

# A new occurrence of vesigniéite from the Gorob–Hope copper deposit, Namibia

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## Abstract

An iron-rich vesigniéite,  $[\text{Ba}(\text{Cu},\text{Fe})_3(\text{VO}_4)_2(\text{OH})_2]$  with Cu:Fe near 4:1, was identified in samples from the submarine-exhalative Gorob–Hope copper deposit, Namibia. The olive-colour mineral occurs as mammillary encrustations and vein fillings in the gossan zone of this deposit; it often has a brownish oxidation coating. The main X-ray lines are 3.21 Å (100) [204, 113], 2.72 Å (63) [313, 002] and 2.94 Å (61) [020, 311]. The cell parameters are  $a = 10.236$ ,  $b = 5.905$ ,  $c = 14.253$  Å and  $\beta = 103.71^\circ$ . The formation of vesigniéite took place during the alteration of the ore under strongly alkaline and slightly reducing to oxidizing conditions. While copper and barium were derived from the submarine exhalative mineralisation, vanadium was leached from the countryrock, a mica schist.

**KEYWORDS:** vesigniéite, vanadate, Gorob–Hope deposit, Namibia.

## Introduction

VESIGNIÉITE is a secondary copper mineral with the ideal chemical formula  $\text{BaCu}_3(\text{VO}_4)_2(\text{OH})_2$ . It was first described by Guillemin (1955) in a specimen from Friedrichsrode, Thuringia. Vesigniéite has a very similar crystal structure to bayldonite  $[\text{PbCu}_3(\text{AsO}_4)_2(\text{OH})_2 \cdot \text{H}_2\text{O}]$  and resembles volborthite  $[\text{Cu}_3(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}]$ , for which it has probably been mistaken in many cases (Guillemin, 1956). Vesigniéite has now been found in samples from the gossan zone of the Gorob–Hope copper deposit, where it had not previously been identified.

## Occurrence and paragenesis

The mineralised lenses of the Gorob–Hope area are situated within the Namib Desert, approximately 90 km inland from the coast in the western part of central Namibia. The geology of the area is dominated by massive mica schists of the Kuiseb Formation of the Pan-African Damara Orogen. Precursors of these metasediments were Proterozoic greywackes, sandstones and shales. Metamorphic conditions were those of the lower amphibolite facies (Miller, 1983).

The stratabound copper mineralisation is associated with amphibolite lenses of the 'Matchless Belt', which is interbedded with the Kuiseb metasediments and has a strike length of 350 km. The amphibolites include metabasalts and intrusive equivalents and have a chemical composition similar to oceanic tholeiites (Miller, 1983). Based on the close association of the deposit and the Matchless amphibolites, the mineralisation is believed to be of submarine-exhalative origin. Minor amounts of lead and zinc as well as trace amounts of gold and silver were deposited together with the copper. In the Gorob–Hope area the mineralisation forms five distinct lenses, namely the Gorob, Vendome, Luigi, Bruna and Hope lenses. Vesigniéite was found in the gossan zone of all except the Luigi lens, the latter having no surface outcrop.

In hand specimen, vesigniéite forms mammillary encrustations up to 2 mm thick on fractures and cleavage planes of the limonitic gossan. It also occurs in small veins up to 3 mm thick. One sample shows vesigniéite coating the walls of small vugs in a calcite–limonite breccia. On the contact between the gossan and the micaceous schist, vesigniéite also penetrates the schist and forms thin films on the schistosity planes. Other

minerals associated with vesigniéite are cryso-colla, malachite, calcite and quartz. In thin section it can be seen that malachite is replaced by vesigniéite, especially in veins and vugs of the limonitic gossan. Vesigniéite is the latest of the secondary minerals in the paragenetic sequence.

### Physical and optical properties

Vesigniéite forms radial aggregates of prismatic, monoclinic crystals. The aggregates have a maximum diameter of 2 mm. Crystal size ranges from cryptocrystalline to 0.15 mm with a length : width ratio of 10 : 1. Twinning is common (pers. comm., W. Joswig, 1989). The massive encrustations have a brownish-black oxidation coating. Smaller, single-crystal aggregates as well as vein fillings display the typical light yellowish olive colour. Vesigniéite has a dull lustre and a dark greenish yellow streak.

Vesigniéite from Gorob has a hardness of approximately 3.5 on the Mohs scale. The density, measured by water displacement, is 4.21 g/cm<sup>3</sup>. The mineral is easily soluble in acids. In thin section, vesigniéite is subtranslucent and exhibits a yellow to greenish yellow colour in transmitted light. Slight pleochroism from greenish yellow to light yellow occurs. The refractive indices could not be established due to the extremely small crystal size, but birefringence was determined to be 0.040.

### Chemical composition

A sample of 0.2 g from a piece of mammillary vesigniéite was dissolved in HF + HNO<sub>3</sub> + HClO<sub>4</sub>. All elements except phosphorus and sulfur were analysed by atomic absorption spectrophotometry with a Perkin Elmer 1100B. Phosphorus was determined by spectrophotometry and sulfur by SO<sub>2</sub> measurement on a LECO CS 044. The results are shown in Table 1. A calculation of the formula of vesigniéite from Gorob according to the assay, after excluding the minor constituents, gives Ba(Cu<sub>0.8</sub>Fe<sub>0.2</sub>)<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub>(OH)<sub>2</sub>. There is a significant replacement of copper by iron. A high iron content has not been reported from any of the other known localities for vesigniéite.

### X-ray diffraction study

The X-ray diffraction studies of the vesigniéite samples were carried out with a Rigaku Geigerflex with Cu-K $\alpha$  radiation at a scanning rate of 0.5° 2 $\theta$ /min. The cell dimensions of vesigniéite from Gorob were determined from the powder

Table 1.

Chemical composition in wt% of vesigniéite from Gorob compared with two other occurrences (\* = after Guillemin (1956), \*\* = after Vesigniéite Research Group (1977), \*\*\* = theoretical value).

	Gorob-Hope	Friedrichsrode*	Shensi**
CuO	34.50	36.50	40.27
PbO	0.06		
ZnO	0.12		0.028
FeO	9.03		
MnO	0.08		
CaO	0.15		0.053
BaO	21.28	23.90	24.22
MgO	0.10		0.011
Na <sub>2</sub> O	0.05		0.007
K <sub>2</sub> O	0.13		0.10
P <sub>2</sub> O <sub>5</sub>	0.27		
As <sub>2</sub> O <sub>5</sub>	0.05		0.023
V <sub>2</sub> O <sub>5</sub>	25.24	31.20	30.08
Al <sub>2</sub> O <sub>3</sub>	0.17		0.42
SiO <sub>2</sub>	4.50		0.49
S <sup>2-</sup>	0.04		
H <sub>2</sub> O	3.50***	3.50	3.62
$\Sigma$	99.27	96.20	98.19

diffraction data using the Pulvex program. The indexed powder data are presented in Table 2. Cell dimensions are as follows:  $a = 10.236$ ,  $b = 5.905$ ,  $c = 14.255$  Å,  $\beta = 103.71^\circ$ . The space group is C2/c.

### Discussion

Copper, barium and vanadate ions in aqueous solution can combine to form vesigniéite according to the following reaction  $\text{Ba}^{2+} + 3\text{Cu}^{2+} + 2(\text{VO}_4)^{3-} + 2\text{H}_2\text{O} \rightarrow [\text{BaCu}_3(\text{VO}_4)_2(\text{OH})_2] + 2\text{H}^+$ . While copper and barium can be attributed to submarine exhalative mineralisation, the vanadium must be of different origin. Hartleb (1988) describes samples of the metasediments of the Kuiseb Formation containing 100–150 ppm V<sub>2</sub>O<sub>5</sub>. Leaching of the parts of the Kuiseb Formation in direct contact with the ore body and its gossan, could therefore provide the necessary vanadate ions.

The (VO<sub>4</sub>)<sup>3+</sup> ion has a limited stability range (Fig. 1). The formation of vesigniéite must hence take place under strongly alkaline and slightly reducing to oxidizing conditions. Changing groundwater levels with varying pH conditions are typical of the desert climate prevailing in the Gorob area. Depletion of SiO<sub>2</sub> typical of the gossan environment points to moderate to high pH values. Since vesigniéite replaces malachite, (CO<sub>3</sub>)<sup>2-</sup> ions released during the breakdown of this carbonate could act as a buffer to promote the

Table 2. Powder X-ray diffraction data for vesigniéite from the Gorob - Hope area.

$I_{\text{obs}}$	$d_{\text{obs}}$ (Å)	$d_{\text{calc}}$ (Å)	hkl
54	6.9100	6.9242	002
49	4.9511	4.9684	111
32	4.5715	4.5866	202
42	3.4502	3.4621	004
100	3.2176	3.2219	204
61	2.9472	2.9527	020
63	2.7200	2.7193	311
40	2.5686	2.5655	115
26	2.5404	2.5388	220
		2.5390	402
37	2.4859	2.4860	314
		2.4860	400
		2.4874	023
37	2.2906	2.2955	222
		2.2933	404
19	1.9278	1.9263	511
		1.9251	422
		1.9247	131
19	1.8226	1.8206	315
		1.8210	226
18	1.7539	1.7544	422
		1.7529	133
		1.7520	515
23	1.7323	1.7311	008
11	1.7054	1.7060	602
		1.7050	331
14	1.6543	1.6558	423
		1.6560	331
		1.6555	604
		1.6551	333
		1.6543	134
18	1.6195	1.6194	135
		1.6188	426
9	1.5400	1.5495	517
		1.5317	602
25	1.4784	1.4771	622
		1.4764	040
		1.4763	227

strongly alkaline conditions necessary to form the  $(\text{VO}_4)^{3-}$  ion. Equilibration of the weathering solutions with oxygen-rich meteoric water leads to increasing Eh conditions. Once the stability field of  $(\text{VO}_4)^{3-}$  is reached, vesigniéite can form.

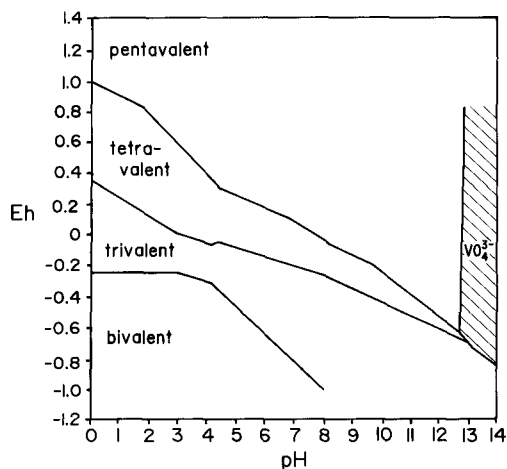


Fig 1. Stability field of  $(\text{VO}_4)^{3-}$  (after Evans and Garrels, 1958).

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