Z(\gamma)$ in the plane (010) and $X(\alpha) \parallel b$ is perpendicular to (010), which is also the plane of cleavage; $Z(\gamma) \wedge c$ is very small (Fig. 1). Owing to the diffuse isogyres we could not determine the dispersion unambiguously.

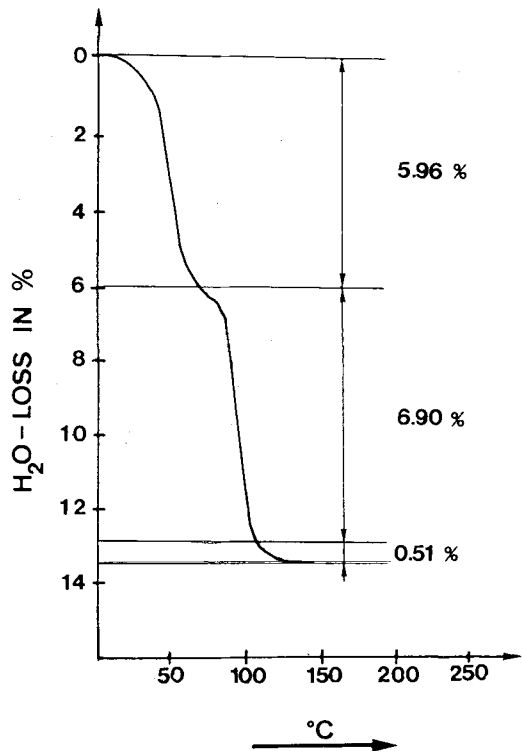


Fig. 2. Thermogravimetric analysis of vochtenite recorded with a DuPont TGA-951 apparatus with a heating rate of $2^\circ\text{C}/\text{min}$.

Chemical composition

Chemical analyses were carried out with a Cameca electron microprobe type Camebax using the following standards: meta-torbernite(U), apatite(P), magnesia-oxide(Mg), and metallic iron(Fe); H_2O was determined by thermo-gravimetric analysis (TGA) using a DuPont TGA-951 apparatus. The microprobe analysis was carried out on three different crystals with 10 data points on each crystal.

The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio was derived from Mössbauer spectrographic data. The analytical results are, Fe_2O_3 4.04 (± 0.10), FeO 3.30 (± 0.15), MgO

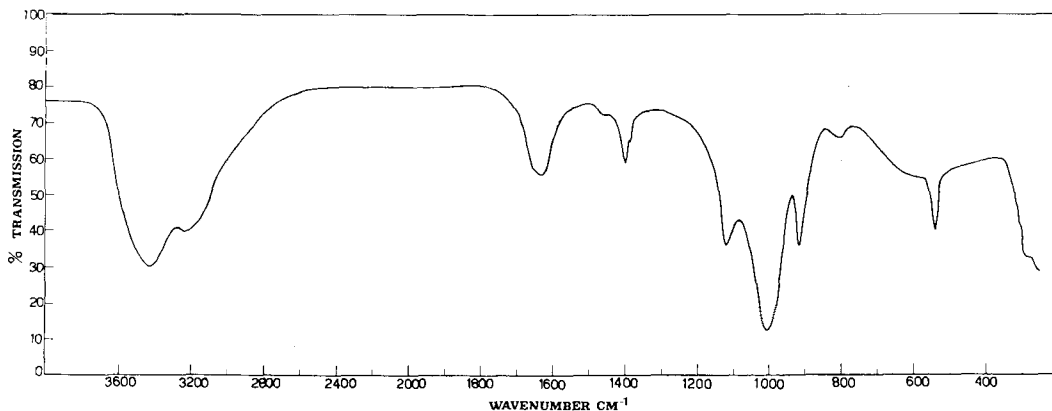
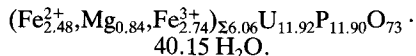


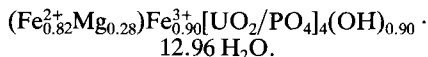
FIG. 3. Infrared spectrum in KBr of vochtenite.

0.63 (± 0.02), UO_3 63.07 (± 0.90), P_2O_5 15.65 (± 0.22), H_2O 13.37 (± 1.0), a total weight percent of 100.96.

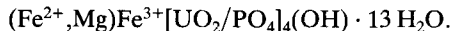
The empirical formula calculated from the analysis is



Taking into account the structural group $[\text{UO}_2/\text{PO}_4]^-$ and the fact that the formation of an Fe^{3+} ion implies a charge compensation with an OH^- ion the formula with $Z = 3$ is to be written as

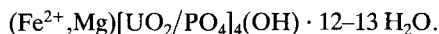


The ideal formula is considered to be



If only 12 molecules of water are bound structurally, this will correspond with 12.55% H_2O . The difference of 0.82% H_2O with respect to the TGA analysis is within the tolerance of 1%. The

difference can be explained by assuming that zeolitic water is present between the structural layers of the mineral. As a consequence it is more desirable to represent the formula as



Taking into account $Z = 3$, the cell volume and the molecular weight, a density of 3.663 g/cm^3 is calculated, while the mean density of 5 determinations, measured in toluene, is 3.650 g/cm^3 at 25°C. Due to the lack of sufficient material more accurate measurements could not be obtained.

Compatibility calculations using the Gladstone-Dale relationship yield $K_p = 0.1616$ and $K_c = 0.1687$ for the analytical formula using constants reported by Mandarino (1981); hence $1 - (K_p/K_c)$ is 0.0421, indicating good compatibility (Mandarino, 1979).

Thermal analysis

The differential scanning calorimetric analysis was obtained using a DuPont DSC-910 apparatus.

Table 1. Mössbauer parameters of vochtenite (V) and an oxidized synthetic bassetite (S) with $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios of 0.44/0.65 and 0.48/0.52 respectively

	Fe^{2+}				Fe^{3+}			
	δ (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)	RA (%)	δ (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)	RA (%)
v	1.38(2)	2.47(4)	0.35(4)	0.48(4)	0.44(3)	0.86(6)	0.48(6)	0.52(4)
s	1.32(1)	2.87(3)	0.35(3)	0.44(3)	0.45(2)	0.70(4)	0.60(5)	0.56(3)

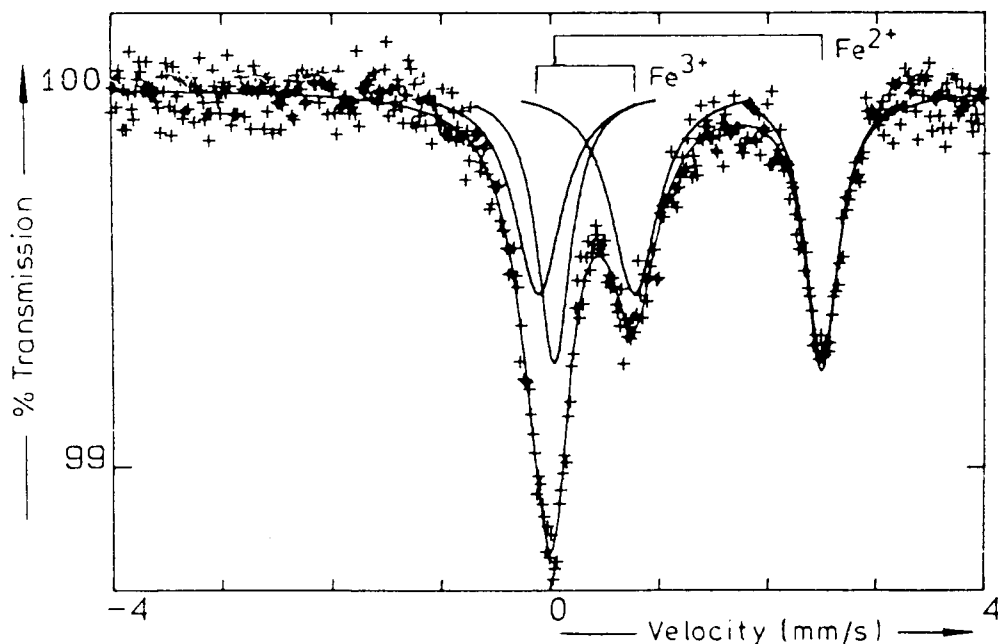


FIG. 4. ^{57}Fe -Mössbauer spectrum at 80 K of vochtenite. Fitted Lorentzian lines and their sum are shown as full lines.

The DSC analysis is characterized by three endothermic peaks at 63, 105 and 150 °C. The thermogravimetric analysis is carried out with a DuPont TGA-951 apparatus with an applied heating rate of 2 °C/min and a constant flow of nitrogen. The results are represented in Fig. 2 from which it is clear that there is a total loss of H_2O of 13.37%, divided into three stages: (i) 40–75 °C, a loss of 5.96% H_2O (3 moles H_2O); (ii) 75–125 °C, a loss of 6.90% H_2O (3.47 moles H_2O); and (iii) 125–200 °C, a loss of 0.51% H_2O corresponding to 0.356 moles of H_2O or 0.51 moles OH.

Infrared spectroscopy

The infrared spectrum was recorded by means of the KBr technique (1 mg/300 mg KBr) with a Beckman infrared spectrometer type 4240. Vochten *et al.* (1984) studied extensively the infrared spectrum of synthetic bassetite and fully oxidized bassetite. The spectrum of vochtenite is presented in Fig. 3 and can be interpreted by considering the vibrations of OH^- , PO_4^{3-} and UO_2^{2+} groups, in addition to the vibrations of water molecules.

According to Gonzalez-Diaz *et al.* (1978) the vibration modes of the PO_4^{3-} group are: ν_1 , PO-stretching (940 cm^{-1}); ν_2 , OPO-bending (420 cm^{-1}); ν_3 , PO-stretching (1020 cm^{-1}); and ν_4 ,

OPO-bending (560 cm^{-1}). The ν_3 and ν_4 vibrations are infrared active. The absorption bands at about 3600–3200, 1650 and 900–500 cm^{-1} are thought to be due to water, corresponding to stretching, deformation and vibrational modes respectively.

The analysis of the vibrational band is very complicated, as pointed out by Ischida *et al.* (1972). Moreover, the $\nu_4(\text{PO}_4)$ mode also occurs in this region. In the region of the water-bending vibration, a relatively broad band is observed. This is due, in general, to the presence of unresolved multiplets, resulting from the presence of a large number of non-equivalent water molecules.

The free OH-stretching vibration is situated in the region of 3500–3600 cm^{-1} for several crystallized salts (Fowler, 1966, 1974*a,b*). Vochtenite is characterized by the presence of one OH group, however, no single peak at frequencies above 3600 cm^{-1} , characteristic for a hydroxyl group, has been detected in the spectrum. On the other hand the intensity of the band due to the OH group may be small, as was demonstrated by a study of hydroxylapatite by Fowler (1966, 1974*a,b*). This could mean that the band overlaps the broad stretching band of the water molecules.

The transformation of $\text{Fe}(\text{H}_2\text{O})^{2+}$ into $\text{Fe}^{3+}(\text{OH})^-$ results in an increase in the electronic

Table 2. X-ray powder diffraction data for vochtenite

d_{obs}	d_{calc}	I_{meas}	hkl
9.998	9.995	100	020
8.733	8.777	10	011
6.573	6.577	20	111
4.999	4.998	30	040
4.892	4.884	45	002
4.818	4.815	30	131
3.574	3.578	15	132
3.475	3.472	70	311
3.333	3.332	50	060
3.087	3.086	40	232
2.828	2.828	30	312
2.642	2.642	10	171
2.500	2.499	30	080
2.463	2.463	10	500
2.205	2.205	40	244
2.152	2.152	45	523
2.111	2.111	45	344;471
2.074	2.074	20	224;291
2.000	1.999	10	0 10 0
1.809		15	
1.735		30	
1.666		40	
1.576		10	
1.428		10	
1.331		10	

Collection of Smithsonian Institution (Reg. File No. 139591). Guinier-Haag camera, 100 mm, Cu-K α radiation, 40 kV, 20 mA. Calculation of the unit cell parameters from powder pattern by the method of McMasters and Larsen (1964).

charge of the cation and a replacement of an H₂O molecule by an OH-group. This effect of a charge transfer has been investigated by Brink (1972) and Maltese *et al.* (1967).

As a consequence of the charge transfer, lower frequencies are obtained for OH groups, which probably explains the shoulder in the lower frequency zone of the OH band illustrated in Fig. 3.

⁵⁷Fe Mössbauer spectroscopy

The ⁵⁷Fe Mössbauer spectrum at 80 K was recorded in the normal transmission geometry using a time-mode spectrometer with triangular reference signal. ⁵⁷Co in a Rh matrix was used as the radiation source. The absorber consisted of the mineral crystallites spread out to a thickness of 1 mg Fe/cm². The folded spectrum contains 512 channels and was calibrated from the room temperature spectrum of a standard Fe foil. The inner

line width for the latter was 0.25 mm/s and each channel has a width of approximately 0.016 mm/s. The spectrum of vochtenite was analysed with a superposition of a ferrous and ferric quadrupole doublet, shown in Fig. 4.

The quadrupole splitting ΔE_Q , the isomer shift δ versus α Fe, the line width Γ and the relative area RA of the two doublets are listed in Table 1 for a synthetic oxidized iron uranyl phosphate with a Fe²⁺/Fe³⁺ ratio of 0.48/0.52 and vochtenite with a Fe²⁺/Fe³⁺ ratio of 0.44/0.56 respectively.

A significant difference exists between the quadrupole splittings of two compounds, which means that the local symmetry around the Fe²⁺ and Fe³⁺ ions is different. This is consistent with the conclusion obtained from X-ray diffraction, that vochtenite does not exhibit the structure of bassetite and oxidized bassetite.

X-ray diffraction data

Since insufficient material was available and the crystal aggregates consist of relatively small, sub-parallel and fractured crystals, it was impossible to do reliable single crystal studies. For this reason the only source of information on the lattice parameters was from X-ray powder diffraction data. These have been obtained at 40 kV and 20 mA with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) using a Philips PW-1140 generator. The photographs were recorded by means of a Guinier-Hägg camera with a diameter of 100 mm and an exposure time of 30 minutes. Silicon powder (NBS-640) was used as an internal calibrant for an accurate determination of the camera constant as a function of the glancing angle.

The relative intensities of the diffraction lines were measured with a Carl Zeiss Jena MD-100 microdensitometer. Table 2 summarizes the d_{hkl} values obtained, with their relative intensities and hkl indices. The X-ray diffraction pattern of fully oxidized bassetite (Vochten *et al.*, 1984) has a strong line at 10.359(85) not occurring in vochtenite. Moreover, the diffraction lines 9.998(100), 8.733(10), 6.573(20), 4.892(45) and 4.818(30) of vochtenite do not occur in fully oxidized bassetite. Therefore, the X-ray diffraction patterns of the two minerals are sufficiently different to distinguish them from each other.

In spite of the fact that the method of McMasters and Larsen (1964) for finding the cell parameters from powder diffraction data can be applied successfully to mineral phases with a relatively high symmetry, they do not always turn out to be fully reliable for monoclinic and triclinic systems. But notwithstanding possible deficiencies, this computer program has been applied to

our data. The parameters obtained from the powder pattern were indexed using the computer program of Visser (1969). The values obtained for a , b , c and α , β , γ are 12.606, 19.999, 9.999 Å and 90°, 102°, 31°, 90° respectively for which a cell volume of 2461 (Å)³ and a ratio $a:b:c = 0.6306:1:0.5002$ has been calculated. It is clear that vochtenite crystallizes in the monoclinic system, with an as yet undetermined space group.

Acknowledgements

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