WODGINITE FROM NORTHEASTERN BRAZIL

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ABSTRACT

Two varieties of wodginite, Fe-rich and Mn-rich, occur in pegmatites at Seridózinho, Paraiba State, Brazil. The mineral is monoclinic with

$$a = 9.46\ \text{Å},\ b = 11.43\ \text{Å},\ c = 5.12\ \text{Å},\ \beta = 91°12'$$

(for the Mn-variety). Optical properties, micro-indentation hardness and reflectance values, and electron-microprobe analyses are presented. A discussion of previously published analyses leads to the conclusion that there seem to be two possible systems to fit the analyses of wodginite into a formula.

INTRODUCTION

During the first months of 1968 a number of samples of Nb-Ta-minerals from the Seridózinho mine, 9 km NW of the city of Juazeirinho, Paraiba State, Brazil, were investigated by the fourth author at the Laboratório de Técnicas Físico-Químicas Aplicadas à Mineralogia e Petrologia in Lissabon. X-ray fluorescence analysis of this material revealed the presence of tin in two specimens labelled "tantalite". After a short stay of the same author at the Institute of Earth Sciences of the Free University at Amsterdam, the material was left there for further investigation.

Subsequent study by X-ray diffraction and electron-microprobe analysis made it possible to identify the rare mineral wodginite in the Sn-bearing samples. Seridózinho is the eighth reported locality for this mineral and the first one in South America.

Wodginite has been first described by N i c k e l et al. (1963) from Wodgina, Australia, from Bernic Lake, Manitoba, Canada, and from the Benson mine, Southern Rhodesia. The mineral has also been found in Ruanda (B o u r g u i g n o n and M é l o n, 1965), at Krasonice, Czechoslovakia (L u n a, 1965), in the Kalbin Range, U.S.S.R. (K h v o s t o v a et al., 1966), and at Sukula, SW FInlan (V o r m a and S i i v o l a, 1967).

OCCURRENCE

The geology of the Rio Grande do Norte and Paraiba pegmatite district (also called the Borborema province) has been described by d e A l m e i d a et al. (1944), J o h n s t o n (1954a and b), R o l l f (1945), R a o (1963) and R o y et al. (1964). The country rocks consist of biotite-schists, gneisses, amphibolites, quartzites and migmatites of Precambrian age. The district is characterized by numerous lens-shaped dikes of granitic pegmatites that accompany the granitic intrusions in the area. J o h n s t o n (1945a and b) classified the pegmatites in homogeneous and heterogeneous types. R o l f f (1945) also distinguished a mixed type. Mineralization in Li, Be, Ta-Nb

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and Sn is common, especially in the last two types. R o y et al. (1964) give details about the zones of the heterogeneous pegmatites and include Seridózinho as an example of this type.

The dimensions of the pegmatite outcrop at Seridózinho, which is explored commercially for tantalite and cassiterite, are about 300 by 40 meters. Minerals present are muscovite, feldspars (microcline and albite), and quartz, characteristic respectively for the zones I (contact with the wall-rock), II and III (intermediate), and IV (nucleus); ambligonite, spodumene (crystals up to 2 meters in length), beryl, Nb-Ta-minerals, cassiterite and some phosphates (apatite, arrojadite) are dispersed in the intermediate zone, but also occur in the quartz core. The Nb-Ta-minerals as well as cassiterite are usually associated with albite.

One of the wodginite specimens (NT-47) is a fragment of a single crystal, but contains very small inclusions of tapiolite. The other specimen (NT-34) is an intergrowth of wodginite and tapiolite in alternating subparallel layers which have a width of up to some millimeters. At the contacts of the two minerals, the tapiolite of specimen NT-34 contains very thin fringes (usually 10-20 microns across) of a new Sn-Ta-mineral, staringite (B u r k e et al., 1969). In the same specimen a vein of albite is also present. The occurrence of wodginite at Seridózinho is genetically conformable to the previous finds of this mineral, all of them being located in pegmatites, more particularly in the feldspars.

OPTICAL PROPERTIES

Under the microscope, in reflected light, wodginite shows a greyish white colour (in oil darker than in air), weak bireflection and distinct anisotropy in greyish tints. Internal reflections are orange-red (only visible in oil). No cleavage or twinning have been observed. The associated tapiolite has a strong bireflection, with colours varying from yellowish grey to grey with a bluish tint, and a very strong anisotropy with greenish yellow to deep blue interference colours. The internal reflections are deep red. Twinning is present. No differences in polishing hardness could be observed between wodginite and tapiolite.

Micro-indentation hardness (VHN) was measured with the Leitz-Durimet Pol (U y t e n b o g a a r d t, 1966). Applied load was 100 g, and the indentation time 15 sec. VHN of wodginite from Seridózinho (mean minimum and maximum values of 15 indentations): 766-820 kg/mm^2 (for the Fe-variety, spec. NT-34) and 849-899 kg/mm^2 (for the Mn-variety, spec. NT-47). K h v o s t o v a et al. (1966) obtained a VHN of 860-1080 kg/mm^2 on wodginite from the Kalbin Range. The higher values may be due to the higher Mn-content of the Russian specimen. The VHN of tapiolite in spec. NT-34 is 893-959 kg/mm^2.

TABLE 1.

Reflectance of wodginite and tapiolite.

Wave-length in nm	1	2	3
470	15.3-15.8	14.7-15.5	16.2-17.0
546	14.9-15.5	14.3-15.1	15.5-17.2
589	14.8-15.4	14.2-15.0	15.2-17.1
650	14.6-15.4	13.9-14.8	15.0-17.0

1. Wodginite, NT-34.
2. Wodginte, NT-47.
3. Tapiolite, NT-34.

Spectral reflectance of wodginite and tapiolite was measured with the Leitz MPV Microscope Photometer (W e b e r, 1965). 10 measurements were performed on both specimens at each of the four standard wave-lengths proposed by the IMA-Commission on Ore Microscopy. As standard the carborundum NPL N.2538.30 was used; the apparatus showed no primary or secondary glare effects. The results are given in Table 1.

The reflectance of wodginite had not been measured before. The conclusion that the reflectance increases with the Fe-content is, therefore, tentative. The difference in reflectance of the two wodginite specimens may, namely, also be due to the different Ta/Nb ratio, as has been proved for the columbite-tantalite series (B e u g n i e s and M o z a f a r i, 1968).

CHEMISTRY

Electron-microprobe[5]) analyses were carried out by the second author. The results are given in Table 2, columns 8 and 9, and compared with analyses of wodginite from other localities. The following standards were used for the analyses: tantalum metal for

[5]) Type Geoscan, Cambridge Instrument Company Ltd., Cambridge, Great Britain.

TABLE 2

Chemical analyses of wodginite.

	1	2	3	4	5	6	7	8	9
Ta_2O_5	70.49	70.05	74.1	67.50	65	60	61	59.4	68.4
Nb_2O_5	7.63	1.35	14.5	7.09	9	16	13	12.8	3.5
SnO_2	8.92	13.20	-	10.26	10	10	10	13.1	13.1
SiO_2	-	0.60	-	-	-	-	-	-	-
ZrO_2	-	-	-	-	-	-	-	1.5	1.5
TiO_2	-	2.39	-	0.81	2	3	4	0.1	0.1
MnO	10.87	9.04	5.5	10.91	5	2	2	3.5	7.2
FeO	1.34	1.87	5.9	3.06	8	6	7	9.1	4.8
CaO	0.42	-	-	-	-	-	-	-	-
MgO	0.37	-	-	-	-	-	-	-	-
Loss ign.	0.18	-	-	-	-	-	-	-	-
Total	100.22	98.50	100.0	99.63	99	97	97	99.5	98.6

1. Wodgina, Australia (Simpson, 1909). Ref. in: Nickel et al. (1963). MgO and CaO due to impurities.
2. Bernic Lake, Manitoba, Canada (Nickel et al., 1963). SiO_2 due to impurities.
3. Ruanda (Bourguignon and Mélon, 1965). Corrected for impurities.
4. Kalbin Range, U.S.S.R. (Khvostova et al., 1966).
5. 6, and 7. Sukula, SW Finland (Vorma and Siivola, 1967). Electron-microprobe analyses.
8. Seridózinho, Brazil, NT-34 (this paper). Mean values of 6 electron-microprobe analyses by C. Kieft.
9. Seridózinho, Brazil, NT-47 (this paper). Mean values of 6 electron-microprobe analyses by C. Kieft; ZrO_2 and TiO_2 not measured, but analogous to NT-34.

Ta, lueshite for Nb, tin metal for Sn, zircon for Zr, TiO for Ti, iron metal for Fe and rhodonite for Mn. The analytical data were corrected for absorption, atomic number and secondary fluorescence. Absorption correction was applied according to the formula of Philibert (1963) with the $\bar{\sigma}$ of Duncumb and Shields (1966); in this correction, the mass absorption coefficients of Heinrich (1966) were used. Atomic number correction was divided into backscatter factor R and retardation factor S. R was calculated by following the data of Bishop (1966), while for S the expression of Reed (1964) was applied. The formula of Reed (1965) was used for the correction of secondary fluorescence.

Discussion of results. The tin-content in wodginite from Seridózinho is rather high, but about the same as for wodginites from most of the other localities. Bourguignon and Mélon (1965) observed 4.8% SnO_2 in the Ruanda wodginite, but assigned this entirely to inclusions of cassiterite. However, some tin might have been incorporated in their material; nevertheless, the tin-content is very low. The Benson mine wodginite contains only 0.30% SnO_2 (Nickel et al., 1963). Moreau and Tramasure (1965) and Turnock (1966) obtained synthetic wodginite-type Mn-Fe-Ta-compounds without tin, proving that this element is not essential for the mineral.

Small contents of zirconium have been measured spectrographically (0.01-0.05% and 0.2% in specimens from Ruanda and Canada respectively) and by means of X-ray fluorescence (O.X.% in wodginite from Czechoslavakia). Compared with these figures the ZrO_2-content in the Seridǒzinho material is rather high (1.5%).

Two varieties of wodginite have been described: an Fe-variety from Ruanda and Finland, and a Mn-variety from Australia, Canada, the U.S.S.R. and Czechoslavakia. At Seridózinho, the two varieties occur together in the same, rather small, deposit: NT-34 is Fe-rich, and NT-47 is Mn-rich. Bourguignon and Mélon (1965) state that they obserbed the two varieties within the same deposit in Ruanda, but no analyses are presented for the Mn-variety.

CRYSTALLOGRAPHY

X-ray powder diagrams of the Seridózinho wodginite were obtained with Debye-Scherrer and Guinier-de Wolff cameras by the first and the third author, respectively. The Guinier-de Wolff method yielded the best photographs with very sharp reflec-

TABLE 3

Analyses of wodginite from Table 2, recalculated to atomic proportions.

	1		2		3		4	5		8		9	
Ta	8.29	9.78	8.40	8.67	8.48	11.25	7.71	7.4	9.1	6.66	9.5	8.24	8.93
Nb	1.49		0.27		2.77		1.35	1.7		2.39		0.69	
Sn	1.54		2.32		-		1.72	1.7		2.16		2.29	
Ti	-	1.54	0.79	3.11	-		0.26	0.6	2.3	0.03	2.49	0.03	2.64
Zr	-		-		-		-	-		0.30		0.32	
Mn^{2+}	3.98	4.46	3.38	4.07	1.92	3.99	3.88	1.8	4.6	1.23	4.38	2.69	4.45
Fe^{2+}	0.48		0.69		2.07		0.22	2.8		3.15		1.76	
Fe^{3+}	-		-		-		0.86	-		-		-	
	15.78		15.85		15.24		16.00	16.0		15.92		16.02	
0	32.00		32.00		32.00		32.00	32.0		32.00		32.00	
A : B	1:2.54		1:2.89		1:2.82		1:2.90	1:2.48		1:2.64		1:2.60	

Column numbers refer to analyses in Table 2.
See text for explanation.
Analysis 4 recalculated for cation: anion ratio 1 : 2; part of ferrous oxide converted into ferric oxide (K h v o s t o v a et al., 1966).

tions, so that these were taken for further calculations. Ni-filtered Cu-radiation was used; the d-values were gauged against alum as a standard, and corrected by the least squares method. The pattern of the Seridózinho material is similar to that of type-locality wodginite as published by N i c k e l et al. (1963). The unit-cell dimensions were calculated for wodginite from spec. NT-47, using the hkl-indices as given by N i c k e l et al. (1963):

$$a = 9.46\,\text{Å},\ b = 11.43\,\text{Å},\ c = 5.12\,\text{Å},\ \beta = 91°12';$$

a, b and c have a precision of ± 0.01 Å. This is in good agreement with previously published wodginite unit-cell parameters.

CRYSTAL CHEMISTRY

A difficulty encountered by all authors describing natural wodginite is to express a formula for this mineral. N i c k e l et al. (1963) concluded from the unit-cell dimensions and from the structural relationship with the columbite-tantalite series that the unit-cell should contain 32 oxygen atoms. Because there was no way to group the cations conformably to the space-group requirements (either two sets of four equivalent positions and one of eight equivalent positions (C 2/c), or four sets of four equivalent positions (Cc)), N i c k e l et al. (1963) suggested that the cations might be distributed at random in the 16 available positions and therefore proposed as a formula for wodginite $A_{16}O_{32}$.

K h v o s t o v a et al. (1966) divided the cations in A (Mn^{2+}, Fe^{2+}) and B (Ta, Nb, Sn, Ti, Fe^{3+}) groups on the basis of their ionic radii and obtained an A : B ratio of about 1 :3 after having converted part of the ferrous oxide into ferric oxide to get a cation : anion ratio nearest 1 : 2. N i c k e l et al. (1963) already pointed out the possibility of a higher valency for one or more of the components in wodginite, in order to explain the discrepancies between the measured and the calculated specific gravities of their specimens. This A : B ratio in the order of 1 : 3 was also obtained on the practically tin-free wodginite from Ruanda and on the Bernic Lake material. The formula of the above-mentioned samples can then be expressed as $A_4B_{12}O_{32}$, with the cations ordered as given by K h v o s t o v a et al. (1966).

Another way to order the 16 cations in accordance with the space-group requirements is:

$$(Fe, Mn)_4^{2+}\,(Sn, Ti, Zr)_4^{4+}(Ta, Nb)_8^{5+}O_{32}.$$

In our opinion, this ordered structure, containing about 22-27 wt.% SnO_2 (depending on varying Fe : Mn and Ta : Nb ratios), might represent the possible Sn-end member of wodginite. It appears from the atomic ratios in Table 3 that the tin-content in the analyses 5, 8, and 9 might be the result of a simple substitution:

$$3(Sn, Ti, Zr)^{4+} \rightleftharpoons 1(Fe, Mn)^{2+} + 2(Ta, Nb)^{5+}.$$

Consequently, the chemical formula for the samples 5, 8, and 9 could be written as:

$$(Fe, Mn)^{2+}_{4+x}(Sn, Ti, Zr)^{4+}_{4-3x}(Ta, Nb)^{5+}_{8+2x}O_{32}$$

with x = 0.57, 0.50 and 0.45 for the analyses 5, 8, and 9 respectively. This also means that the iron in these specimens is present as divalent ions. The substitution cannot be applied to the analyses 2, 3, and 4 which have an A : B ratio about 1 : 3; in turn, the analyses 5, 8, and 9 have an A : B ratio of about 1 : 2.5 to 1 : 2.6 only. Analysis 1 does not fit in either of the two systems; this may partly be due to shortcomings in the analytical techniques since it was carried out in 1909. The analyses 6 and 7 are not taken in consideration, their total being only 97%.

The conclusion of these observations is that there seem to be two possible systems to fit the analyses of wodginite into a formule. Both systems are consistent with the space-group requirements, but contradictory to each other. Single crystal study will have to decide which space-group wodginite belongs to. Perhaps the fact that the analyses 2, 3, and 4 were carried out by wet-chemical methods, and the analyses 5, 8, and 9 by electron-microprobe should be regarded as more than pure coincidence.

Comparison with synthetically prepared wodginite gives no solution for this problem. Moreau and Tramasure (1965) obtained two compounds giving diffraction patterns similar to that of natural wodginite: one by fusing Mn_2O_3 and Ta_2O_5, and the other by heating tapiolite with composition

$$(Fe_{0.1-0.3}Mn_{0.9-0.7})Ta_2O_6;$$

no formulas are given for these products. Turnock (1966) obtained a wodginite-type product to which he attributes the formula

$$Mn^{2+}_{2-2w}Fe^{3+}_{3w}Ta_{4-w}O_{12}, \text{ with } 0.08 < w < 0.29.$$

This formula is not in accordance with 32 oxygen atoms needed in the unit-cell of wodginite, and is not consistent with the space-group requirements.

The question of the structure of wodginite apparently can not be answered with the data available at this moment.

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