New data on sincosite

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Abstract

Microprobe analysis of sincosite confirms the formula $Ca(VO)_2(PO_4)_2 \cdot 5H_2O$, assuming tetravalent vanadium. The density of sincosite is 2.98(3) g/cm³. Sincosite is tetragonal with a = 8.895(3) and c = 12.727(2)Å. The space group could not be determined, but sincosite is isostructural with meta-autunite.

Introduction

In the course of an examination of meta-autunite minerals in the Vaux mineral collection at Bryn Mawr College a wrongly identified specimen was found. This sample, #7996 from the Black Hills of South Dakota, consisted of a rosette of quarter-inch green plates on a black siliceous matrix. It was misidentified as metatorbernite. The provenance of the specimen was not in doubt, but the color was too pale and the luster too vitreous for the mineral metatorbernite. Detailed crystallographic and chemical examination showed it to be the rare hydrated calcium vanadyl phosphate, sincosite.

Chemical and physical properties

The mineral was analyzed with a MAC Etec microprobe using an operating voltage of 15 kV, specimen current of 0.01 μ A, and a beam diameter of 25 μ m to minimize volatilization. The results of three energy dispersive analyses are shown in Table 1. As there was inadequate material for the direct determination of water, it was estimated by difference. The calculated formula is Ca(VO)₂(PO₄)₂ · 5H₂O, essentially identical to that proposed by Schaller (1924). This formula presupposes that the vanadium is tetravalent.

Sincosite is dark leek green to pale green in this specimen. Schaller (1924) notes that it can also be olive-green to brown-green. The luster is vitreous, becoming submetallic in partially dehydrated crystals.

Individual crystals form thin plates with perfect {001}, good {110} and poor {100} cleavages. All crystals show striations parallel to [100] and [110]. The specific gravity as determined by the sink or swim method in methylene iodide-toluene was 2.98(3) g/cm³. This value is appreciably higher than that found by Schaller (2.84 g/cm³), but agrees closely with the calculated value of 2.97 g/cm³, as determined below.

Crystallography

Crystals of sincosite proved to be of uniformly low quality, due to the turbostratic nature of the crystals. Only one hk0 precession photograph was successful, showing a few weak reflections suggesting a cell with a = b = 6.30Å. The

powder diffraction pattern was collected using a Gandolfi camera, with silicon as an internal standard. The pattern was indexed by analogy with the meta-autunite cell, and the unit cell was refined using the program Unit Cell (Appleman and Evans, 1973). The powder diffraction pattern of sincosite is listed in Table 2. As presumed by Schaller (1924), sincosite is tetragonal, with cell parameters a=8.895(3) and c=12.727(2)Å. The reflections from the hk0 precession photograph thus define a pseudocell, turned 45° from the true cell and having half of its volume. The space group could not be determined. Assuming Z=2, D calc. =2.970 g/cm³.

Discussion

Sincosite almost certainly has the meta-autunite structure, as first suggested by Schaller (1924). In this structure, apical oxygens from four different phosphate tetrahedra octahedrally coordinate each uranyl ion (Zolensky and Smith, in prep.). Square pyramidal coordination is typical for tetravalent vanadium (Evans and Block, 1966), the average apical bond lengths being 1.60 and 1.91Å respectively. However, a sixth oxygen atom or water molecule, from 2.18 to 2.97Å from the V⁴⁺, often completes a distorted octahedral coordination. These distorted vanadium octahedra may substitute into the meta-autunite structure in place of the uranyl octahedra. The short V–O double bonds are oriented normal to the plane of the phosphate tetrahedra, and the opposite bonds project out into the interlayer region to become possible V–H₂O bonds. How-

Table 1. Analytical results for sincosite (in wt. %)

0xide	Variability range	Average	Ideal
P205	31.37	31.37	31.26
V204	36.42-36.46	36.44	36.54
Ca0	12.43-12.58	12.51	12.35
H ₂ 0*		19.68	19.85
Total		100.0	100.0
* Water	estimated by dif	forence	

Water estimated by difference

Table 2. X-ray powder patterns of sincosite

h	k	1	I/I_0	d _{calc} .	dobs.	
0	0	1	20	12.73	12.72	_
1	0	D	10	8,90	8.90	
1	0	1	10	7.29	7.31	
0	0	2	100	6.36	6.35	
1	1	2	20	4.47	4.47	
0	0	3	20	4.24	4.26	
1	0	3	25	3.829	3.841	
2	1	1	15	3.797	3.792	
1	1	3	60	3.517	3.511	
0	0	4	80	3.182	3.190	
2	0	3	10	3.070	3.069	
2	1	3	40	2.901	2.907	
3	0	2	50	2,688	2.682	
1	1	5	15	2.360	2.362	
3	2	2	10	2.300	2.290	
4	0	2	40	2.099	2.100	
4	2	0	15	1.999	1.991	
3	1	5	5	1.887	1.884	
5	1	0	10	1.744	1.743	
2	2	7	15	1.574	1.570	
4	4	1	10	1.561	1.563	
4	1	1 0 1 2 2 3 3 1 3 4 3 3 2 5 2 2 0 5 0 7 1 7	10	1.390	1.392	
5	4	2	5	1.357	1.360	
0 1 1 0 1 0 1 0 2 2 3 1 3 4 4 4 5 1 4 4 5 1 4 5 1 4 5 1 4 5 1 5 1	0 0 0 1 1 0 0 1 1 0 0 1 2 0 2 1 1 2 4 1 4 0 4	10	25	1.260	1.264	
4	4	8	5	1.118	1.120	

ever, the detailed configuration must await a structure analysis of sincosite.

"Meta-autunites" from known vanadium containing environments should be re-examined, as sincosite is easily confused with meta-autunite and may be more common

than the number of reported occurrences would suggest. Sincosite can easily be distinguished from the meta-autunites by its lack of radioactivity. It seems likely that sincosites containing interlayer cations other than calcium will be found, in an analogy to the meta-autunites.

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