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## Holtite and dumortierite from the Szklary Pegmatite, Lower Silesia, Poland

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### ABSTRACT

The Szklary holtite is represented by three compositional varieties: (1) Ta-bearing (up to 14.66 wt.% Ta<sub>2</sub>O<sub>5</sub>), which forms homogeneous crystals and cores within zoned crystals; (2) Ti-bearing (up to 3.82 wt.% TiO<sub>2</sub>), found as small domains within the core; and (3) Nb-bearing (up to 5.30 wt.% Nb<sub>2</sub>O<sub>5</sub>) forming the rims of zoned crystals. All three varieties show variable Sb+As content, reaching 19.18 wt.% Sb<sub>2</sub>O<sub>3</sub> (0.87 Sb a.p.f.u.) and 3.30 wt.% As<sub>2</sub>O<sub>3</sub> (0.22 As a.p.f.u.) in zoned Ta-bearing holtite, which constitutes the largest Sb+As content reported for the mineral. The zoning in holtite is a result of Ta-Nb fractionation in the parental pegmatite-forming melt together with contamination of the relatively thin Szklary dyke by Fe, Mg and Ti. Holtite and the As- and Sb-bearing dumortierite, which in places overgrows the youngest Nb-bearing zone, suggest the following crystallization sequence: Ta-bearing holtite → Ti-bearing holtite → Nb-bearing holtite → As- and Sb-bearing, (Ta,Nb,Ti)-poor dumortierite → As- and Sb-dominant, (Ta,Nb,Ti)-free dumortierite-like mineral (16.81 wt.% As<sub>2</sub>O<sub>3</sub> and 10.23 wt.% Sb<sub>2</sub>O<sub>3</sub>) with (As+Sb) > Si. The last phase is potentially a new mineral species, Al<sub>6</sub>□B(Sb,As)<sub>3</sub>O<sub>15</sub>, or Al<sub>5</sub>□<sub>2</sub>B(Sb,As)<sub>3</sub>O<sub>12</sub>(OH)<sub>3</sub>, belonging to the dumortierite group. The Szklary holtite shows no evidence of clustering of compositions around ‘holtite I’ and ‘holtite II’. Instead, the substitutions of Si<sup>4+</sup> by Sb<sup>3+</sup>+As<sup>3+</sup> at the Si/Sb sites and of Ta<sup>5+</sup> by Nb<sup>5+</sup> or Ti<sup>4+</sup> at the Al(1) site suggest possible solid solutions between: (1) (Sb,As)-poor and (Sb,As)-rich holtite; (2) dumortierite and the unnamed (As+Sb)-dominant dumortierite-like mineral; and (3) Ti-bearing dumortierite and holtite, i.e. our data provide further evidence for miscibility between holtite and dumortierite, but leave open the question of defining the distinction between them. The Szklary holtite crystallized from the melt along with other primary Ta-Nb-(Ti) minerals such as columbite-(Mn), tantalite-(Mn), stibiotantalite and stibiocolumbite as the availability of Ta decreased. The origin of the parental melt can be related to anatexis in the adjacent Sowie Mountains complex, leading to widespread migmatization and metamorphic segregation in pelitic-psammitic sediments metamorphosed at ~390–380 Ma.

**KEYWORDS:** holtite, dumortierite, Szklary pegmatite, Poland, electron microprobe analyses, solid solutions.

### Introduction

HOLTITE is a very rare Ta- and Sb-bearing aluminium borosilicate belonging to the dumor-

tierite group, known from pegmatites at only three localities worldwide. The mineral was first identified by Pryce (1971) in pegmatite specimens from an alluvial tin deposit near Greenbushes, southwestern Western Australia; Voloshin *et al.* (1977) found holtite in a pegmatite at Mount Vasin-Myl’k, Voron’i Tundry, Kola Peninsula,

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Russia, and Pieczka and Marszałek (1996) described the mineral from a pegmatite at Szklary in Lower Silesia, Poland.

Hoskins *et al.* (1989) obtained a formula for holtite from the type locality of  $(\text{Si}_{2.25}\text{Sb}_{0.75})\text{B}[\text{Al}_6(\text{Al}_{0.43}\text{Ta}_{0.27}\square_{0.30})\text{O}_{15}(\text{O},\text{OH})_{2.25}]$ , and discussed two main substitutions,  $\text{Sb}^{3+} + \square \rightarrow \text{Si}^{4+} + \text{OH}^-$  and  $^{3/5}\text{Ta}^{5+} + ^{2/5}\square \rightarrow \text{Al}^{3+}$ , incorporating  $\text{Sb}^{3+}$  in triangular pyramidal coordination at sites close to the tetrahedral sites and  $\text{Ta}^{5+}$  at the Al(1) octahedral site of the dumortierite-holtite structure. Voloshin *et al.* (1987) recognized low-Sb ‘holtite I’ and high-Sb ‘holtite II’ in the material from the Kola Peninsula. However, Locock *et al.* (2006) discouraged use of these terms because: (1) Si is dominant at the tetrahedral sites in both varieties; (2) there are no known structural differences between them; and (3) the Commission of New Minerals, Nomenclature and Classification of the International Mineralogical Association had not approved such usage.

Groat *et al.* (2009) presented structural results of holtite from all of the known occurrences, along with a discussion on substitution and ordering in the holtite structure. Assuming the substitutions presented above are the only significant ones in relating dumortierite compositions to holtite compositions, Groat *et al.* (2009) gave a general holtite stoichiometry of  $\text{Al}_{7-(5x+y+z)/3}(\text{Ta}, \text{Nb})_x \square_{(2x+y+z)/3} \text{BSi}_{3-y}(\text{Sb}, \text{As})_y \text{O}_{18-y-z}(\text{OH})_z$ , where  $x$  denotes the total number of pentavalent cations,  $y$  is the total amount of Sb+As, and  $z$  is the total amount of OH, with  $z \leq y$ . This formula does not take into account divalent and tetravalent cations at the Al(1) site or substitutions at the Si or (Sb,As) sites of the dumortierite-holtite structure. Moreover, Groat *et al.* (2009) noted that their crystal-structure refinements did not reveal any differences in cation ordering that might distinguish ‘holtite I’ from ‘holtite II’. Given also that the two varieties do not qualify as distinct species according to the dominant-valency rule (Hatert and Burke, 2008), Groat *et al.* (2009) advised that “use of the terms holtite I and holtite II be discontinued”.

There are relatively few analyses of holtite and no studies sufficiently systematic to fully characterize holtite composition from any one locality. However, the compositional variation in the Voron’i Tundry holtite and zoning in the Szklary holtite reported by Voloshin *et al.* (1977, 1987) and Pieczka (2010), respectively, clearly

point to the need for systematic studies of holtite from each locality. Such chemical characterization could also provide information about stages of holtite crystallization in the geochemical evolution of pegmatites. In this paper, we present a systematic chemical study of the Szklary holtite and coexisting As- and Sb-bearing dumortierite, both of which show extensive compositional variations. These data can be applied to examining the complex relationships between holtite and dumortierite. For the purposes of description of these two dumortierite-group minerals from the Szklary pegmatite, compositions with  $\text{Ta} + \text{Nb} + \text{Ti} > 0.25$  atoms per formula unit (a.p.f.u.) are being called holtite and compositions with  $\text{Ta} + \text{Nb} + \text{Ti} < 0.1$  a.p.f.u., dumortierite.

## Geological setting

The Szklary massif is situated ~60 km south of Wrocław and 6 km north of Ząbkowice Śląskie in the southern part of the Mississippian Niemcza shear zone (Fig. 1). The zone extends along the eastern edge of the Sowie Mountains block in the northeastern part of the Bohemian Massif (the Central Sudetes and the Fore-Sudetic block, southwestern Poland). The Szklary massif is one of several small bodies of serpentinized ultramafic and mafic rocks that rim the Sowie Mountains gneissic complex, considered parts of a tectonically fragmented Sudetic ophiolite suite (Majerowicz and Pin, 1986) ~420 Ma old (Oliver *et al.*, 1993), composed of weakly serpentinized harzburgites, lherzolites and pyroxenites containing enclaves of amphibolites and rodingites. The serpentinites are crosscut by numerous aplite, and less commonly, lamprophyre veins. The Szklary pegmatite (~390 Ma, Pb-U-Th dating of cheralite; Pieczka, unpubl. data) is similar to pegmatites in the nearby Sowie Mountains gneissic complex with respect to the mode of occurrence, internal structure, mineral composition and age of formation.

In the Sowie Mountains complex, metamorphism of pelitic–psammitic sediments reached upper amphibolite facies and led to widespread migmatization and metamorphic segregation. Intrusion of granitic magma during uplift of the Sowie Mountains complex at ~374–380 Ma (van Breemen *et al.*, 1988, Timmermann *et al.*, 2000) led to the formation of dykes and veins of pegmatite containing abundant black tourmaline and ranging in

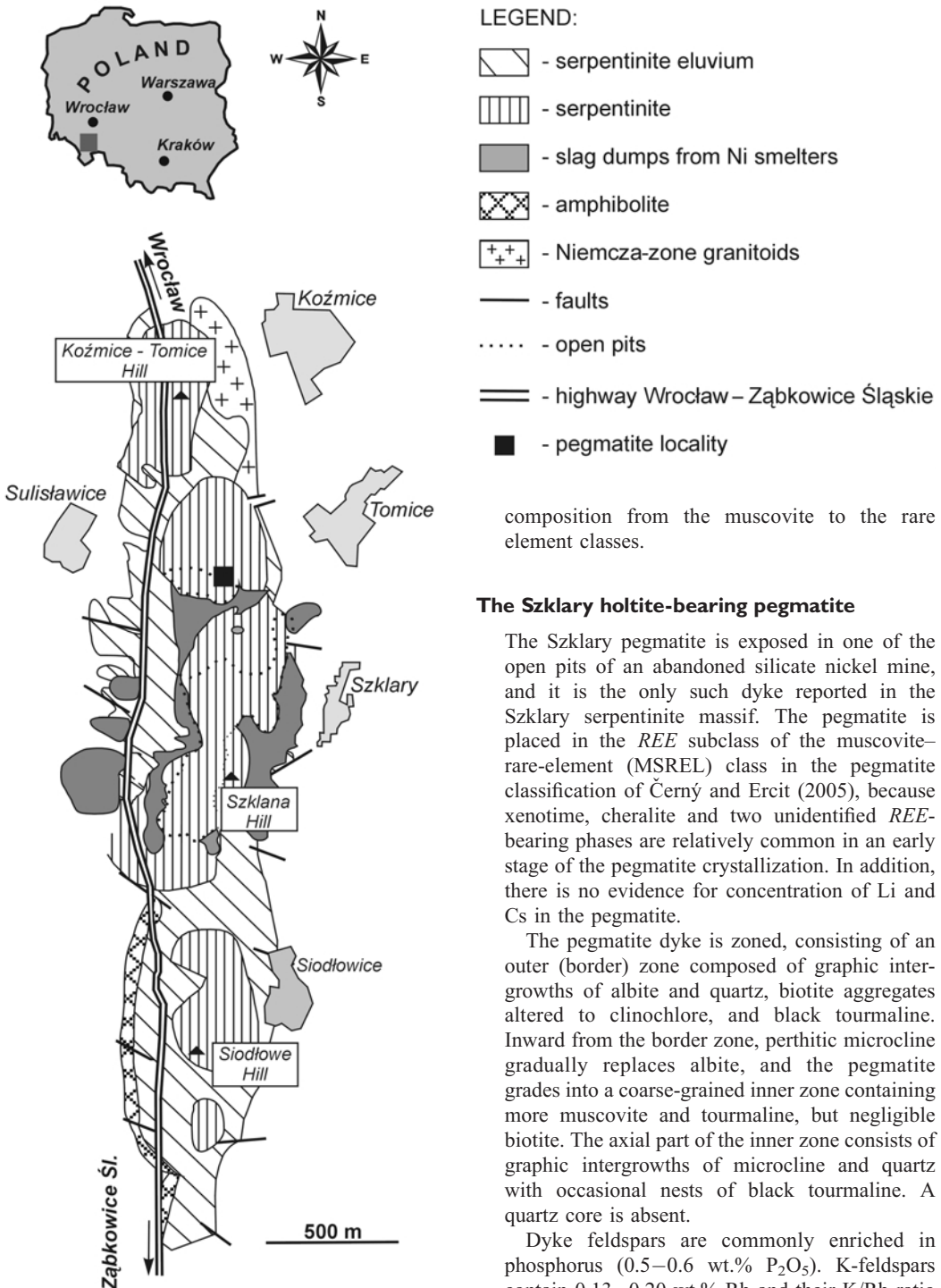


FIG. 1. Geological sketch of the Szklary massif (after Niśkiewicz, 1967, Michalik, 2000).

mediate members of the schorl–dravite series (Pieczka and Kraczk, 1996) or, much less frequently, by blue dravite representing a transitional member among the dravite, schorl and olenite end-members (Pieczka, 2007).

Aggregates of holtite crystals, up to 5 mm in size and creamy-white to yellow, yellow with a brownish tint and yellowish-grey in colour, are generally found in the inner zone of the dyke among crystals of microcline, quartz and black tourmaline; holtite is less common within aggregates of Mn-bearing oxide minerals or as inclusions in quartz. Holtite crystals range from prismatic and acicular to asbestiform and are up to 1 mm long and to 50  $\mu\text{m}$  in diameter, though usually they are smaller. Holtite is associated with

stibiocolumbite and microcline having numerous disseminated inclusions of native antimony, native bismuth, paradocrasite, stibarsen and less commonly native arsenic. Locally, in interstices between holtite crystals, stibiocolumbite forms larger aggregates enclosing holtite (Fig. 2). Stibiotantalite has never been found in close proximity to holtite in the pegmatite.

Rare chrysoberyl occurs within muscovite aggregates, and less commonly in the graphic intergrowths of feldspars with quartz. It forms single tabular or twinned crystals on  $\{130\}$ , usually a few millimeters in size, light green to yellowish green, transparent to translucent, in places intergrown with xenotime or zircon. No beryl has been found either within crystals of

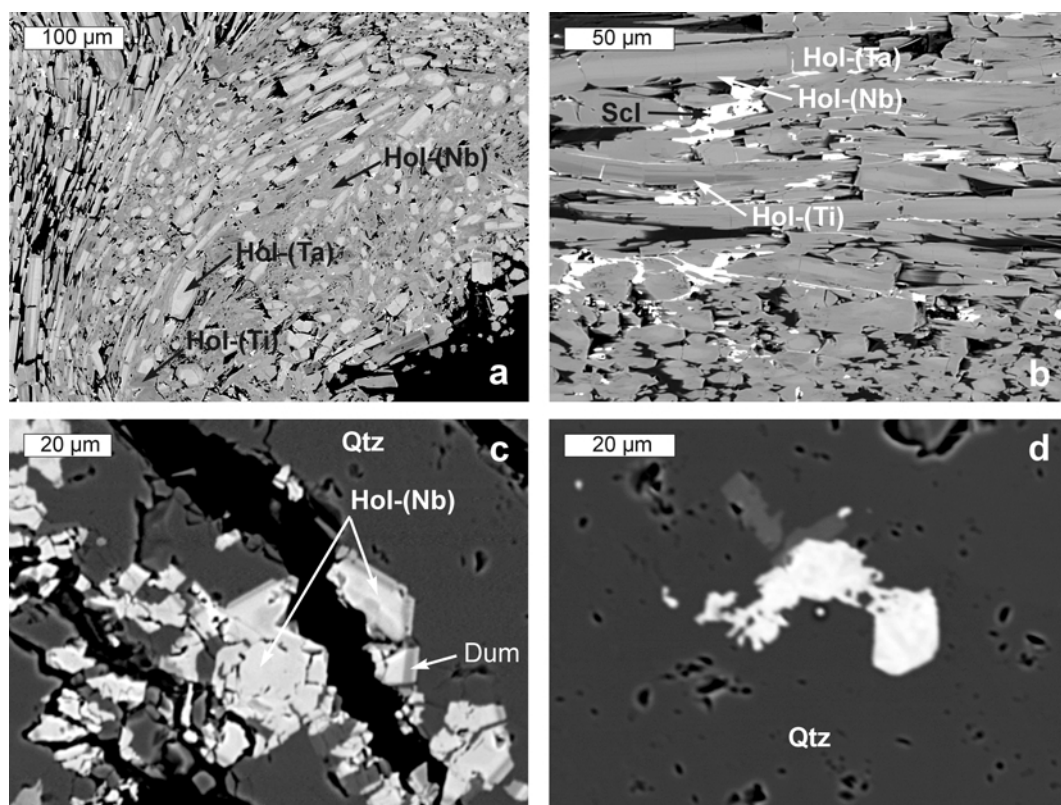


FIG. 2. Representative BSE images of holtite and dumortierite in the Szklary pegmatite: (a) crosswise sections of holtite showing Ta-bearing core and Nb-bearing rim; (b) longitudinal sections of zoned holtite with streaks of Ti-bearing holtite (dark grey) and stibiocolumbite in interstices among holtite crystals; (c) crystal of Nb-bearing holtite overgrown by As- and Sb-bearing dumortierite surrounded by quartz; (d) inclusions in quartz of an extremely (As,Sb)-enriched dumortierite-like phase containing negligible Ta, Nb and Ti. Abbreviations: Hol-(Ta) – Ta-bearing holtite, Hol-(Nb) – Nb-bearing holtite, Hol-(Ti) – Ti-bearing holtite, Scl – stibiocolumbite, Dum – dumortierite, Qtz – quartz.

chrysoberyl or anywhere else in the Szklary dyke. Although the presence of cordierite in the border zone suggests that the pegmatite has been affected by metamorphism, we doubt that chrysoberyl formed by the breakdown of beryl + alkali feldspar reported in metamorphosed pegmatites elsewhere (Franz and Morteani, 1984). Instead, we suggest that chrysoberyl crystallized directly from an anatectic melt. A talc + chlorite + vermiculite contact zone up to ~10 cm thick between the pegmatite on one side and serpentinite or amphibolite on the other (Piecza, 2000) could be an altered skarn formed by reaction between the melt and country rocks, resulting in loss of SiO<sub>2</sub> and increase of Al<sub>2</sub>O<sub>3</sub> in the melt, thereby favouring the crystallization of chrysoberyl.

Based on conditions of metamorphism in the Sowie Mountains complex (from 5–7 kbar and 500–600°C to 4–5 kbar and 620–670°C to 700–730°C; Żelaźniewicz, 1987, 1990), and the same age of the metamorphic events (374–380 Ma; van Breemen *et al.*, 1988; Timmermann *et al.*, 2000) as the age of the Szklary pegmatite, we conclude that the Szklary dyke represents an injection of mobilized anatectic melt during a significant HT–MP thermal event into a part of the Sudetic ophiolite currently corresponding to the Szklary massif, which in the Late Devonian was already in contact with the Sowie Mountains complex (Żelaźniewicz, 1990).

### Analytical methods and formula calculation

Compositions of zoned holtite crystals were analysed at the Inter-Institute Analytical Complex for Minerals and Synthetic Substances of the University of Warsaw using a Cameca SX-100 electron microprobe (EMP) operating in wavelength-dispersive spectroscopic (WDS) mode under the following conditions: accelerating voltage – 15 kV, beam current – 20 nA, peak count-time – 20 s, background time – 10 s, beam diameter – 1–2 µm. The following standards, analytical lines and crystals were used: Al – orthoclase (Kα, TAP), Si – diopside (Kα, TAP), P – apatite (Kα, PET), Sc – pure Sc (Kα, PET), Ti – rutile (Kα, LIF), Fe – hematite (Kα, LIF), As – GaAs (Lα, TAP), Nb – pure Nb (Lα, PET), Sb – InSb (Lβ, PET), Ta – pure Ta (Mα, TAP). The amounts of Mg, Mn, Zr, Sn, W and Bi were below detection using WDS. Compositions of homogeneous holtite (WPH) were obtained at the University of British Columbia using a Cameca

SX-50 microprobe (WDS mode) with the following operating conditions: accelerating voltage – 20 kV, beam current – 20 nA, peak count-time – 20 s, background time – 10 s, beam diameter – 10 µm. The following standards and X-ray analytical lines were used: kyanite – Al(Kα), Si(Kα); apatite – P(Kα), pure Sc – Sc(Kα), rutile – Ti(Kα), synthetic fayalite – Fe(Kα), tennantite – As(Kα), columbite – Nb(Lα), tetrahedrite – Sb(Lα) and microlite – Ta(Mα). Data reduction was done with the ‘PAP’ procedure (Pouchou and Pichoir, 1985) in both laboratories.

Most analyses gave acceptable totals ranging from 97.94 to 100.90 wt.%; an exception is WPH holtite, for which totals range from 93.85 to 96.62 wt.%. The low totals could have resulted from infiltration of epoxy between very fine holtite fibres in this sample, creating a situation analogous to epoxy soaking very finely porous materials (Sorbie *et al.*, 2004; Grew *et al.*, 2008), in which analytical totals decreased because the target material was diluted by epoxy hit by the relatively wide 10 µm electron beam used at the University of British Columbia. This problem appears to have been averted at the University of Warsaw using a 1–2 µm beam, sufficiently narrow to fit on the holtite crystals without hitting epoxy.

Holtite is a mineral the formula of which is very difficult to calculate due to vacancies present not only at the cationic, but also at the anionic sites. Therefore all analyses were normalized by iteration to (O+OH) = (18–As–Sb) a.p.f.u. Assuming 1.000 B a.p.f.u. and OH<sup>–</sup> to be = (Sb+As), i.e. z = y, which gave reasonable H<sub>2</sub>O contents for holtite from Greenbushes and Voron'i Tundry (Groat *et al.*, 2009), these authors' formula for holtite simplifies to  $A_{17-(5x+2y)/3} (Ta, Nb)_x \square_{(2x+2y)/3} BSi_{(3-y)}(Sb,As)_y O_{18-2y}(OH)_y$ . Because the sum Si+P+As+Sb is always <3 a.p.f.u., we have assumed that Al also occupies a tetrahedral site and have added sufficient Al to make up the deficiency, i.e. Si+P+As+Sb+<sup>IV</sup>Al = 3. This assumption is supported by structural evidence for tetrahedrally coordinated Al in dumortierite, e.g. Alexander *et al.* (1986) reported up to 0.15 <sup>IV</sup>Al a.p.f.u. substituting for Si<sup>4+</sup> in some Fe- and Ti-poor samples, and Fuchs *et al.* (2005) found a similar content of 0.15–0.17 <sup>IV</sup>Al a.p.f.u. in two samples of dumortierite from Lower Austria. The vacancy at the octahedral sites was calculated from a modified version of the

relationship given by Groat *et al.* (2009) and taking into account various divalent and tetra-valent cations present in the holtite. We have assumed that the small amount of Fe present (mostly <0.4 wt.% FeO, and none >0.77 wt.% FeO, Table 1a) is entirely Fe<sup>2+</sup> because Fe<sup>3+</sup> contents are not significant in associated primary Nb-Ta oxides in the pegmatite (Piecicka, 2010).

### Compositional variations in the Szklary holtite

Of the three known localities for holtite, only the Szklary pegmatite has Nb-bearing and Ti-bearing holtite in addition to Ta-bearing holtite. A complete set of spot EMP analyses of the Szklary holtite and dumortierite is presented in Table 1 (Table 1a, containing all the data has been deposited with the editor and available from [www.minersoc.org/pages/e\\_journals/dep\\_mat\\_mm.html](http://www.minersoc.org/pages/e_journals/dep_mat_mm.html); a representative selection of these data are given in Table 1b): (1) homogeneous holtite WPH; (2–5) holtite richest in Ta, Nb, Ti or Sb in the zoned crystals; (6, 7) holtite overgrown by As- and Sb-bearing dumortierite (Fig. 2c); (8) As- and Sb-bearing dumortierite and (9) a dumortierite-like phase containing negligible Ta, Nb and Ti, as well as more Sb+As than Si ('X-phase'). The dumortierite-like phase is found

as a few tiny inclusions not exceeding 20 µm across in quartz (Fig. 2d). It has a composition suggesting a relationship with dumortierite, but we do not yet have crystallographic data to confirm this suggestion.

The Szklary holtite varies widely considering Ta, Nb and Ti amounts substituting for Al at the Al(1) site (Fig. 3), and in occupancy of the (Sb, As) sites (Fig. 4). This compositional heterogeneity is evident in the majority of holtite crystals, which show a distinct zoning with a core formed by a Ta-bearing variety surrounded by a rim of a Nb-bearing variety a few micrometers wide. There are also dark grey streaks up to 5 µm wide of Ti-bearing holtite located within the core or along the core/rim boundary. Holtite without visible compositional zoning was found in only a few aggregates that are generally composed of very thin acicular to asbestiform crystals.

Figure 4a shows the relationship between Sb+As and Si, which refers only to occupancy of the Si and (Sb<sup>3+</sup>, As<sup>3+</sup>) sites, the latter being partially occupied triangular pyramids. The compositions plot close to the line Si+As+Sb = 3 showing an inverse relationship between the Si<sup>4+</sup> content and the (Sb<sup>3+</sup>+As<sup>3+</sup>) content, which is consistent with each of the two (Sb, As) sites being

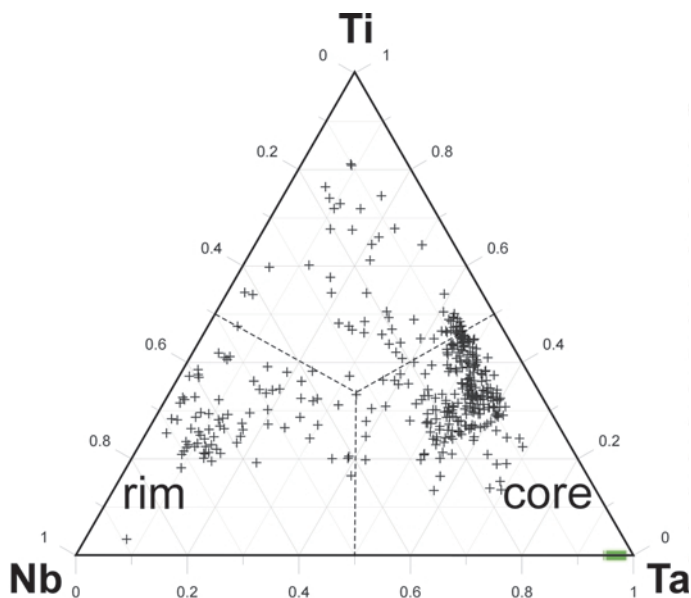


FIG. 3. Composition of the Szklary holtite in the Nb-Ta-Ti ternary system (black crosses – zoned holtite, green crosses clustered near Ta corner – homogeneous WPH holtite).

## HOLTITE AND DUMORTIERITE FROM POLAND

TABLE 1(b). Selected compositions of the Szklary holtite, As- and Sb-rich dumortierite, and a dumortierite-like mineral containing negligible Ta, Nb and Ti.

	1	2	3	4	5	6	7	8	9
	WPH-10	Sz43a/28	Sz32/9	Sz34/54	Sz39d/81	Sz5B/1	Sz5B/3	Sz5B/5	Sz5A/2
Wt.%									
P <sub>2</sub> O <sub>5</sub>	0.55	0.00	0.00	0.00	0.25	0.14	0.31	0.23	0.99
Nb <sub>2</sub> O <sub>5</sub>	0.19	0.91	5.30	0.79	1.14	4.37	5.16	0.36	0.00
Ta <sub>2</sub> O <sub>5</sub>	14.66	7.73	1.06	1.12	5.33	1.57	1.15	0.21	0.00
SiO <sub>2</sub>	20.45	17.27	17.88	21.57	15.87	19.65	19.58	23.38	12.90
TiO <sub>2</sub>	0.00	0.78	0.95	3.82	1.12	0.56	0.26	0.24	0.27
B <sub>2</sub> O <sub>3</sub> *	5.06	5.18	5.43	5.58	5.28	5.51	5.58	5.83	5.75
Al <sub>2</sub> O <sub>3</sub>	45.85	44.61	47.55	50.07	46.11	50.44	50.84	56.09	51.88
Sc <sub>2</sub> O <sub>3</sub>	0.15					0.21	0.25	0.17	0.20
As <sub>2</sub> O <sub>3</sub>	1.98	1.70	2.14	2.88	3.30	3.90	4.39	5.56	16.81
Sb <sub>2</sub> O <sub>3</sub>	5.57	18.85	18.25	11.78	19.18	10.64	10.97	6.50	10.23
FeO	0.00	0.16	0.22	0.12	0.27	0.75	0.45	0.38	0.20
H <sub>2</sub> O*	0.53	1.32	1.32	0.99	1.49	1.01	1.08	0.91	2.16
Total	94.99	98.50	100.11	98.72	99.35	98.75	100.01	99.85	101.39
Atomic contents									
P <sup>5+</sup>	0.053	0.000	0.000	0.000	0.024	0.013	0.027	0.019	0.084
Si <sup>4+</sup>	2.343	1.933	1.908	2.238	1.742	2.068	2.032	2.324	1.300
As <sup>3+</sup>	0.138	0.115	0.138	0.182	0.220	0.249	0.276	0.336	1.035
Sb <sup>3+</sup>	0.264	0.871	0.804	0.504	0.868	0.462	0.470	0.267	0.429
<sup>(4)</sup> Al <sup>3+</sup>	0.202	0.081	0.150	0.076	0.146	0.208	0.195	0.055	0.162
ΣT	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000
B <sup>3+</sup>	1	1	1	1	1	1	1	1	1
Nb <sup>5+</sup>	0.010	0.046	0.256	0.037	0.056	0.208	0.242	0.016	0.000
Ta <sup>5+</sup>	0.457	0.235	0.031	0.032	0.159	0.045	0.032	0.006	0.000
Ti <sup>4+</sup>	0.000	0.066	0.076	0.298	0.092	0.044	0.020	0.018	0.021
<sup>(6)</sup> Al <sup>3+</sup>	5.989	5.803	5.829	6.048	5.816	6.048	6.025	6.515	6.000
Sc <sup>3+</sup>	0.015					0.019	0.023	0.015	0.018
Fe <sup>2+</sup>	0.000	0.015	0.020	0.011	0.025	0.066	0.039	0.031	0.017
<sup>(6)</sup> vac.	0.529	0.835	0.788	0.574	0.851	0.570	0.619	0.400	0.944
O <sub>2</sub> <sup>-</sup>	17.197	16.028	16.116	16.628	15.823	16.578	16.508	16.796	15.092
OH <sup>-</sup>	0.401	0.986	0.942	0.686	1.088	0.711	0.746	0.602	1.454
vac.	0.401	0.986	0.942	0.686	1.088	0.711	0.746	0.602	1.454
	HOL	HOL	HOL	HOL	HOL	HOL	HOL	DUM	X-phase

Notes: \* calculated from stoichiometry. 1 – WPH holtite, 2–5 – zoned holtite, 6–8 – holtite overgrown by dumortierite, 9 – X-phase. Abbreviations: HOL – holtite, DUM – dumortierite, X-phase – an unnamed dumortierite-like phase.

too close to the corresponding Si site for either of the (Sb, As) sites and its corresponding Si site to be occupied at the same time. The small deviation from the total of Si+As+Sb being 3 is due to the substitution of Si by P and tetrahedral Al.

Incorporation of Ti<sup>4+</sup> is considered to result mostly from the substitution  $\frac{3}{4} \text{Ti} + \frac{1}{4} \square \rightarrow \text{Al}$  at the octahedral Al(1) site, which is analogous to the substitution  $\frac{3}{5} \text{Ta}(\text{Nb})^{5+2/5} \square \rightarrow \text{Al}$ , and to a lesser extent from the substitution  $\text{Fe}^{2+} + \text{Ti}^{4+} \rightarrow 2\text{Al}$ . The proportion of Ti [=Ti/(Ti+Ta+Nb)] in

most samples increases with increasing Si (Fig. 4b), such that Ti/(Ti+Ta+Nb) reaches a maximum when the amount of Si at the T sites exceeds 2.2 a.p.f.u., whereas the proportions of Ta and Nb taken individually show no such relationship. However, in contrast to the inverse relationship between As+Sb and Si, the holtite samples from Greenbushes and Voron'i Tundry (H1–H3, Groat *et al.*, 2009) do not plot in this trend, suggesting that it cannot be generalized to other holtite samples.



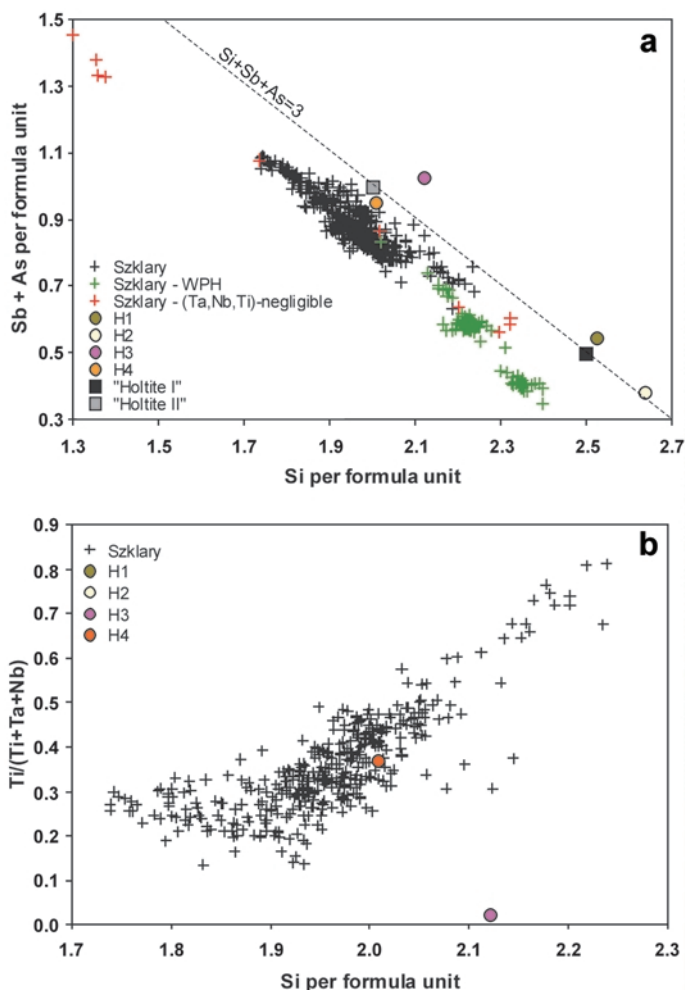
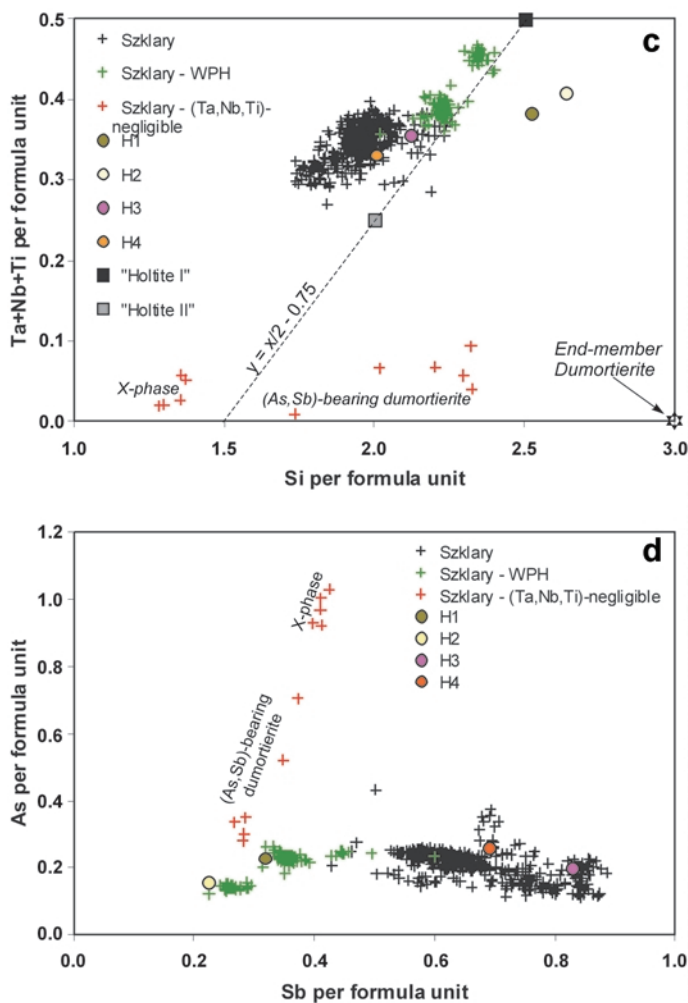


FIG. 4 (*this and facing page*). Compositional relations in the Szklary holtite and dumortierite: (a) Sb+As (a.p.f.u.) vs. Si (a.p.f.u.); (b)  $Ti/(Ti+Ta+Nb)$  vs. Si (a.p.f.u.); (c) Ta+Nb+Ti (a.p.f.u.) vs. Si (a.p.f.u.); (d) As (a.p.f.u.) vs. Sb (a.p.f.u.). The data for H1–H4 and idealized ‘holtite I’ and ‘holtite II’ are from Groat *et al.* (2009). H1 and H2 do not plot in the area shown in Fig. 4b.

Figure 4c shows the relationship between Ta+Nb+Ti substituting for Al at the Al(1) site and the Si content. Compositions of the Szklary holtite and H1–H3 holtites (Groat *et al.*, 2009) plot mostly to the low-Si (left) side of the line marked by ‘holtite I’ and ‘holtite II’, with Ta+Nb+Ti decreasing as  $Si^{4+}$  is being replaced by  $Sb^{3+}+As^{3+}$ . The As- and Sb-bearing dumortierite plots as a separate cluster of points with Ta+Nb+Ti  $\leq 0.1$  a.p.f.u. and Si  $> 2$  a.p.f.u., whereas the dumortierite-like ‘X-phase’ containing negligible (Ta+Nb+Ti) plots at Si  $< 1.5$  a.p.f.u., because of extensive substitution of Si by As+Sb.

Figure 4d shows two linear trends. Most holtite from Szklary, together with H1–H4 (Groat *et al.*, 2009), plot in a horizontal trend at constant As  $\approx 0.2$  a.p.f.u. with Sb ranging from 0.2 to 0.9 a.p.f.u. In contrast, (As, Sb)-bearing dumortierite and the dumortierite-like ‘X-phase’ plot in a nearly vertical trend. The two trends intersect at As  $\approx$  Sb  $\approx 0.2$  a.p.f.u. A distinct change in the type of replacement appears in dumortierite crystallized after holtite and in the dumortierite-like ‘X-phase’ with As+Sb  $> Si$ , where the As content is always greater than the Sb content, even if the latter is relatively large. The co-variation of As and Sb

## HOLTITE AND DUMORTIERITE FROM POLAND



(Fig. 4d) indicates miscibility between dumortierite, the As- and Sb-bearing dumortierite and the (As+Sb)-dominant dumortierite-like 'X-phase' containing negligible Ta+Nb+Ti.

The homogeneous Ta-bearing holtite (WPH) reaches the composition  $(Al_{5.99}Ta_{0.46}Nb_{0.01}Sc_{0.01}\square_{0.53})_{\Sigma 7.00}B(Si_{2.34}Sb_{0.26}As_{0.14}P_{0.05}Al_{0.20})_{\Sigma 3.00}[O_{17.20}(OH)_{0.40}\square_{0.40}]_{\Sigma 18.00}$  (Table 1b). This holtite has the greatest Ta content reported to date: 14.66 wt.%  $Ta_2O_5$  (cf. Greenbushes, 11.24 wt.%  $Ta_2O_5$ ; Pryce, 1971; 12.06–13.15 wt.%  $Ta_2O_5$ ; Groat *et al.*, 2009; Voron'i Tundry, 13.79 and 11.03 wt.%  $Ta_2O_5$ ; Kazantsev *et al.*, 2005; 10.93 wt.%  $Ta_2O_5$ ; Groat *et al.*, 2009). Given the presence of 0.46 Ta p.f.u.,

which presumably is located only at the Al(1) site, and the likelihood for vacancies at the Al(2), Al(3) and Al(4) sites, it is possible that  $Ta > Al$  and  $Ta > \text{vacancy}$  at the Al(1) site, i.e. Ta is the dominant occupant, which has not been reported previously in holtite. However, the dominance of Ta at Al(1) can be demonstrated only by refinement of the crystal structure of the WPH holtite. In any case, this Ta content exceeds 75% of the maximum possible, because charge balance constrains substitution of  $Al^{3+}$  by  $Ta^{5+}$  or  $Nb^{5+}$  at the Al(1) site to 0.6 (Ta+Nb) a.p.f.u. (Groat *et al.*, 2009).

Compositions of Ta-bearing holtite forming the core of zoned crystals vary from a Ta-rich composition  $(Al_{5.80}Ta_{0.23}Ti_{0.07}Nb_{0.06}$

$\text{Fe}_{0.01}^{2+} \square_{0.83} \Sigma_{7.00} \text{B}(\text{Si}_{1.93} \text{Sb}_{0.87} \text{As}_{0.12} \text{Al}_{0.08}) \Sigma_{3.00} [\text{O}_{16.03}(\text{OH})_{0.99} \square_{0.99}] \Sigma_{18.00}$  to compositions with Ta only slightly dominant over Nb or Ti. With a further decrease in Ta, compositions become Ti-dominant in tiny streaks within the core or locally on the core/rim margin, and Nb-dominant in the rim. The maximum of 7.73 wt.%  $\text{Ta}_2\text{O}_5$  (0.23 Ta a.p.f.u.) in the cores of zoned crystals is distinctly smaller than that in WPH. The Ta-bearing holtite richest in Sb+As contains 19.18 wt.%  $\text{Sb}_2\text{O}_3$  and 3.30 wt.%  $\text{As}_2\text{O}_3$ , reaching the composition  $(\text{Al}_{5.82} \text{Ta}_{0.16} \text{Ti}_{0.09} \text{Nb}_{0.06} \text{Fe}_{0.02}^{2+} \square_{0.85}) \Sigma_{7.00} \text{B}(\text{Si}_{1.74} \text{Sb}_{0.87} \text{As}_{0.22} \text{Al}_{0.15} \text{P}_{0.02}) \Sigma_{3.00} [\text{O}_{15.82}(\text{OH})_{1.09} \square_{1.09}] \Sigma_{18.00}$ , with more Sb or Sb+As than reported in any holtite to date.

The Nb-bearing variety contains up to 5.30 wt.%  $\text{Nb}_2\text{O}_5$ ,  $(\text{Al}_{5.83} \text{Nb}_{0.26} \text{Ti}_{0.08} \text{Ta}_{0.03} \text{Fe}_{0.02}^{2+} \square_{0.79}) \Sigma_{7.00} \text{B}(\text{Si}_{1.91} \text{Sb}_{0.80} \text{As}_{0.14} \text{Al}_{0.15}) \Sigma_{3.00} [\text{O}_{16.12}(\text{OH})_{0.94} \square_{0.94}] \Sigma_{18.00}$ , whereas the Ti-bearing variety contains up to 3.82 wt.%  $\text{TiO}_2$ ,  $(\text{Al}_{6.05} \text{Ti}_{0.30} \text{Nb}_{0.04} \text{Ta}_{0.03} \text{Fe}_{0.01}^{2+} \square_{0.57}) \Sigma_{7.00} \text{B}(\text{Si}_{2.24} \text{Sb}_{0.50} \text{As}_{0.18} \text{Al}_{0.08}) \Sigma_{3.00} [\text{O}_{16.63}(\text{OH})_{0.69} \square_{0.69}] \Sigma_{18.00}$ , comparable with the maximum Ti content reported in dumortierite, ~0.33 Ti a.p.f.u. (Huijsmans *et al.*, 1982).

As- and Sb-bearing dumortierite forming a rim around the Nb-bearing holtite core has the composition:  $(\text{Al}_{6.52} \text{Fe}_{0.03}^{2+} \text{Nb}_{0.02} \text{Ti}_{0.02} \text{Ta}_{<0.01} \text{Sc}_{0.01} \square_{0.40}) \Sigma_{7.00} \text{B}(\text{Si}_{2.32} \text{As}_{0.34} \text{Sb}_{0.27} \text{Al}_{0.05} \text{P}_{0.02}) \Sigma_{3.00} [\text{O}_{16.80}(\text{OH})_{0.60} \square_{0.60}] \Sigma_{18.00}$ . However, inclusions disseminated around the crystal contain up to 0.71 As a.p.f.u. and 0.50 Sb a.p.f.u., more than reported previously in dumortierite (e.g. Cempírek *et al.*, 2010). Lastly, (As, Sb)-dominant dumortierite-like ‘X-phase’ contains up to 16.81 wt.%  $\text{As}_2\text{O}_3$  and 10.23 wt.%  $\text{Sb}_2\text{O}_3$ , but negligible Ta and Nb,  $(\text{Al}_{6.00} \text{Ti}_{0.02} \text{Fe}_{0.02}^{2+} \text{Sc}_{0.02} \square_{0.94}) \Sigma_{7.00} \text{B}(\text{Si}_{1.30} \text{As}_{1.04} \text{Sb}_{0.43} \text{Al}_{0.16} \text{P}_{0.08}) \Sigma_{3.00} [\text{O}_{15.09}(\text{OH})_{1.45} \square_{1.45}] \Sigma_{18.00}$ , i.e.  $\text{As} + \text{Sb} > \text{Si}$ .

The full range of  $\text{Sb}^{3+} + \text{As}^{3+}$  for  $\text{Si}^{4+}$  substitution in the Szklary holtite, ~0.35 to 1.09 a.p.f.u., suggests an extensive solid solution between (Sb,As)-poor and (Sb,As)-rich holtite (Fig. 4a). This range is wider than that between ‘holtite I’ (Si = 2.50 a.p.f.u., Sb+As = 0.50 a.p.f.u.) and ‘holtite II’ (Si = 2.0 a.p.f.u., Sb+As = 1.0 a.p.f.u.; Groat *et al.*, 2009), i.e. our compositional data based on 500 spot analyses of holtite from the Szklary dyke show no evidence for clustering of holtite compositions around compositions corresponding to ‘holtite I’ and ‘holtite II’ (Voloshin *et al.*, 1987; Voloshin and Pakhomovskiy, 1988). Although the homogeneous Ta-bearing holtite

WPH has compositions closer to ‘holtite I’ and the zoned holtite has compositions closer to ‘holtite II’, the compositions of all the holtite analysed cover almost the full range of possible holtite composition. As noted by Groat *et al.* (2009), a limited number of localities for holtite and a small number of holtite analyses from any one occurrence could give the illusion of clustering. Evolution of holtite composition in terms of  $\text{Sb}^{3+} + \text{As}^{3+}$  substitution for  $\text{Si}^{4+}$  is instead a reflection of geochemical evolution of the pegmatite melt from which holtite crystallized.

In summary, our data provide further evidence for miscibility between phases identified as holtite and phases identified as dumortierite, and that the distinction between the two minerals is even more blurred than earlier thought. We have arbitrarily called a phase holtite if  $\text{Ta} + \text{Nb} + \text{Ti} > 0.25$  a.p.f.u. and dumortierite if  $\text{Ta} + \text{Nb} + \text{Ti} < 0.1$  a.p.f.u. because of the gap in  $\text{Ta} + \text{Nb} + \text{Ti}$  contents evident in Fig. 4c. However, we realize that some dumortierite from other localities, e.g. Norway (Huijsman *et al.*, 1982), contain enough Ti to be called ‘holtite’ using this criterion. Groat *et al.* (2009) concluded that a more precise definition of holtite and its distinction from dumortierite awaited detailed study of both minerals and that differences in diffraction behaviour need to be considered. Despite the large number of analyses presented here, we concur that it is still premature to propose new definitions of these two minerals, a prerequisite for which are systematic crystallographic studies.

### Origin of holtite in the Szklary pegmatite

Crystallization of holtite in the Szklary pegmatite as a primary Ta-Ti-Nb mineral with columbite-(Mn), tantalite-(Mn), stibiotantalite and stibio-columbite is due to the parental melt being enriched in Ta, Nb, Sb, As, Al and B, and to S fugacity being too low for sulphides such as arsenopyrite and löllingite to form. Both textural relationships among holtite and coexisting minerals, as well as Ta-Nb fractionation in the holtite varieties, indicate the following crystallization sequence: Ta-bearing homogeneous holtite WPH [ $\text{Ta}/(\text{Nb} + \text{Ta}) = 0.99 - 0.95$ ] → Ta-bearing holtite forming the core in zoned crystals [ $\text{Ta}/(\text{Nb} + \text{Ta}) = 0.90 - 0.45$ ] → Ti-bearing holtite [ $\text{Ta}/(\text{Nb} + \text{Ta}) = 0.85 - 0.07$ ] → Nb-bearing holtite forming the rim in zoned crystals [ $\text{Ta}/(\text{Nb} + \text{Ta}) = 0.49 - 0.03$ ] → As- and Sb-bearing (Ta,Nb,Ti)-poor dumortierite [ $\text{Ta}/(\text{Nb} + \text{Ta}) = 0.15 - 0.03$ ] →

(As and Sb)-dominant dumortierite-like ‘X-phase’ containing negligible Ta+Nb+Ti. Although Ti-bearing holtite is found mostly in the core of Ta-bearing holtite and only locally between Ta-bearing cores and Nb-bearing rims, its position between the other two varieties in even a few places is sufficient to justify our conclusion that it is intermediate in the crystallization sequence.

Elevated Ti contents, which have not been reported in holtite from Greenbushes and Voron’i Tundry, could be due to contamination of the Szklary pegmatite-forming melt by ultramafic and mafic wall rocks. In contrast, the rare homogeneous Fe- and Ti-free WPH holtite probably reflects only local changes in melt composition that had not been contaminated by Mg, Fe, and Ti.

Holtite–stibiocolumbite textural relationships and zoning in the holtite crystals suggest that zoned holtite crystallized with stibiocolumbite

following a stage of melt evolution indicated by trend II for columbite-group minerals (Fig. 5). Holtite crystallization began during a stage when the availability of Ta in the melt reached a maximum, inducing crystallization of the mineral with the highest Ta/(Ta+Nb) ratio, i.e. WPH holtite and Ta-bearing holtite in the core in the zoned crystals. Crystallization of Ta-holtite consumed Ta in the melt and prevented the crystallization of tantalite or stibiotantalite. Subsequently, holtite, columbite-(Mn) and stibiocolumbite, which in places encloses holtite fibres, became progressively richer in Nb, resulting in an anomalous trend that has been reported as trend I for columbite-group minerals in this pegmatite and in a few pegmatites elsewhere (Pieccka, 2010). In summary, Ta, Nb and Ti contents of the zoned holtite provide a record of the availability of these elements in the melt from which it

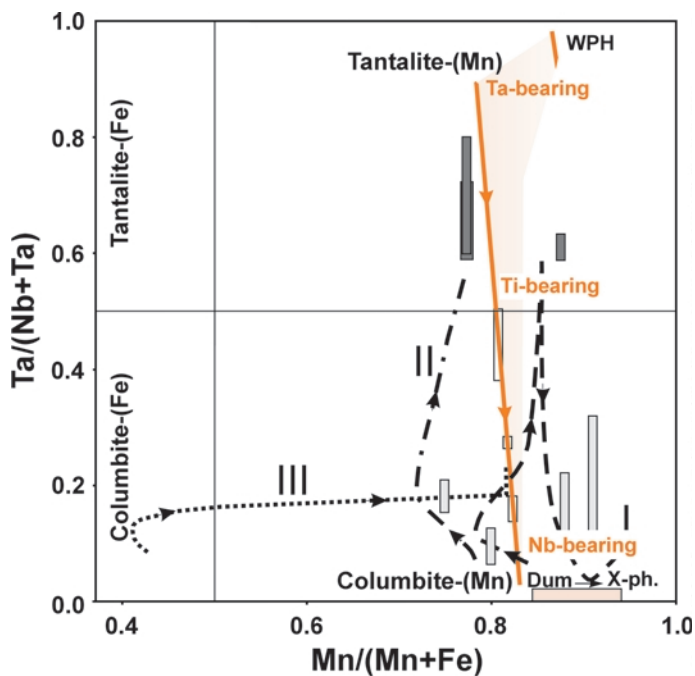


FIG. 5. Paragenetic-chemical diagram showing relationships between holtite and dumortierite and the primary Nb-Ta minerals in the Szklary pegmatite in terms of Mn-Fe and Ta-Nb fractionation (modified from Pieczka, 2010; fig. 9). Fractionation trend in holtite is denoted by the solid orange line; compositional trends exhibited by the columbite-group minerals are indicated by the dashed black line (Trend I), dotted-dashed line (Trend II), and dotted line (Trend III); other symbols show the compositional fields of stibiocolumbite coexisting with the CGM (light grey rectangles), stibiotantalite (dark grey rectangles), and stibiocolumbite coexisting with holtite (unfilled rectangles). A crystallization stage for holtite is indicated by the orange area to the right of the Ta-Nb fractionation trend and for As- and Sb-bearing dumortierite passing into the (As,Sb)-dominant dumortierite-like ‘X-phase’ indicated with an orange rectangle.

crystallized; this information supplements what can be learned from compositions of the oxides (Pieczka, 2010). Preservation of the fine zoning in holtite is probably due to the slow diffusion of Ta, Nb and Ti in this mineral. Although no diffusivity data are available for holtite or dumortierite, the diffusion coefficients for quadrivalent and pentavalent cations are expected to be relatively low (Brady and Cherniak, 2010). There is no need to invoke disequilibrium crystallization to explain the zoning in holtite.

## Conclusions

(1) The compositions of all the holtite varieties in the Szklary pegmatite, which cover a very wide range of possible holtite compositions, including Nb-bearing and Ti-bearing holtite, as well as Ta-bearing holtite, do not corroborate earlier proposals that holtite analyses clustered around compositions corresponding to 'holtite I' and 'holtite II' (Voloshin *et al.*, 1987; Voloshin and Pakhomovskiy, 1988).

(2) Instead, the substitution of  $\text{Si}^{4+}$  by  $\text{Sb}^{3+} + \text{As}^{3+}$  at the Si/Sb sites and of  $\text{Ta}^{5+}$  by  $\text{Nb}^{5+}$  or  $\text{Ti}^{4+}$  at the Al(1) site suggest possible solid solutions between: (a) (Sb,As)-poor and (Sb,As)-rich holtite; (b) dumortierite and the unnamed (As+Sb)-dominant dumortierite-like mineral; and (c) Ti-bearing dumortierite and holtite.

(3) Textural relationships between Nb-bearing, Ti-bearing, and Ta-bearing holtite, as well as As- and Sb-bearing dumortierite overgrowing Nb-bearing holtite, suggest the following crystallization sequence for the Szklary pegmatite: Ta-bearing homogeneous holtite → Ta-bearing holtite forming the core in zoned crystals → Ti-bearing holtite → Nb-bearing holtite forming the rim in zoned crystals → As- and Sb-bearing, (Ta,Nb,Ti)-poor dumortierite → (As and Sb)-dominant dumortierite-like mineral containing negligible Ta, Nb and Ti. The last phase is potentially a new mineral species,  $\text{Al}_6 \square \text{B}(\text{Sb,As})_3 \text{O}_{1.5}$  or  $\text{Al}_5 \square_2 \text{B}(\text{Sb,As})_3 \text{O}_{1.2}(\text{OH})_3$ , belonging to the dumortierite group.

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