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ARSENOPALLADINITE FROM ITABIRA, BRAZIL, AND FROM THE STILLWATER COMPLEX, MONTANA*

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Abstract

Type arsenopalladinite from Itabira, Minas Gerais, Brazil, is triclinic $Pd_8(As,Sb)_3$ with As:Sb$\simeq$5:1 and with *a* 7.43, *b* 13.95, *c* 7.35Å, α 92°53′, β 119°30′ and γ 87°51′. Stillwaterite from the Stillwater Complex, Montana, is hexagonal Pd_8As_3, but crystals with the general composition $Pd_8(As,Sb,Sn)_3$ and As:(Sb,Sn)$\simeq$5:1 are most probably triclinic and therefore must be considered to be arsenopalladinite. X-ray powder data are reported for arsenopalladinite from both localities.

Sommaire

L'arsénopalladinite, $Pd_8(As,Sb)_3$, avec As:Sb$\simeq$5:1, provenant de Itabira, Minas Gerais, au Brézil, est triclinique: *a* 7:43, *b* 13.95, *c* 7.35Å, α 92°53′, β 119°30′ et γ 87°51′. La stillwatérite, Pd_8As_3, provenant du Stillwater Complex, au Montana, est hexagonale, mais ses cristaux, dont la composition générale est $Pd_8(As,Sb,Sn)_3$ et avec As:(Sb,Sn)$\simeq$5:1, sont très probablement tricliniques. Par conséquent, ils doivent être considérés comme étant de l'arsénopalladinite. On fournit les données des diagrammes de poudre aux rayons X pour l'arsénopalladinite provenant des deux gîtes.

Introduction

Arsenopalladinite from Itabira, Minas Gerais, Brazil, originally thought to be hexagonal Pd_3As, was redefined by Clark *et al.* (1974) as triclinic $Pd_5(As,Sb)_2$. The study of arsenopalladinite has been complicated by many factors, the most significant of which were the very poor X-ray diffraction characteristics of the mineral and the lack of information on the phases and phase relations in the Pd-As-Sb system. The discovery by Cabri *et al.* (1975) of the new hexagonal mineral stillwaterite, $Pd_8(As,Sb)_3$, as well as a closely related unnamed Pd_5As_2 mineral from the Stillwater Complex, Montana, resulted in a joint examination of the arsenopalladinite-stillwaterite relation. This was particularly pressing since the composition of stillwaterite reported by Cabri *et al.* extended along the hypothetical Pd_8As_3–Pd_8Sb_3 join to the point that it overlapped some arsenopalladinite compositions.

Materials and Methods of Investigation

The thirteen arsenopalladinite grains from Itabira, Brazil reported by Clark *et al.* (1974) were re-examined. These grains contain inclusions of hematite, PdO, quartz, palladian Au, and atheneite, $(Pd,Hg)_3As$. "Stillwaterite" grain No. 7 from the Stillwater Complex, Montana, whose composition was given as $Pd_{8.01}(As_{2.52}Sb_{0.27}Sn_{0.21})$ (Cabri *et al.* 1975, Table 2, No. 8) was extracted from the polished section and studied by X-ray diffraction.

Compositions of the arsenopalladinites were determined at CANMET with an MAC probe, at 25 kV and 0.03 μA specimen current, using the following X-ray lines and synthetic standards: Pd$L\alpha$, As$K\alpha$ (Pd_3As); Sb$L\alpha$ ($Pd_5As_{1.49}Sb_{0.51}$); and Cu$K\alpha$($Pd_{4.85}Cu_{0.15}Sb_2$). The standards and the arsenopalladinites were freshly polished before analysis because of tendencies to tarnish, even when carbon-coated. Corrections to the X-ray data were applied using the EMPADR VII computer program of Rucklidge & Gasparrini (1969) and the homogeneity of the analyzed minerals determined from the homogeneity index built into the program. A homogeneity index

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TABLE 1. ELECTRON PROBE ANALYSES OF ARSENOPALLADINITE FROM ITABIRA, BRAZIL.

Grain no.	Weight percent Pd	Cu	As	Sb	Total	Atomic proportions Pd	Cu	ΣPd	As	Sb	ΣAs
1.	76.8(2)*	tr.**	17.0(1)	5.4(1)	99.2	8.00	-	8.00	2.51	0.49	3.00
2.	77.6(2)	tr.	17.0(1)	5.5(1)	100.1	8.01	-	8.01	2.49	0.50	2.99
3.††	77.3(2)	0.06	18.2(1)	3.8(1)	99.36	7.98	0.01	7.99	2.67	0.34	3.01
4.†	77.2(1)	0.05	17.0(1)	5.6(1)	99.85	7.99	0.01	8.00	2.50	0.50	3.00
5.	78.3(2)	tr.	16.5(4)	5.4(2)	100.2	8.09	-	8.09	2.42	0.49	2.91
6.	77.9(2)	tr.	16.5(6)	5.2(2)	99.6	8.09	-	8.09	2.44	0.47	2.91
7.††	77.5(1)	0.10	18.6(1)	3.1(1)	99.30	7.98	0.02	8.00	2.72	0.28	3.00
8.	77.2(2)	tr.	17.0(1)	5.6(1)	99.8	7.99	-	7.99	2.50	0.51	3.01
9.	77.3(1)	tr.	16.8(1)	5.4(1)	99.5	8.03	-	8.03	2.48	0.49	2.97
10.	78.2(2)	tr.	17.1(1)	5.6(1)	100.9	8.01	-	8.01	2.49	0.50	2.99
11.	77.5(2)	tr.	16.4(5)	5.4(1)	99.3	8.08	-	8.08	2.43	0.49	2.92
12.	78.5(3)	tr.	16.9(2)	5.5(1)	100.9	8.05	-	8.05	2.46	0.49	2.95
13.†	77.0(2)	0.04	17.1(2)	5.5(1)	99.64	7.98	0.01	7.99	2.51	0.50	3.01

*The number in parentheses represents the homogeneity index. **tr = trace, i.e., <0.03 wt. %. †Grain X-rayed.
††Identity as arsenopalladinite requires X-ray analysis.

greater than 3 is equivalent to $>3\sigma$ in observed variance and thus such samples are inhomogeneous. X-ray powder diffraction photographs were taken with a 57.3 mm Gandolfi camera and single-crystal studies were performed using a precession camera.

Electron Probe Analysis

Arsenopalladinite

The analyses of arsenopalladinite are reported in Table 1 and represent 7 or 8 spot analyses for all but grain No. 13 which was analyzed by 15 spot analyses. Au and Hg were sought but not detected. Two observations may be made: first, the results for the homogeneous grains may be calculated on the basis of eleven atoms where an 8:3 stoichiometry for Pd:(As,Sb) is apparent. The actual range for the homogeneous grains is 7.99-8.05:2.95-3.01. This range is further narrowed to 7.99-8.03:2.97-3.01 if one removes a grain with borderline homogeneity (No. 12). The three inhomogeneous grains (Nos. 5, 6, and 11) show the largest scatter of values for As. The second observation is that eight of the ten grains considered to be homogeneous have As:Sb=5:1.

The thirteen grains were then re-analyzed at the British Museum (Natural History) with a Cambridge Geoscan microanalyzer, using the synthetic standard $Pd_5As_{1.49}Sb_{0.51}$ and the computer program by Mason *et al.* (1969). The results confirmed the suggested 8:3 stoichiometry. The data comparison was excellent for As and Sb (up to 0.7 wt. % for As and 0.1 wt. % for Sb) but the BM(NH) analyses for Pd were slightly higher by up to 1.4 wt. % with the totals averaging 100.4%. This is within acceptable experimental error, considering that different instruments and correction programs were used.

Stillwaterite

Seven of the thirteen stillwaterite grains quantitatively analyzed by Cabri *et al.* (1975) had no elemental substitutions for As and were essentially Pd_8As_3. None of these thirteen grains needed re-analysis with the microprobe but six grains with some substitution for As required a detailed re-examination by X-ray diffraction because of composition overlap with the arsenopalladinite.

X-Ray Diffraction Investigation

Arsenopalladinite

As indicated in Table 1, two grains of arsenopalladinite were removed from the polished section for X-ray diffraction. The powder pattern of grain 13 proved too poor for any conclusive interpretation or measurements. Half of grain 4 was removed from the section and four fragments were examined by the X-ray precession method using Mo$K\alpha$ radiation. All four fragments were polycrystalline and for only one was it possible to determine the space-group symmetry with reliability. The cell chosen, P1 or $P\bar{1}$, is dimensionally pseudohexagonal (Table 2).

The X-ray powder diffraction patterns obtained from fragments of grain 4 were also of poor quality but better resolved than the pattern given by grain No. 13. The pattern of fragment 4c is compared in Table 3 to that of a grain from the Stillwater Complex as is discussed below. The diffraction lines were indexed, guided by the intensities on the single-crystal

TABLE 2. CRYSTAL DATA OF ARSENOPALLADINITE

	Itabira, Brazil		Stillwater Complex
	Clark *et al.* (1974)*	Gr. 4c**	Montana, Gr. 7.***
a Å	7.399	7.43	7.38
b	14.063	13.95	13.85
c	7.352	7.35	7.36
α	92°03'	92°53'	91°06'
β	118°57'	119°30'	119°53'
γ	95°54'	87°51'	86°49'
Z	6	6	6

* Back-reflection oscillation photographs
** Precession method
***Calculated from powder diffraction data

photographs, using the reduced cell given in Table 2.

Stillwaterite

Six of the thirteen stillwaterite grains quantitatively analyzed by Cabri *et al.* (1975) had some substitution of As, usually by Sb and Sn. The weak Gandolfi pattern of one of these (No. 13) had been indexed by Cabri *et al.* as hexagonal stillwaterite though there were intensity differences with both natural and synthetic Pd_8As_3. This grain as well as another (Cabri *et al.*, Table 2, grain 7, No. 8) gave precession photographs that were too poor for cell-dimension measurements due to the polycrystalline nature of the grains. The grains are pseudo-hexagonal, hence the previous indexing as hexagonal, but are considered to have a unit cell similar to that of arsenopalladinite grain 4. The cell parameters of grain 7 (Table 2) were calculated from the powder diffraction data which were indexed in the same manner as those of the arsenopalladinite grain 4 (Table 3).

Discussion

A detailed re-examination of type arsenopalladinite from Itabira has confirmed the triclinic symmetry of the mineral and has shown that the ideal composition is close to $Pd_8(As,Sb)_3$ with As:Sb=5:1. Some grains of "arsenopalladinite" are not homogeneous and a few have less Sb substitution for As. It is not certain whether the latter also have triclinic symmetry. The arsenopalladinite powder pattern is reported for the first time.

"Stillwaterite" with Sb and Sn substitution for As close to 5:1 is pseudo-hexagonal and is considered to have the same symmetry as arsenopalladinite. The effect of Sn substitution on the intensities of the powder pattern or on the symmetry is not known. Though stillwaterite of composition Pd_8As_3 is definitely hexagonal,

TABLE 3. X-RAY POWDER DIFFRACTION DATA OF ARSENOPALLADINITE

Itabira, Brazil*				Stillwater Complex Montana**		
I	d_{meas}	d_{calc}	$h\ k\ l$	I	d_{meas}	d_{calc}
1B	2.63	2.64	$\bar{2}\ 3\ 0$			
1	2.49	2.49	$\bar{2}\ 4\ 1$			
½	2.39	2.39	$\bar{3}\ 1\ 1$			
6	2.34	2.35	$\bar{2}\ 1\ 3$	5	2.35	2.36
½	2.31	2.31	$2\ 2\ \bar{3}$	½	2.30	2.30
2	2.28	2.28	$1\ 5\ \bar{2}$			
2	2.19	2.19	$3\ 3\ \bar{2}$	2	2.18	2.18
10	2.13	2.13	$0\ 0\ 3$	10	2.13	2.13
			$2\ 4\ 1$	½	2.02	2.02
½	1.90	1.90	$2\ 6\ 0$	½	1.92	1.92
½	1.85	1.85	$4\ 1\ \bar{2}$	2	1.84	1.84
1	1.78	1.78	$2\ 7\ \bar{1}$			1.83
½	1.75	1.75	$\bar{4}\ 1\ 3$	1	1.75	1.75
1	1.67	1.67	$3\ 3\ 1$			
1	1.64	1.64	$\bar{3}\ 6\ 2$	½	1.62	1.62
½	1.54	1.54	$\bar{4}\ 2\ 4$	½	1.54	1.54
½	1.52	1.52	$1\ 9\ \bar{1}$	1	1.51	1.51
1	1.47	1.47	$\bar{4}\ 5\ 3$			
4	1.41	1.41	$\bar{2}\ 6\ 4$	1B	1.43	1.43
2	1.39	1.39	$1\ 1\ 4$	1B	1.39	1.39
1	1.36	1.36	$5\ 3\ \bar{1}$	1	1.35	1.35
			$3\ 9\ 0$	½B	1.28	1.28
3	1.24	1.24	$\bar{5}\ 2\ 5$	½	1.24	1.24
3	1.21	1.21	$\bar{4}\ 7\ 4$	2	1.22	1.22
½	1.206	1.206	$5\ 7\ \bar{2}$	1	1.209	1.209
			$4\ 8\ 0$	½	1.205	1.205
½	1.192	1.192	$\bar{4}\ 1\ 6$	½	1.197	1.197

57.3 mm Gandolfi camera; Co radiation (λ=1.7902Å)
*Grain 4c; **grain 7; B = broad.

it is also not known whether those grains with 8:3 stoichiometry and As: (Sb,Sn) greater than 5:1 have hexagonal or triclinic symmetry.

It is noteworthy that though the cell edges of the three grains reported in Table 2 are reasonably close to each other, there are larger differences in the angles, especially in γ. These may represent genuine, grain-to-grain variations or may be due to the poor quality of the material, and are a further aspect of the complications associated with arsenopalladinite.

Conclusions

Type arsenopalladinite is triclinic $Pd_8(As,Sb)_3$ with As:Sb $\simeq$5:1 and with cell dimensions a 7.43, b 13.95, c 7.35Å, α 92°53′, β 119°30′, γ 87°51′ and Z = 6. Type stillwaterite is Pd_8As_3, with hexagonal symmetry, but compositionally similar grains of $Pd_8(As,Sb,Sn)_3$ with As:(Sb,Sn) $\simeq$5:1 are considered to be tin-bearing arsenopalladinite.

The composition at which a change from hexagonal to triclinic symmetry occurs between Pd_8As_3 and $Pd_8As_{2.5}(Sb,Sn)_{0.5}$ has not been determined.

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