

MINERALOGY OF WOOD TIN FROM THE DZHALINDA DEPOSIT

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Mineralogy of wood tin from the Dzhalinda deposit located in the Khingan-Olonoy tin district has been studied. The wood tin is reniform aggregates up to 5 cm in size of concentric zoned cassiterite. Significant later quartz filling tiny fractures in cassiterite layers is close intergrown with cassiterite. Microinclusions of dzhalindite were identified in wood tin; acanthite, preisingerite (?), native bismuth and thorium-bearing monazite-group minerals were found at the deposit for the first time.

11 figures, 2 tables, 8 references.

Keywords: wood tin, Dzhalinda tin deposit, Khabarovsk krai, cassiterite, dzhalindite, acanthite, preisingerite, native bismuth, monazite.

The Dzhalinda deposit located in the central part of the Malyy Khingan ridge belongs to the Khingan-Olonoy tin-district; it is a typical member of the rhyolitic assemblage (Geology..., 1986). The deposit is related to the paleovolcanic neck filled with the Upper Cretaceous effusive quartz porphyry. These porphyries are silicified, sericitized, and kaolinitized along northeast striking fault zone. Ore mineralization is reniform aggregates of wood tin filling cavities and fractures in silicified rocks (Betekhtin, 1964).

Previously, we studied gemmological features of wood tin from the Dzhalinda deposit for possible usage as gem material (Petrochenkov, 2011). This article discussed the mineralogical features of mineral of wood tin.

Mineralogy and structure of wood tin

According to the X-ray examination performed on a X^o PetroPRO device, analyst I.S. Naumova, wood tin from the Dzhalinda deposit consists of cassiterite, quartz, and X-ray amorphous phase (average 76, 17, and 7%, respectively). The X-ray amorphous phase can be related to both cassiterite and opal; the latter frequently occurs at the deposits of rhyolitic assemblage.

The typical structural feature of the ores is the reniform cryptocrystalline aggregates of cassiterite up to 5 cm in size (Komarova, 1959). These aggregates are concentric zoned that is caused by the alternated variously colored zones. Large kidneys frequently composed of intergrown fine kidneys (from 3 to 15 mm) which are overgrown by new layers of cassiterite and include predominantly quartz zones (Figs. 1, 2).

Cassiterite occurs as dark grey and black concentric layers ranging from 0.05 to 0.5 mm in width (Figs. 3a, 3b). Part of these layers consist of fine (< 0.01 mm) crystals or are cryptocrystalline (Figs. 3c, 3d). Another part is massive aggregates of long prismatic and spear-shaped crystals reaching 0.3 mm along long axis (Fig. 3b). Parallel twins with size increased to 0.5 mm are common. Sector extinction in crossed polars is observed. Red and orange thin layers of cassiterite (~0.015 mm) are also characteristic (Fig. 3a).

Tiny spherulites of cassiterite of 0.01 to 0.04 mm in diameter occur in the quartz dominant zones (Fig. 3b). Black core of these spherulites is composed of cryptocrystalline or amorphous cassiterite. Rims of the spherulites consist of light brown tiny (0.005–0.008 mm) prismatic crystals. Aggregates of intergrown spherulites reach 0.3 mm in size. The spherulites are later than cassiterite forming kidneys and are simultaneous with quartz.

Quartz fills small veinlets up to 0.1 mm wide occurring as rather dense grid on separate places of wood tin (Fig. 3c). Concentric quartz veinlets and predominantly quartz areas up to 2 mm in size with tiny inclusions of cassiterite, and areas composed of quartz and cassiterite are typical (Figs. 2, 3d). Predominantly isometric complexly outlined centered crystals of quartz ranging from 0.005 to 0.07 mm in size of complex are randomly oriented, their forms are mainly isometrical with a complex contour, their size vary from (Figs. 3c, d). According Betekhtin (1964) and Genkin and Murav'eva (1963), quartz in wood tin is later than cassiterite and replaces the latter.



Fig. 1. Polished plate of wood tin from the Dzhallindadeposit. Vernadsky State Geological Museum, Russian Academy of Sciences, No 46722.

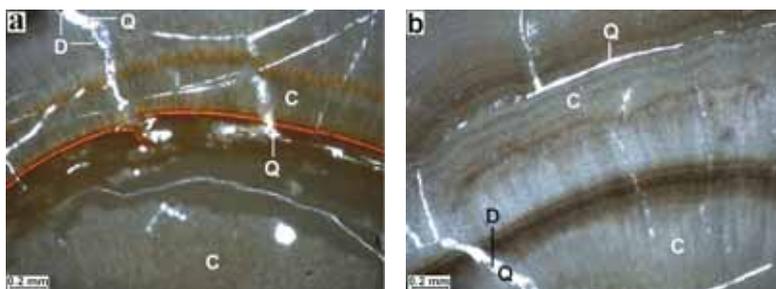


Fig. 2. Polished section of wood tin from the Dzhallinda deposit. (C) Cassiterite, (Q) quartz.



Fig. 3. Photomicrograph of fragments of wood tin: (a, b) nickols //, (c, d) nickols +. (C) Cassiterite, (Q) quartz, (D) dzhallindite.

Electron microprobe study

The chemical composition of wood tin was measured with a "Superprobe-8100" electron microprobe equipped with an "Inca" energy dispersion system at All-Russia Institute of Mineral Resources, analyst N.I. Chistyakova.

Electron microprobe measurements indicate that grey and black cassiterite, the contains (wt.%): up to 0.33 Fe, up to 1.0 Si up to 3 As up to 0.7 In, and up to 0.5 Ta. These are resulted from microinclusions of quartz and other minerals. We studied red veinlet in wood tin between the zone of filled by of grey cassiterite and the fine-grained cassiterite-quartz aggregate composed of (Fig. 3a). This veinlet is about 30 microns in thickness. In its central part a small crack (3 microns thick) is

observed. Red cassiterite contains Fe (0.67 – 1.69 wt.%), which is significantly higher than in grey cassiterite. Content of other measured elements is comparable. Probably, red color of cassiterite in wood tin is caused by inclusions of iron oxides formed as a result of recrystallization of cassiterite. Extremely fine size prevents accurate determination of these microinclusions with electron microprobe.

As a result, numerous inclusions of dzhallindite and for the first time inclusions of acanthite, preisingerite (?), native bismuth, and monazite were found in wood tin at the Dzhallinda deposit

Dzhallindite $\text{In}(\text{OH})_3$ was discovered by Genkin and Murav'eva (1963) at the Dzhallinda deposit. They reported dzhallindite as a

secondary supergene mineral replacing indite (FeIn_2S_4) that was also described for the first time at this deposit (Genkin, Murav'eva, 1963). Later, dzhallindite was identified in gold-base metal ore at the Bugdaya deposit (Eastern Transbaikalia). According to Kiseleva *et al.* (2008), dzhallindite was resulted from neutralization of thermal solutions corroding In-bearing sphalerite.

We have found dzhallindite in quartz veinlets and cassiterite-quartz zones of, where it occurs as numerous isometric inclusions ranging from 1–2 to 100 microns in size (Figs. 4–8). In binocular loupe, in polished section, inclusions of dzhallindite are white. The composition of dzhallindite studied here is consistent with previous data (Genkin, Murav'eva, 1963; Kiselev, 2008). The content of In in dzhallindite varies from 61 to 63 wt.%. Permanent Si (up to 0.61 wt.%) in dzhallindite indicates microinclusions of quartz in the mineral. The following elements are occasionally detected in dzhallindite, wt.%: up to 4.1 Fe, up to 0.56 P up to 0.99Al and up to 0.52 As.

In large segregations of dzhallindite, there are darker in back-scattered electron image square or trapezoidal zones of predominant size 7–12 microns (Fig. 6). Concentration of Fe in the dark zones is 1.5–4.1 wt.%, whereas in the bulk dzhallindite it does not exceed 0.13 wt.%. In the dark Fe-bearing zones of dzhallindite, concentration of In decreases that was previously observed in dzhallindite

from the Bugdaya deposit (Kiseleva, 2008). Proper iron minerals in the ark zones were not identified. Bivalent iron is probably replaces indium in the lattice of dzhallindite by close ionic radii of these elements.

The composition of dzhallindite calculated from theoretical formula $\text{In}(\text{OH})_3$ is as follows, wt.%: 69.2 In, 30.8 (OH) group. At the same time, according to previous articles (Genkin, Murav'eva, 1963; Kiselev, 2008) and this study, concentration of In in the mineral does not exceed 63 wt.% and content of the (OH) group is 28 wt.%, i.e., the deficiency of total is 9 wt.%, that is probably caused molecular water.

Rare elongated irregular-shaped inclusions of Ag sulfide of 0.5–3 microns in size are observed in dzhallindite (Fig. 7). According to the electron microprobe data, these inclusions contain, wt%: 85–88 Ag and 12.5–13 S that corresponds to the chemical composition of **acanthite** – Ag_2S .

Rare Bi arsenate (Table 1) closely intergrown with dzhallindite is observed in quartz. Isometric or elongated segregation of this mineral up to 20 microns in size is complexly countered (Fig. 8). In reflected light, "large" segregations of bismuth arsenate is black. Lamellar structure of the mineral (Fig. 9) is exhibited at high magnification. Width and length of lamella reaches 2 and 10 microns, respectively. Fan-shaped aggregates up to 15 microns in size are formed as a result of intergrowing.

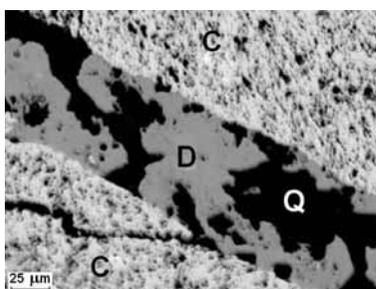
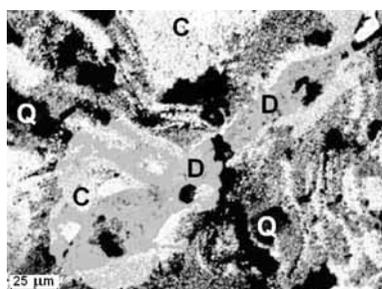


Fig. 4. Back-scattered electron image of inclusions of dzhallindite (D) in cassiterite (C) and quartz (Q).

Fig. 5. Back-scattered electron image of quartz veinlet (Q) with inclusions of dzhallindite (D) in cassiterite.

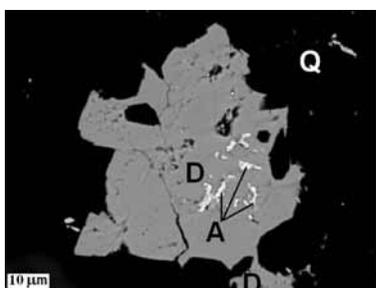
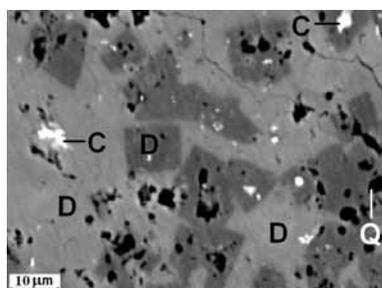


Fig. 6. Back-scattered electron image of Non-uniform structure of dzhallindite exhalations (D) with cassiterite (C) and quartz (Q) inclusions.

Fig. 7. Back-scattered electron image of inclusions of acanthite Ag_2S (A) in dzhallindite (D); (Q) quartz.

Table 1. Chemical composition of preisingerite (?) inclusions in wood tin

№ spectrum	Component, wt.%				Total
	As	Pb	Bi	O*	
1	16.23	4.44	60.23	15.96	96.86
2	15.39	3.62	58.58	15.23	92.82
3	15.00	3.66	59.42	15.14	93.22
4	15.05	1.91	58.76	15.20	90.92
5	14.76	1.80	58.75	15.24	90.55
6	14.48	0.80	60.54	15.80	91.62
7	14.28	0.76	59.33	15.19	89.56
8	15.90	4.76	58.74	15.60	95.00
9	16.29	4.21	58.47	15.74	94.71
10	15.86	6.03	56.81	15.46	94.16
11	16.43	5.22	58.17	15.85	95.67
12	15.64	4.18	58.48	15.39	93.69

Notes: A JXA-8100 electron microprobe (Jeol, Japan) operating at accelerating voltage 20 kV, current 20 nA, and beam diameter 2 microns. Analytical lines are AsLa, PbMa, BiMa. Standards were used: natural FeAsS, synthetic PbS, and Bi₂S₃. Analyst N.I. Chistyakova. * – oxygen calculated by stoichiometry.

Preisingerite Bi₃O(OH)(AsO₄)₂ and rooseveltite BiAsO₄ (Semenov, 2002) are similar in chemical composition to the revealed bismuth arsenate. Theoretical composition of preisingerite is as follows (wt.%): 66.9 Bi, 16 As, 0.1 H, and 17 O. The composition of rooseveltite is as follows (wt.%): 60 Bi, 21.5 As, and 18.5 O. According to electron microprobe data (Table 1), the average chemical composition of bismuth arsenate is as follows, wt.%: 58.86 Bi, 15.44 As, and 3.45 Pb, that is closer to the formula of preisingerite Bi_{2.79}Pb_{0.17}O(OH)(As_{1.02}O₄)₂ than to that of rooseveltite (Bi_{1.11}Pb_{0.07})_{1.18}As_{0.82}O₄ (calculated on the basis of total cations). Taking in to account oxygen calculated by stoichiometry, average total is 93.4 wt.%. The deficient total is caused by the fine size segregations of bismuth arsenate and hydroxyl groups in the mineral. Presumably, Bi⁺³ is replaced by Pb⁺², due to their close ionic radii and charge deficiency of cation group is balanced by hydroxyl group presenting in preisingerite. Additional study is required to accurately determine this phase.

Previously, rooseveltite and preisingerite were reported from the Oranzheviy ore field related in the Upper Kalganinsky pluton, Magadan region (Krinov, 2011). Rooseveltite occurring as tiny aggregates replacing bismuthinite and occasionally arsenopyrite is closely intergrown with preisingerite. Micro-

veinlets of these minerals also cut quartz. Interestingly, rooseveltite contains high Pb (3–6 wt.%, average 4.4 wt.%). These data are consistent with our results indicating possible existence of both minerals in wood tin at the Dzhalinda deposit. Krinov *et al.* (2011) referred the formation of rooseveltite and preisingerite to low-temperature decomposition of the earlier arsenic and bismuth minerals that also could occur at the Dzhalinda deposit.

Inclusions of **native bismuth** are found in the cassiterite-quartz zone (Fig. 10). These irregular-shaped inclusions reach 15 microns in size. According to the electron microprobe data, the inclusions contain Bi up to 99.8 wt.% (one analysis shows 0.4 wt.% Cu).

Numerous inclusions of Ce- and Th-bearing mineral – presumably **monazite-(Ce)** – (Ce,La,Y,Th)[PO₄] – were observed in dzhalindite enclosed in quartz (Fig. 11, Table 2). The larger idiomorphic prismatic crystals of this mineral reach 16 microns in length along long axis and 7 microns in width (Fig. 11).

The examination of single crystal testifies to the highly variable content of constituents (Table 2). Ca, Pr, Nd, Cm, Pb which can incorporate into the monazite structure were also measured. The presence of In appears to be caused by the inclusions of dzhalindite in which monazite is enclosed. The total content varies from 86.4 to 92.9 wt.% resulting from the size of monazite crystals (first microns) and complex chemical composition of these crystals. The absence of enhanced radiation in the specimens of wood tin indicates insignificant microinclusions of monazite.

The hourglass structure (Fig. 11) is clearly displayed in the crystal of this mineral enriched in Ce and Th. Three symmetrical zones are distinguished in the crystal: black rim and grey and white zones in the central part. Black rim (Table 2, spectra 5–6) has higher Y, La, Ce, Pr, Nd, Cm and lower Th and Ca in comparison with white zone in which Y was not detected (Table 2, spectra 3–4). Average composition of black rims corresponds to the formula calculated on the basis of total cations (Ca_{0.08}Y_{0.08}La_{0.20}Ce_{0.42}Pr_{0.03}Nd_{0.15}Sm_{0.02}Pb_{0.02}Th_{0.01})_{1.01}[P_{0.99}O₄], that of white zones corresponds to the formula – (Ca_{0.23}La_{0.12}Ce_{0.21}Pr_{0.02}Nd_{0.07}Sm_{0.01}Pb_{0.02}Th_{0.31})_{0.99}[P_{1.01}O₄]. The intermediate content of these elements in grey zones (Table 2, spectra 1–2) corresponds to the following formula (Ca_{0.12}Y_{0.02}La_{0.16}Ce_{0.28}Pr_{0.02}Nd_{0.09}Sm_{0.02}Pb_{0.03}Th_{0.20})_{0.94}[P_{1.03}O₄]. Thus, the formula of

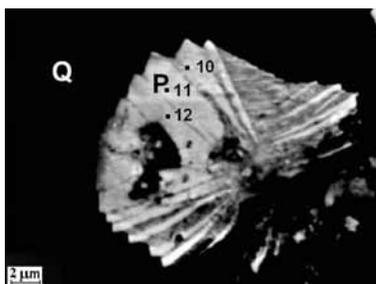
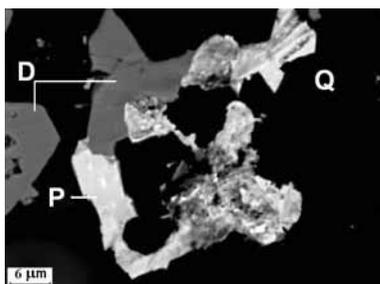


Fig. 8. Back-scattered electron image of inclusions of dzhalindite (D) and preisingerite (?) (P) in quartz (Q).

Fig. 9. Back-scattered electron image of inclusions of preisingerite (?) (P) in quartz (Q). 10–12 correspond to the spectrum numbers in Table 1.

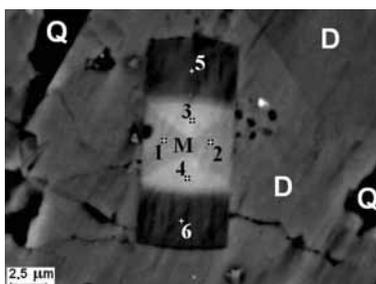
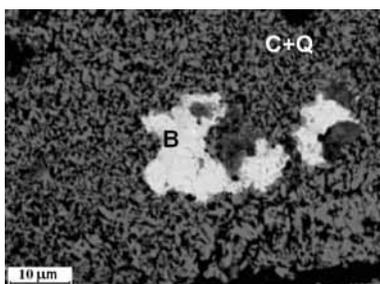


Fig. 10. Back-scattered electron image of inclusions of native bismuth (B) in cassiterite – quartz layer (C+Q).

Fig. 11. Back-scattered electron image of hourglass crystal of the monazite group mineral (M) in dzhalindite (D). 1–6 correspond to the spectrum numbers in Table 2.

Table 2. Chemical composition of inclusions of monazite group minerals in wood tin

№ spectrum	Component, wt. %												
	P	Ca	Y	In	La	Ce	Pr	Nd	Sm	Pb	Th	O*	Total
1	11.84	2.84	0.81	1.92	8.32	15.50	1.68	4.67	0.86	1.61	17.61	25.25	92.92
2	11.42	2.80	0.63	1.59	8.00	13.84	0.52	4.43	0.96	2.75	16.99	24.02	87.95
3	11.12	3.21	0.00	0.56	5.97	11.82	0.82	3.42	0.44	2.04	25.64	23.51	88.55
4	11.45	3.20	0.00	0.53	5.32	10.28	0.79	3.57	0.71	1.22	25.89	23.69	88.65
5	12.47	1.16	2.24	1.41	9.94	20.67	1.43	7.50	1.59	2.28	0.64	25.08	86.41
6	12.51	1.10	2.72	1.60	9.90	20.80	1.64	8.10	1.24	1.37	0.50	25.27	86.75

Notes. A JXA-8100 electron microprobe (Jeol, Japan) operating at accelerating voltage 20 kV, current 2 nA, and beam diameter 2 microns. Analytical lines are PK α , CaK α , YL α , InL α , LaL α , CeL α , PrL α , NdL α , SmL α , PbM α , ThM α . Standards were used: synthetic AlPO $_4$, Ca $_2$ Fe $_2$ O $_7$, Y $_2$ O $_3$, InAs, LaPO $_4$, CeP $_3$ O $_{14}$, PrPO $_4$, NdP $_3$ O $_{14}$, SmP $_3$ O $_{14}$, PbS, ThO $_2$. Analyst N.I. Chistyakova.
* – oxygen calculated by stoichiometry.

black rims corresponds to monazite-(Ce), whereas central zones are Th-rich analogue of this mineral.

In this case, grey zones are considered as monazite-(Ce) because Ce is higher in formula than Th, while white zones correspond to Th-dominant analogue of monazite. More accurate determination of this mineral was failed due to fine aggregates of this phase. Note that microinclusions of the monazite group minerals of the similar chemical composition we found in spacimans of wood tin from the Dominion Creek placer, Canada.

Conclusions

Abundant wood tin consisting of fine to cryptocrystalline and amorphous cassiterite

as reniform aggregates is the feature of ore mineralogy at the Dzhalinda. Quartz filling thin fractures and small cavities in cassiterite and in places intimately intergrowing with the latter is in large quantities in wood tin.

In our opinion, the extensive replacement of cassiterite by quartz as reported by Betekhtin (1964) and Genkin and Murav'eva (1963) at comparable low pressure and temperature of fluids characteristic of the deposition of wood tin at the deposits of the rhyolitic assemblage is unlikely. Microinclusions of dzhalindite and bismuth minerals (preisingerite (?) and native bismuth) are undoubtedly later than cassiterite and are simultaneous with quartz. Usually magmatic monazite group minerals were probably in-

roduced into hydrothermal solution as a result of dissolution of quartz porphyries hosting orebodies.

The conclusion of the conditions of wood tin deposition at the Dzhalinga deposit is debatable and the decision of this problem requires the additional facts.

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