

TEMAGAMITE, A NEW PALLADIUM-MERCURY TELLURIDE FROM THE TEMAGAMI COPPER DEPOSIT, ONTARIO, CANADA *

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ABSTRACT

Temagamite is a newly characterized mineral with the composition Pd_3HgTe_3 and is named after the locality. The mineral is indexed tentatively as orthorhombic with the unit-cell a 11.57(1), b 12.16(1), c 6.76(1) Å. The strongest lines on the x-ray powder pattern of synthetic Pd_3HgTe_3 are 2.912(10), 2.187(9), 1.959(7), 1.661(5), 1.624(5), 1.462(5), and 1.155(5). The choice of cell is not unequivocal because one reflection could not be adequately indexed.

The mineral occurs as rounded to irregular inclusions (115 microns or less) in chalcopyrite and is often closely associated with merenskyite ($PdTe_2$) and/or stuetzite ($Ag_{5-x}Te_3$) and/or hessite (Ag_2Te). Under reflected light in air, the mineral is white with a grey tinge, shows no birefractance, and is weakly anisotropic. Under oil, the anisotropism is enhanced with colours pale grey to dark grey. Reflectance measurements at 470, 546, 589, and 650 nm gave 52.8 and 51.8, 53.9 and 52.9, 55.0 and 54.2, and 57.7 and 57.1%, respectively for R_g' and R_p' . One micro-indentation hardness measurement gave $VHN_{25} = 92$. The mineral has been synthesized. It decomposes at about 570°C to $PdTe + Hg$, mercury vapour beginning to form below 500°C.

An unnamed Pd-Hg-Ag telluride associated with temagamite has also been discovered. This mineral appears darker grey than temagamite and is distinctly birefractant in oil, with colours brownish grey and bluish grey. It is distinctly to strongly anisotropic with colours from yellow-orange to dull greyish brown. The small size of the one grain found prevents further characterization at this time.

INTRODUCTION

While examining chalcopyrite samples for other projects in the Mineral Research Program of the Mineral Sciences Division, inclusions were observed in one of these samples which resulted in the discovery and study of the new mineral temagamite**, Pd_3HgTe_3 . The new min-

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** The mineral and the mineral name were approved by the Commission on New Minerals and Mineral Names, IMA. A polished section containing the mineral is preserved in the Royal Ontario Museum (M 32528).

eral is named after the Temagami deposit, Ontario, which was first drilled by the Temagami Mining Company in 1954.

The name Timagami (an Ojibway word for "deep clear water") was approved by the geographic board on June 25, 1906 and is now apparent on all official maps and related documents. However, at the instigation of the local population, the Canada Post Office, early in 1968, applied to the Canadian Permanent Committee on Geographic Names for a change in spelling to Temagami. The Executive Secretary of this Committee, in turn, applied to the Lands and Surveys Branch of the Ontario Department of Lands and Forests. The Ontario Department approved that the spelling of Timagami in Lake Timagami, Timagami Island, Timagami River, and Timagami (hamlet) be changed to Temagami on the 20th of March 1968; the Canadian Permanent Committee on Geographic Names also approved of this change on the 27th of March, 1968.

The Temagami deposit was one of the first discoveries made by means of airborne magnetometer (Copperfields Mining Corporation Limited, 1972) though sulphide showings on Temagami Island were first reported by Moorhouse (1942, p. 25). The Temagami mine closed in 1972 after producing \$34 million worth of copper.

The mineralogy and geology of the deposit are described by Rose (1965, 1966), and in the unpublished theses of Franklin (1967) and Scott (1969). As the result of conversations with personnel at the mine the authors of these reports suggest the presence of silver, sperrylite and gold in the ore, but no sperrylite or silver have been positively identified. Rose (1966) states that platinum and palladium have been reported in the ores of the Temagami deposit and the presence of "rare minute specks possibly of silver and sperrylite". A recent conversation (March 7, 1973) with Mr. G. MacIntosh, geologist with the company, indicated that palladium and a smaller amount of platinum occurred erratically in the copper concentrates. However, mineralogical and trace element studies made on this

deposit, during its lifetime, did not result in the discovery of the source and distribution of the palladium. The sample in which temagamite was found assayed 0.124 oz/ton Pd, and Pt was not detected.

MATERIAL AND METHOD OF INVESTIGATION

The massive chalcopyrite hand specimen (~500 g.), in which temagamite was found, was obtained from the Royal Ontario Museum. The Royal Ontario Museum had received a large quantity of massive chalcopyrite from the Temagami Mining Company Limited as a gift for their collection. This sample originated from the massive chalcopyrite ore which is in contrast to the low grade Ni-Cu pyrite zone described by Franklin (1967).

The Temagami deposit is on Temagami Island, Lake Temagami, in the Timiskaming Mining Division and about 100 kilometers northwest of North Bay. Access to the area and the geological maps available are discussed by Rose (1966).

The minerals were studied by ore microscopy, x-ray diffraction analysis, and by the electron probe microanalyser. The initial discovery of temagamite (Anal. #1 in Table 1) was in a polished section of massive chalcopyrite. Several other grains were found by crushing the hand specimen and making gravity separations of sized fractions with separatory funnels (2.96 liquid) and with an elutriating tube (3.33 liquid). The samples were mounted in cold-setting plastic, polished on lead laps, and lightly buffed on a cloth lap using minus 0.05- μ alumina. The reflectance values were obtained with reference to a silicon standard N2538.42 calibrated by the National Physical Laboratory, Great Britain, using a 45:1 objective of 0.85 numerical aperture on an area ten microns square. The micro-indentation hardness was measured with a Leitz Durimet tester. X-ray diffraction powder data were obtained by the film method using 57.3- and 114.6-mm Gandolfi and Debye-Scherrer cameras. Film shrinkage corrections were applied and the unit cell parameters were refined by a least-squares computer program (using 38 and 9 reflections for synthetic Pd_3HgTe_3 and temagamite, respectively). A Guinier-de Wolff multiple-sample focussing camera was used for qualitative work.

The compositions were determined using a Materials Analysis Company model 400 electron-probe microanalyser, operated at 25 kv with a specimen current of about 0.03 microamperes, except for three analyses at 20 kv and 0.025 microamperes (discussed below). Corrections

were applied using the program of Rucklidge & Gasparrini (1969). For the unknown Pd-Hg-Ag telluride, additional corrections were applied to compensate for the interference between $\text{PdL}\beta_1$ ($\lambda = 4.146$) and $\text{AgL}\alpha_1$ ($\lambda = 4.154$). Standards used were synthetic Pd_3HgTe_3 , PdBi, PdSb, PdTe, $\text{Pd}_{2.9}\text{Sb}$, and metallic Ag. Pd_3HgTe_3 was synthesized by reacting high-purity elements in an evacuated silica tube. The phase relations in the Pd-Hg-Te system being unknown, the following procedure was employed. The weighed elements were heated at 300°C for 2 days, at 500°C for 1 day, finally at 600°C for 3 days. The charge appeared to have melted but did not seem homogeneous and there was a very small amount of mercury condensed along the tube walls. The regulus was crushed and ground in a mortar, pelletized, and annealed in an evacuated tube at 500°C for 15 days. Microscopic and electron probe examination showed a homogeneous single phase which was subsequently used as the probe standard. Other experiments will be described below.

OPTICAL, PHYSICAL AND CHEMICAL PROPERTIES

Temagamite

Under reflected light in air, the mineral is white with a grey tinge, shows no birefractance, and is weakly anisotropic. Under oil, the mineral appears the same, but the anisotropism is enhanced with colours pale grey to dark grey. The mineral appears considerably greyer when it occurs with the more reflectant and whiter merenskyite. Temagamite has approximately the same polishing characteristics as merenskyite, polishes better than stuetzite, but poorer than chalcopyrite. The reflectances in air at the four standard wavelengths 470, 546, 589, and 650 nm are 52.8 and 51.8, 53.9 and 52.9, 55.0 and 54.2, and 57.7 and 57.1%, respectively (mean values for three measurements R_g' and R_p' on one grain). One micro-indentation hardness measurement gave $\text{VHN}_{25} = 92$, but the indentation was fractured in two corners.

The temagamite was always found as small rounded to irregular inclusions in chalcopyrite. The most common inclusions in chalcopyrite were millerite and siderite; other inclusions were galena, merenskyite, hessite, and stuetzite. One grain of an unknown Pd-Hg-Ag telluride was found. Temagamite was usually closely associated with either merenskyite, hessite, stuetzite, or a combination of them. The largest composite inclusion measured about 30×115 microns (Fig. 1), and the smallest was only a few microns wide. Fourteen temagamite grains were identified qualitatively with the electron

probe, and four others were analysed quantitatively (Table 1).

The first microanalyses of temagamite, using PdTe, HgS, PdBi, and Pd₂Sb as standards, indicated small amounts of Sb and Bi. Re-analysis, using synthetic Pd₃HgTe₃, PdBi and PdSb as standards, indicated that no Bi or Sb was present. This is ascribed to the difficulty in obtaining the proper background correction for

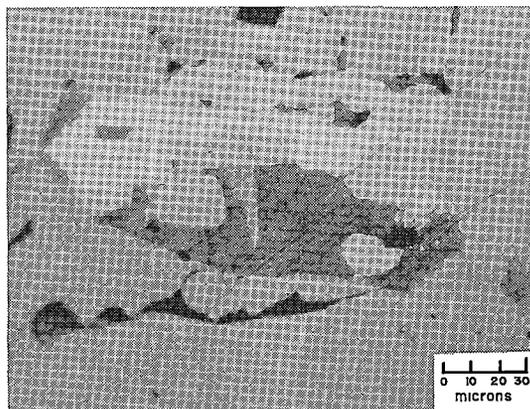


FIG. 1. Photomicrograph of composite grain in chalcopyrite. The merenskyite (white) is intergrown with temagamite (pale grey) which is itself intergrown with stuetzite (dark, poor polish). A lamellar grain of the unnamed Pd-Hg-Ag telluride (slightly darker grey than temagamite, oriented N-S) is seen in the stuetzite and is also in contact with temagamite. This section is preserved in the Royal Ontario Museum (M 32528).

TABLE 1. ELECTRON PROBE ANALYSES OF TEMAGAMITE, MERENSKYITE, STUETZITE, AND UNNAMED MINERAL

Wt. %	1	2	3	4	5	6*	7*
Pd	34.9	34.6	35.1	34.8	29.2	n.d.**	19.4
Hg	22.1	21.5	22.6	22.1	n.d.	n.d.	38.2
Te	42.1	41.6	42.3	41.6	67.8	40.7	23.1
Ag	n.d.	n.d.	n.d.	n.d.	n.d.	57.1	18.2
Sb	n.d.	0.3	n.d.	n.d.	0.3	----	----
Bi	n.d.	0.5	n.d.	n.d.	2.6	----	----
Totals	99.1	98.5	100.0	98.5	99.9	97.8	98.9

* Analyses at 20 kv and a specimen current of 0.025 microamperes.

** Not detected.

1. Temagamite, Pd_{2.99}Hg_{1.00}Te_{3.01}, Area 1, with merenskyite, stuetzite and unnamed mineral.
2. Temagamite, Pd_{3.04}Hg_{1.00}(Te_{3.05}Bi_{0.02}Sb_{0.03})₂=3.10, #8, with hessite in chalcopyrite.
3. Temagamite, Pd_{2.98}Hg_{1.02}Te_{3.00}, #15, with merenskyite and stuetzite.
4. Temagamite, Pd_{3.00}Hg_{1.01}Te_{2.99}, #1.
5. Merenskyite, Pd_{1.00}(Te_{1.94}Bi_{0.04}Sb_{0.01})₂=1.99, Grain 1 with temagamite and stuetzite or hessite.
6. Stuetzite, Ag_{4.98}Te_{3.00}, Area 1, with temagamite, merenskyite, and unnamed mineral.
7. Unnamed Pd-Hg-Ag telluride, Area 1, with temagamite, stuetzite, and merenskyite.

this combination of elements and stresses the importance of having standards with compositions very similar to the unknown, as was discussed recently by Cabri & Harris (1972) for insizwaite. Therefore, analysis 2 in Table 1 is suspect in this regard, but could not be repeated because this grain had been removed for x-ray powder diffraction.

The x-ray powder pattern obtained for temagamite (Table 2) consists of a few weak reflections which were partly masked by film darkening due to sample fluorescence. This pattern could not be indexed initially and was suspected to contain some chalcopyrite and hessite impurities. Dr. A. Kato, (pers. comm., 1973) suggested that the pattern be indexed on an orthorhombic pseudohexagonal cell by analogy to minerals such as moncheite. We have used this cell in an attempt to index synthetic Pd₃HgTe₃ which was prepared subsequently. However, the pattern of this synthetic phase was considerably more detailed (Table 2) and one reflection (~3.75Å) could not be accounted for and there was poor correspondence for another reflection (2.479Å). These two reflections were apparent after the sample was subjected to long exposures (e.g. over 34 hours for 114.6-mm cameras). Though no impurity was observed in the first polished section of the synthetic phase, two later sections, following annealing first at 500°C and then at 400°C and 425°C, showed about ½ area % impurity. These impurity grains ranged from a maximum size of 10 microns a side down to submicron dimensions and appear more strongly anisotropic than Pd₃HgTe₃. A qualitative analysis gave approximately a Pd₁Hg_{0.1}Te_{0.9} composition. If this impurity, which probably formed due to loss of Hg vapour, is more abundant in the submicron range, it could account for the extra reflection.

The phases Pd₂Te, Pd₅Te, and Pd₃Te are not fully characterized (Grønvold & Røst 1956); therefore, the contribution to the x-ray pattern of the impurity cannot be better defined.

The proposed orthorhombic symmetry for temagamite with cell dimensions a 11.57(1), b 12.16(1), c 6.76(1)Å must be considered tentative until such time as either a single crystal is studied by the precession method or a completely homogeneous synthetic phase with all reflections indexed can be obtained. It compares reasonably well with the unit-cell for synthetic Pd₃HgTe₃: a 11.608(2), b 12.186(1), c 6.793(1). The measured density of the synthetic material is about 9.5 g/cc. For $Z=6$, the calculated density of synthetic Pd₃HgTe₃ is 9.36 g/cc and that of the mineral is 9.45 g/cc.

Unnamed Pd-Hg-Ag telluride

Only one grain of this unnamed mineral was found (Fig. 1). The mineral appears darker grey than temagamite, is slightly bireflectant in air but distinctly bireflectant in oil. The colours in

TABLE 2. X-RAY DIFFRACTION DATA FOR TEMAGAMITE AND SYNTHETIC Pd₃HgTe₃

Temagamite			Synthetic Pd ₃ HgTe ₃			
$a=11.57(1)$	$b=12.16(1)$		$a=11.608(2)$	$b=12.186(1)$		
$c=6.76(1)\text{\AA}$			$c=6.793(1)\text{\AA}$			
<i>I</i>	$d_{\text{meas.}}$	$d_{\text{calc.}}$	<i>hkl</i>	<i>I</i>	$d_{\text{meas.}}$	$d_{\text{calc.}}$
			001	1	6.8	6.79
			020	1/2	6.1	6.09
			201	1/2	4.4	4.41
				3/4	3.75	
10	3.04*	3.041	040	<1/2	3.05	3.046
6	2.89	2.894	400	10	2.912	2.902
			122	1/2	2.871	2.874
			041	1	2.780	2.779
			222	4	2.639	2.641
			312	1	2.479	2.498
			421	2	2.441	2.444
2	2.30**					
1	2.24**					
5	2.17	2.176	113	9	2.187	2.186
1	2.07	2.079	123	4	2.089	2.088
4	1.95	1.951	342	7	1.959	1.956
			502	3	1.914	1.916
4	1.87*					
			620	2b	1.844	1.844
			612	5	1.661	1.665
1/2	1.62	1.618	542	5	1.624	1.622
			461	1/2	1.617	1.616
1b	1.59*	1.585	362	1/2b	1.591	1.589
			371	3	1.546	1.546
			560	1/2	1.528	1.528
			280	1/2	1.474	1.473
1b	1.45	1.459	263	5	1.462	1.463
			543	4	1.431	1.431
			472	2	1.367	1.366
			282	3	1.351	1.351
			463	1	1.340	1.340
			354	1/2	1.311	1.311
			614	3b	1.269	1.269
1b	1.24	1.249	581	4	1.251	1.251
			145	1	1.234	1.234
			1,10,0	1	1.212	1.212
1b	1.20	1.202	902	1	1.205	1.206
1/2	1.16	1.166	833	4	1.169	1.170
			10,1,0	5	1.155	1.155
			1,10,2	1/2	1.142	1.141
			772	3	1.132	1.132
			913	2	1.115	1.116
			206	1	1.111	1.111
1	1.07	1.080	365	2	1.084	1.084
			782	3	1.065	1.065
			275	1/2	1.053	1.053
			645	2	1.045	1.044
			10,0,3	1/2	1.030	1.033
			185	1b	1.010	1.010
			5,11,1	1b	0.9892	0.9892
			385	3	0.9809	0.9809
			456	1	0.9680	0.9681
			5,11,2	1	0.9591	0.9592
			636	2	0.9501	0.9501
			4,10,4	2	0.9375	0.9371
			12,3,1	1/2	0.9321	0.9322
			327	4	0.9303	0.9303
			4,12,2	1	0.9228	0.9225
			855	4b	0.9189	0.9187
			5,11,3	2	0.9145	0.9147

b - BROAD; * - CHALCOPYRITE; ** - HESSITE.

Additional weak reflections corresponding to the following indices were observed on the Guinier powder pattern of synthetic Pd₃HgTe₃: 201, 221, 002, 012, 112, 140, 410, 410, 103, 501, 332, 512.

The temagamite pattern was obtained with a 57.3 mm Gandolfi camera and that of Pd₃HgTe₃ with a 114.6 Debye-Scherrer camera. Both with Co/Fe radiation.

oil are brownish grey and bluish grey. The mineral is distinctly to strongly anisotropic in air and in oil. The colours are yellow-orange to a dull greyish brown. The latter colour changes to a greenish blue a few degrees away from extinction. The molecular proportions are very nearly the same for Pd, Hg, and Te whereas that of Ag is slightly lower. The small size of the grain and the presence of minerals containing these same elements preclude further speculation as to this mineral's stoichiometry, except that it is distinct from temagamite both in composition and in optical properties.

THERMAL STABILITY OF SYNTHETIC TEMAGAMITE

The behaviour of synthetic Pd₃HgTe₃ on heating was studied by DTA and by examination of quenched products. The DTA experiments were performed in evacuated and sealed silica tubes with quartz as internal standard. The use of quartz as internal standard proved to be a poor choice because of the superposition of some heat effects. Two separate DTA determinations were made on Pd₃HgTe₃, previously annealed at 425°C, and these are shown in Table 3.

The first endothermic reaction, noted at 496°C or 472°C, was observed as a drift from the base line and is interpreted as the result of loss of Hg vapour. The second (at 570 or 573°C) and third (at 670°C) endothermic reactions were sharp and were interpreted as the peritectic reaction Pd₃HgTe₃ → 3PdTe + Hg followed by the congruent melting of the PdTe at about 670°C. The PdTe, produced on the decomposition of Pd₃HgTe₃, contained 3 to 4 wt % Hg which may explain the compound's melting at a lower temperature than pure PdTe (720°C, Elliott 1965). Elliott's compilation of earlier work states that this area of the Pd-Te phase diagram needs to be re-investigated.

DISCUSSION

It is likely that temagamite is the same mineral that had earlier been reported by Kingston (1966) from Rustenburg (called unnamed M) from Cabri 1972) and by Genkin (1968, p. 84) from Monchegorsk. Kingston's description of his mineral's optical properties agree reasonably well with ours except for the report that it was iso-

TABLE 3. DTA RESULTS FOR SYNTHETIC Pd₃HgTe₃

Exp.	Heating: endothermic reactions at °C	Cooling: exothermic reactions at °C	Remarks
#1	0496, 570	0536, 475	Only heated to ~620 °C
#2	0472, 573, 670	0657, 643, 530, 477	Exothermic curves are broader and poorly defined

tropic. This may be due to the small grain size (2-5 μ in diameter) as well as being present as intergrowths with merenskyite.

The source of the precious metals for these massive chalcopyrite ores has not previously been positively related to the mineralogy (Franklin 1967; Rose 1966). The abundant temagamite and merenskyite in the specimen examined, however, makes it likely that these two minerals were responsible for the palladium values, while the occurrence of sperrylite has not been verified.

The identification of merenskyite and stuetzite was made only by comparing their optical properties and electron probe analyses. These minerals were too small to extract from the polished sections for confirmation by x-ray diffraction. The presence of hessite was established by some of the extra reflections on the x-ray powder pattern of temagamite, its optical properties being very similar to stuetzite. The abundance of stuetzite and hessite also suggests that these minerals may account for the silver values in the ore. The presence of siderite had not previously been reported. These observations are, however, open to the criticism that the specimen examined was unrepresentative of the massive chalcopyrite ore.

It is interesting to note the melting or decomposition points of temagamite ($\sim 570^\circ\text{C}$ and $\sim 670^\circ\text{C}$), stuetzite ($420(5)^\circ\text{C}$, Kracek *et al.* 1966), hessite ($960(1)^\circ\text{C}$, Kracek *et al.* 1966) and merenskyite (740°C , Elliott 1965). Their textural association suggests that they may have collected together in the molten state and crystallized into these four minerals on cooling. The eutectic temperatures in the Pd-Hg-Ag-Te system are not known, but will be well below the melting point of hessite. The detailed description and discussion of the porous pyrite nodules that occur in the Temagami chalcopyrite by Rose (1965, 1966) suggest a closed high-temperature system (above $\sim 550^\circ\text{C}$) which may have acted as a large-scale duplication of the heating experiments of MacLean *et al.* (1972). These experiments showed that, if chalcopyrite is heated in a sealed capsule above 550°C , it exsolves pyrite as small clusters of crystals, often related to holes which may be of gaseous origin. Therefore, the suggested origin for these nodules, as expressed by Rose (1965) that "... they were formed within invading chalcopyrite ore magma.", appears consistent with this experimental evidence.

CONCLUSIONS

The palladium minerals in the massive chalcopyrite ore from the Temagami deposit consist of three tellurides, temagamite, merenskyite, and an unnamed Pd-Hg-Ag telluride. This is the third reported occurrence of merenskyite in Can-

ada and stuetzite, hessite, and siderite are reported from the Temagami deposit for the first time. The close textural association of these five tellurides suggests a similar paragenesis and is consistent with a moderately high-temperature emplacement of the massive chalcopyrite orebodies.

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