First U.S. occurrence of wodginite from Powhatan County, Virginia

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Abstract

Wodginite occurs as black subhedral grains in the Be, Nb-Ta, Sn bearing Herbb #2 pegmatite in Powhatan County, Virginia. The wodginite is associated with amazonite and topaz in the intermediate zone of the pegmatite. Other Nb-Ta-bearing minerals found associated with wodginite are cassiterite, in part as inclusions in wodginite, and partially ordered manganocolumbite. The Herbb wodginite is compositionally similar to previously studied wodginites and has an average formula $(Mn_{2.86}Fe_{1.5}^{2+})_{\pm 4.01}(Sn_{2.04}Ti_{1.14}Ta_{0.57}Fe_{0.14}^{3+})_{\pm 3.89}(Ta_{7.02}Nb_{0.98})_{\pm 8.00}O_{32}$. The average unit cell dimensions are a 9.471(2), b 11.431(2), c 5.108(1)Å, β 90°47'(1), V 553.1(1)Å³.

Introduction

A black mineral, at first believed to be columbitetantalite, was collected by the first author from the Herbb #2 pegmatite in Powhatan County, central Virginia. Griffitts et al. (1953) noted "small lustrous tabular to equant crystals of columbite-tantalite" in albitized portions of this pegmatite, a species also quoted by Jahns et al. (1952). Recent examination of Nb,Ta-bearing minerals from this locality has led to the identification of the rare Mn,Sn,Ta-oxide mineral, wodginite.

Wodginite, $(Mn,Fe)_4(Sn,Ta,Ti)_4(Ta,Nb)_8O_{32}$, was first described by Nickel et al. (1963) from the type localities Wodgina, Australia and Bernic Lake, Manitoba. Since its discovery, 18 wodginite localities have been cited in the literature. To date this is the first occurrence of wodginite in the U.S., along with wodginite from the Peerless pegmatite at Keystone, South Dakota (Černý et al., in review). This paper describes the occurrence, chemistry and properties of the Virginian wodginite and associated Nb,Ta-bearing minerals.

Occurrence

The Herbb #2 pegmatite lies within a NE-trending belt of pegmatites approximately 5.75 km NE of Flat Rock in Powhatan County, Virginia (Fig. 1). The area lies within the Piedmont province of the central Appalachians in central Virginia. The pegmatite is enclosed within a feldspathic biotite schist. The pegmatite is lenticular in shape, strikes N20°E and dips steeply to the east. It is approximately 75 meters long and 2 to 15 meters thick in outcrop.

This zoned pegmatite is mineralogically complex, and is similar to the Morefield and Rutherford pegmatites of the Amelia pegmatite district, except that it is deeply weathered. Blocky, green perthitic microcline (amazonite), quartz and muscovite are the dominant minerals present. Beryl, topaz, columbite-tantalite, wodginite, cassiterite, and minor spessartine also occur in the pegmatite, mainly in the clayey decomposition products.

Wodginite is found scattered throughout the kaolinized feldspar of the intermediate zones. Veinlets of wodginite also occur near perthitic amazonite bodies and to a lesser extent are also associated with topaz.

Physical properties

Wodginite occurs as black anhedral to subhedral crystals, typically 0.5 cm to 6 cm in length. The largest crystal found at the locality to date was nearly 13 cm in length (D. Richardson, pers. comm.). In transmitted light, the wodginite is translucent, has a reddish brown color along the edges of thin splinters and is grayish-white in reflected light. The streak is light brown. A specific gravity determination was not attempted due to the presence of cassiterite inclusions.

X-ray crystallography

X-ray powder-diffraction data were obtained on a Philips diffractometer using Ni-filtered CuK α radiation ($\lambda = 1.5418$ Å) and scanning speed 1/2° 2 θ /min. X-ray powderdiffraction data were calibrated with annealed CaF₂ (a = 5.4620Å). Unit cell dimensions were calculated by the CELREF computer program on both natural and heated samples of wodginite. The unit cell parameters are given in Table 1. The results show good agreement with previously published wodginite cell dimensions (e.g., Graham and Thornber, 1974).

After heating in air at 1000°C for 16 hours, a slight shift in the cell dimensions was noticed. Sample VA-3 showed a significant decrease in the a, c and β dimensions. This decrease in cell dimension upon heating may be indicative of an increase in ordering. The significance of such a shift



Fig. 1. Location of the Herbb #2 and neighboring pegmatites in the Powhatan area.

in wodginite is not known; it may possibly be related to reduction of mosaicity or improved ordering of the structure.

Chemical composition

Chemical analyses were performed on the MAC 5 electron microprobe in the wavelength dispersive mode. The following standards were used for the analyses: manganotantalite (Mn,Ta), chromite (Fe), stibiotantalite (Nb), cassiterite (Sn), $SrTiO_3$ (Ti), and microlite (Na,Ca). The specimen current was 0.04 mA at 15 kV. Data reduction was made using a modified version of the EMPADR VII computer program of Rucklidge and Gasparrini (1969). Table 1 gives the results of the electron microprobe analyses.

The Herbb wodginites fall within the compositional limits of other wodginites cited in the literature. The average chemical formula calculated on the basis of 32 oxygens, and with Fe > 4.00 A-cations allocated as Fe³⁺ to the C-site, is $(Mn_{2.86}Fe_{1.15}^{2+})_{\Sigma4.01}(Sn_{2.04}Ti_{1.14}Ta_{0.57})_{\Sigma4.01}$

 $Fe_{0.14\Sigma3,89}^{3,+}(Ta_{7.02}Nb_{0.98})_{\Sigma8.00}O_{32}$ (cf. Ferguson et al., 1976 for preferences in site occupancies).

Cassiterite

A second phase in the X-ray powder diffraction pattern of samples VA-4 and VA-6 was identified as cassiterite. Unit cell dimensions are given in Table 1. The cassiterite occurs as elongated inclusions within the wodginite but shows no apparent orientation with respect to the wodginite structure. Under reflected light it is grayish-white like the wodginite; however, it is distinguishable from wodginite under crossed nicols by its granular texture. Chemical composition of a cassiterite inclusion is given in Table 1. The Ta₂O₅, Nb₂O₅ and FeO contents are considerably higher than those normally found in cassiterites, but correlate well with compositions of cassiterites from Nb,Ta-enriched pegmatites, particularly wodginite-bearing ones (Černý et al. 1981b).

Manganocolumbite

Manganocolumbite was found as isolated euhedral crystals in the pegmatite dumps. It is indistinguishable in hand specimen from wodginite and was identified by Xray powder diffraction. In its natural state, the sample can be described as a partially ordered columbite. This sample became fully ordered upon heating in air at 1000°C for 16 hours (cf. Komkov 1970, Černý and Turnock 1971 for order-disorder relationships in the columbite-tantalite series).

The chemical composition of manganocolumbite (Table 1) shows a Ta/Nb ratio of 0.40 and a Fe/Mn ratio of 0.90.

Table 1. Chemical composition of wodginite, manganocolumbite and cassiterite

Sample number	Ta205	Nb205	Ti02	Sn0 ₂	Fe203	MnO	Fe0	Na ₂ 0	Total
VA-2(w)	65.9	5.7	3.6	12.8	0.6	8.1	3.4	0.02	100.12
VA-3(w)	66.7	6.3	4.0	11.3	0.5	8.0	3.5	0.04	100.34
VA-4(w)	68.3	4.0	3.5	12.6	0.0	8.0	3.2	0.0	99.6
VA-6(w)	67.8	5.0	3.5	12.5	0.7	8.4	3.1	0.0	101.0
VA-7(cb)	31.2	46.8	1.9	0.4	0.0	9.4	8.6	0.02	98.32
VA-6B(c)	10.6	0.6	0.8	88.8	0.0	0.2	1.6	0.0	102.6
	Ta ⁵⁺	Nb ⁵⁺	Ti ⁴⁺	Sn ⁴⁺	Fe ³⁺	Mn ²⁺	Fe ²⁺	Na ¹⁺	Total
VA-2(w)	7.42	1.07	1.12	2.11	0.19	2.84	1 18	0.02	15 95
VA-3(w)	7.46	1.17	1.24	1.85	0.16	2.79	1.20	0.03	15.90
VA-4(w)	7.85	0.76	1.11	2.12	0.00	2.86	1.13	0.00	15.83
VA-6(w)	7.62	0.93	1.09	2.06	0.22	2.94	1.07	0.00	15.93
VA-7(cb)	2.20	5.49	0.37	0.04	0.00	2.07	1.87	0.00	12.05
VA-6B(c)	0.14	0.01	0.03	1.74	0.00	0.01	0.07	0.00	2.00
Natural	<u>a</u> , 8		b, 8		c, 8		ß		v, 8 ³
VA-2(w)	9,469(2)		11 433(2)		5 108(1)		90048(1)		552 0(1)
VA-3(w)	9,472(1)		11.427(2)		5,110(1)		90 45(1	í.	553.0(1)
VA-4(w)	9.469(3)		11,433(2)		5,109(1)		90 49 1		553.1(1)
VA-6(w)	9.474(2)		11,436(3)		5.106(1)		90°47(1)'		553.2(1)
VA-7(cb)	14.322(3)		5.739(1)		5,085(2)		-		418.0(1)
VA-6B(c)	4.736(1)				3.174(1)		-		71.21(3)
Heated									
VA-2(w)	9,469(3)		11,430(4)		5,099(1)		90 ⁰ 54(2)'		551 9(2)
VA-3(w)	9.457(2)		11.427(3)		5.098(2)		90 55(2)		550.8(2)
VA-4(w)	9.467(3)		11.426(4)		5.100(2) 5.100(2)		90°55(2)' 90°57(2)'		551,6(2)
VA-6(w)	9.470(3)								551.6(2)
/A-7(cb) 14.336(3)		5.738(1)		5.071(2)		-		417.1(1)	

(w) - wodginite, (cb) - manganocolumbite, (c) - cassiterite * based on 32 oxygens for wodginite, 12 oxygens for manganocolumbite, and 2 oxygens for cassiterite



Fig. 2. The Herbb #2 minerals in the $(Nb,Ta)O_{2.5}$ -(Fe,Mn)O-(Ti,Sn)O₂ triangle and in the columbite-tantalite quadrilateral (W-wodginite, CT-manganocolumbite, C-cassiterite).

As is the case with the wodginites, the manganocolumbite shows appreciable amounts of TiO_2 , but less than is usual in columbite-tantalites coexisting with Ti-rich phases (Černý et al. 1981a).

Figure 2 demonstrates a general compliance of all three analyzed minerals with the substitution $(Fe,Mn)^{2+} + 2(Nb,Ta)^{5+} \rightleftharpoons 3(Sn,Ti)^{4+}$, which is dominant in incorpo-

rating R^{4+} into the minerals of the columbite-tantalite group sensu lato, and $R^{2+} + R^{5+}$ into rutile-type phases. Figure 2 also shows the preference of tetragonal rutiletype structures for Fe and Ta, and the Mn and Ta enrichment of wodginite relative to the manganocolumbite.

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