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Research Article

New Data on the Crystallography and Mineralogy of Tsumoite

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Abstract

Tsumoite is a very rare and usually associated mineral on the Earth. As a result, its existing crystallographic and mineralogical data is neither complete nor reliable. Using the relatively abundant tsumoite produced in the world's first independent tellurium deposit; namely, the Dashuigou tellurium deposit in Sichuan, China, this paper conducts a relatively detailed study on the crystallography and mineralogy of this mineral, which can be regarded as a supplement and correction to the existing data. Tsumoite, as the second richest tellurium mineral from the deposit, occurs in the form of irregular vermiforms and/or fine veinlets at the contact between pyrrhotite, wall rock breccia including dolomite, and tetradymite, and in fractures of the pyrrhotite. In several cases, tsumoite appears in the form of interlocking crystals with tetradymite, and coexists with native gold, chalcopyrite, and so on. Tsumoite is anisotropic with glossy white color and low hardness. Its reflectance and micro-pressure hardness are respectively 36.2 (470 nm), 43.5 (546 nm), 44.8 (589 nm) and 47.3 (650 nm), and 192 kg/mm2 (Hv25). Its chemical compositions are Te=35.58% ~ 37.54%, Bi=61.56% ~ 62.20%, and chemical formula is calculated as BiTe0.97. Results of the quantitative phase analysis (wt.%) XRD-Rietveld and lattice parameters of the tsumoite are respectively a = 4.432 Å, c = 23.995 Å, and v = 408.294 Å3.

Keywords: Tsumoite, Chemical formula, Micro-pressure hardness, Reflectance, Lattice parameters based on the X-ray diffractogram analyses

Introduction

Due to the insufficient stock in nature, it is not easy to obtain enough pure single minerals, so the crystallographic and mineralogical data of some minerals cannot be perfected or are inaccurate. This is what the Chinese saying "a good cook cannot cook without rice" means. Most, if not all, rare elements have this problem. As the name implies, rare elements are very rare on the surface of the earth, that is, in the crust that we humans can easily access. Therefore, many minerals composed of these rare elements are even rarer. In other words, it is even more difficult to find such minerals in sufficient quantities for us humans to analyze and study. Because of this inherent deficiency, the crystallographic and mineralogical data of some minerals we know today are relatively limited, or the existing data lacks precision.Tellurium, discussed in this article, is one of the above rare elements. For a long time, all rare elements, including tellurium, have been judged by traditional mineral deposit and geochemical theories to be unable to form independent deposits, and can only appear as associated components of other bulk deposits such as copper and nickel, which is what the author of this article calls parasitic minerals.

In a sense, the above traditional mineral deposit theory is correct. The Clark values of these rare elements like tellurium in the earth's crust are extremely low, and it is thus difficult for them to form independent mineral deposits. For instance, the average content of Te in the Earth's crust is 2.0 × 10–8 in China, and only 1.34 × 10–9 worldwide [1-3]. With such a low crustal Clarke value, it is indeed difficult for tellurium to form independent deposits. Therefore, the crystallographic and mineralogical data of those minerals composed of tellurium as one of the main elements are relatively limited or lacking. These tellurium minerals include tsumoite studied in this article. In the 1990s, with the discovery, development and research of the Dashuigou independent tellurium deposit in Sichuan, China [4 -13], it became possible to supplement, improve and refine the crystallographic and mineralogical data of some tellurium minerals in terms of sample quantity and quality. As a result, this article provides some new crystallographic and mineralogical data on tsumoite, one of the tellurium minerals.

This paper uses samples from the Dashuigou tellurium deposit to obtain the chemical formula of tsumoite, micro-pressure hardness and reflectance under international standard light waves, and X-ray powder diffraction data. This is a supplement and update to the crystallographic and mineralogy data of tsumoite.

Petrography

As the second most common telluride after tetradymite, tsumoite makes up around 2%~3% of all tellurides from the Dashuigou tellurium deposit. In the form of irregular vermiform and/or fine veinlet, most of the tsumoite distributes at the contacts between pyrrhotite, wall rock breccia, and tetradymite and in fractures of the pyrrhotite (Figures 1~3). Under the microscope, tsumoite demonstrates a greasy, yellowish white color, anisotropic or nonhomogeneous characteristics, and low hardness.

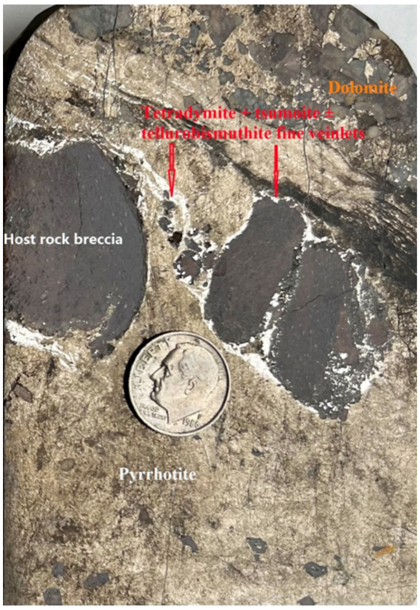

Figure 1: Silvery white colored tetradymite + tsumoite ± tellurobismuthite fine veinlets in massive pyrrhotite (earthy yellow colored) + dolomite (grey to dark grey) + host rock breccia (dark brown) (sample #: SD34, Ore body #I-1 in Drift 3)

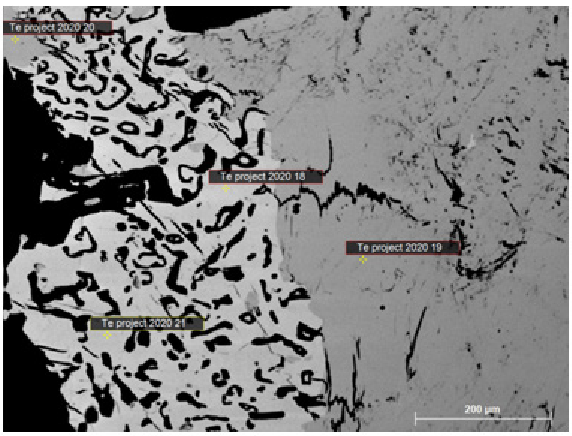

Figure 2: Reflection color and their mutual relationships between tsumoite (bright white), tetradymite (light grey), and pyrrhotite (black) under scanning-electron microscopy (image of the Slide 6 by the lab of UBC)

As Bayliss pointed out that members of the tetradymite group present complex problems, many of which remain unsolved due to incomplete data (1991). In several cases, tsumoite appears in the form of interlocking crystals with tetradymite, and coexists with native gold, chalcopyrite and so on. Tsumoite coexists with chalcopyrite, indicating unmixing characteristics of solid solution. Tsumoite's reflectance under the four international standard wavelengths is listed in Table 1, and its micro-pressure hardness is listed in Table 2. Both reflectance and micro-pressure hardness of the tsumoite are the first groups of data of their kind thus far. Conversely, reflectance of tsumoite under microscope is clearly higher than that of pyrrhotite, but a little bit lower than that of tetradymite from the same deposit.

Table 1: Reflectance (R) of the tsumoite from the Dashuigou deposit.

Wave length (nm)	470	546	589	650
Sample #	*R* %			
1	36.2	43.5	44.8	47.3
Standard sample	Black glasss: *R* % (air) ~4.5%			

Instrument: German Leitz MPV-3 microscopic photometer

Lab of the College of Earth Sciences, Jilin University, China

Instrument: German Leitz ORTHO PLAN microhardness tester

Lab of the College of Earth Sciences, Jilin University, China

The Bi-Te-Se-S compound system faces significant challenges due to the limited documentation of its naturally occurring phases, the rarity of these species, and the variability in quality and quantity of published data, such as reflectance and micro-pressure hardness. These difficulties are further heightened by the typically small grain size and intergrown nature of minerals like tsumoite. The lack of extensive data on tsumoite's reflectance and micro-pressure hardness prevents comprehensive comparison or confirmation of the existing results' normality [14].

Table 2: Micro-pressure harness (Hv) of tsumoite from the Dashuigou deposit

Sample #	Kg/mm^2	
	Hv25	Average
1	192.0	192.0

Chemical composition

The tsumoite's chemical compositions from samples collected from different ore bodies of the Dashuigou tellurium deposit and analyzed by electronic probe are listed in Table 3.

Table 3: Electron microprobe analyses of the tsumoite from the Dashuigou deposit (%)

Sample #	**Test point**	**Te**	**Bi**	**S**	**Fe**	**Cu**	**As**	**Ni**	**Zn**	**Au**	**Ag**	**Total %**	**G.C.F.***	**Data source**
D (Tsumoite)	1	37.54	62.02	0.01	0.03	0.04	0.00	0.02	0.06	0.03	0.04	99.79	$BiTe_{0.99}$	This paper
	2	36.58	62.00	0.71	0.09	0.05	0.05	0.09	0.10	0.03	0.00	99.70	$BiTe_{0.97}$	
	3	36.57	62.20	0.11	0.09	0.05	0.05	0.09	0.11	0.03	0.00	99.30	$BiTe_{0.96}$	
	4	36.18	61.56	0.87	0.11	0.23	0.15	0.07	0.06	0.01	0.06	99.30	$BiTe_{0.96}$	
	5	35.58	61.61	0.73	0.11	0.14	0.04	0.14	0.07	0.00	0.09	98.51	$BiTe_{0.95}$	
	6	36.87	61.63	0.64	0.09	0.14	0.04	0.14	0.07	0.00	0.09	99.71	$BiTe_{0.98}$	
	Average	34.60	60.08	4.61	0.08	0.04	0.05	0.06	0.09	0.02	0.03	99.66	$BiTe_{0.97}$	
Tetradymite	Average	34.60	60.08	4.61	0.08	0.04	0.05	0.06	0.09	0.02	0.03	99.66	$Bi_{2.00}Te_{1.89}S_{1.00}$	Yin & Shi, 2020a
Note and comparison	Hedleyite	17.59	80.95									98.54	Bi_7Te_3 and/or /$Bi_{14}Te_6$ (natural)	Lindahl, 1975
	Telluro-bismuthite	47.80	52.20	Tellurobismuthite, or tellurbismuth								100.00	Bi_2Te_3	Tellurobismuthite, 2024
	Wehrlite or Pilsenite	31.41	68.59	Material described by Huot in 1841 was named wehrlite and thought to contain Bi, Te, and Ag. Kenngot, in 1853, used the name pilsenite for similar material. It was later found that wehrlite was a mixture								100.00	Bi_4Te_3	Li and Xue, 1987

Note: G.C.F.* - general chemical formula. By the electron microprobe lab, Chinese Academy of Geological Sciences, China

From the results of different samples, it can be seen that the compositions are very similar and stable: Te varies between 35.58%~37.54%, with an average of 36.55% and a maximum difference of 1.96%; Bi varies between 61.56%~62.20%, with an average of 61.84% and a maximum difference of 0.64%. The total of the two elements takes up to 97.09%, while other impure elements, including S, Fe, Cu, Au, Ni, Zn, As, and Ag et. al., take up approximately 2.81%. At this stage, it is unclear in what form these trace elements appear in the tsumoite. The calculated chemical formula of tsumoite from the deposit is BiTe0.95~0.95, and the average formula is BiTe0.97.

X-ray power diffraction

The quantitative phase analysis of one powder sample (#SD-40, Figure 2-3) using the RIETVELD method and X-ray powder diffraction data was conducted at the lab of Department of Earth, ocean and Atmospheric Sciences, University of British Columbia, Canada. Detailed information of the analysis is described as follows.

Brief experimental process and method

A McCrone Micronizing Mill was used to grind sample SD-40 from Project #1902410 in ethanol for 10 minutes, achieving an optimal grain size of less than 10 mm for quantitative X-ray analysis. CoKα radiation was applied in a Bruker D8 Advance Bragg-Brentano diffractometer, equipped with an Fe filter foil, 0.6 mm (0.3°) divergence slit, and incident- and diffracted-beam Soller slits, as well as a LynxEye-XE detector, to collect continuous-scan X-ray powder diffraction data within a 3-80°2θ range. The long fine-focus Co X-ray tube functioned at 35 kV and 40 mA with a 6° take-off angle.

Results

Utilizing the International Centre for Diffraction Database PDF-4 and Bruker's Search-Match software, the X-ray diffractogram was analyzed. The Rietveld program Topas 4.2 (Bruker AXS) was employed to refine the X-ray powder diffraction data of the sample, with the outcomes of the quantitative phase analysis from Rietveld refinements presented in Table 4.

These values signify the relative quantities of crystalline phases normalized to 100%. The Rietveld refinement plot can be observed in Figure 4, while unit cell/lattice parameters and volumes are listed in Table 5. Experimental and calculated two theta values with hkl indices are presented in Table 6.

Table 4: Results of quantitative phase analysis (wt.%)

Mineral	ICSD collection code	Ideal formula	SD-40
Tsumoite	100654	BiTe	11.5
Tetradymite	26720	Bi2Te2S	51.5
Tellurobismuthite	74348	Bi_2Te_3	1.9
Pyrrhotite 4C	42491	Fe_7S_8	26.1
Ankerite – dolomite	66333	$Ca(Fe^{2+},Mg,Mn)(CO_3)_2$ - $CaMg(CO_3)_2$	8.1
Chalcopyrite	80095	$CuFeS_2$	0.5
Quartz	174	SiO_2	0.4
Total			100.0

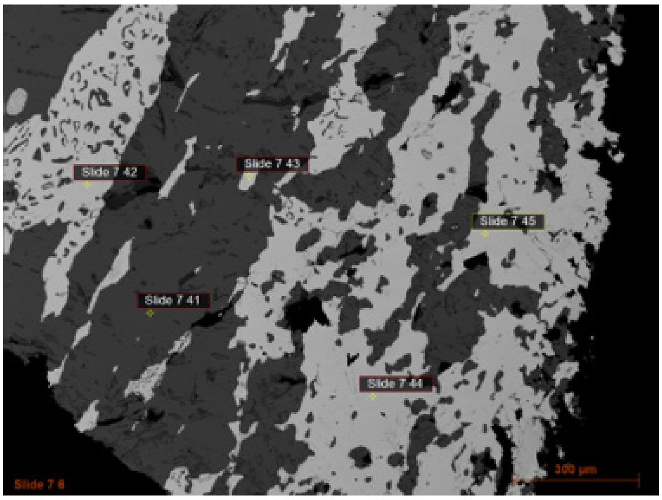

Figure 3: The scanning-electron microscopy image indicating mineral distribution of telluride including tetradymite and tsumoite (light grey) that are interlocked, and pyrrhotite (black) (image of the Slide 7 by the lab of UBC)

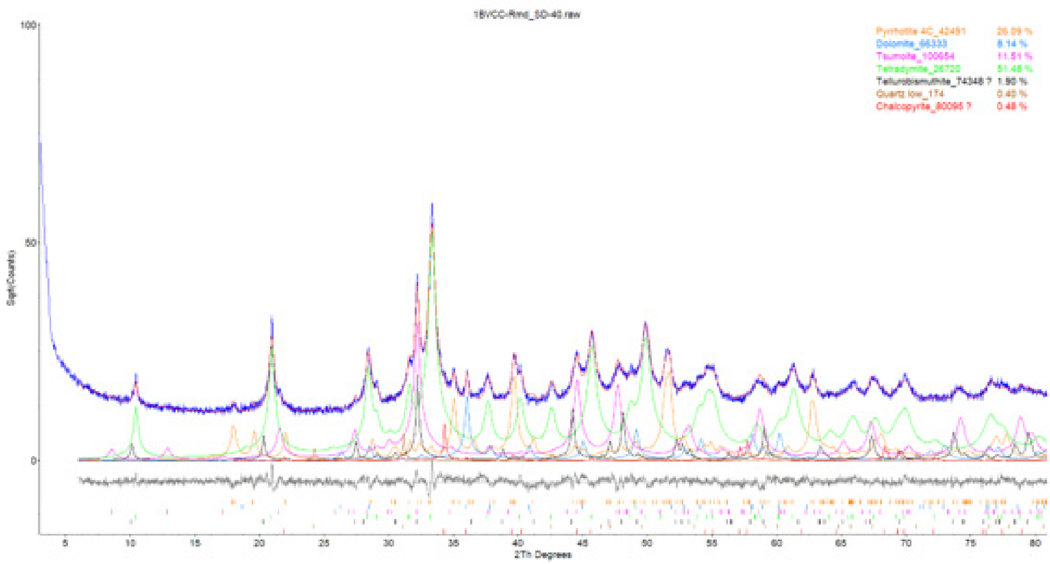

Figure 4: The Rietveld refinement plot
Blue line: observed intensity at each step; Red line: calculated pattern; Solid grey line below: difference between observed and calculated intensities; Vertical bars: positions of all Bragg reflections. Coloured lines are individual diffraction patterns of all phases

Blue line: observed intensity at each step; Red line: calculated pattern; Solid grey line below: difference between observed and calculated intensities; Vertical bars: positions of all Bragg reflections. Coloured lines are individual diffraction patterns of all phases

Table 5: Results of quantitative phase analysis (wt.%) XRD-Rietveld and lattice parameters

Phase name	ICSD collection code	SG	Refined values						
			wt.%	a (Å)	b (Å)	c (Å)	alpha(°)	beta(°)	V (Å^3)
Tsumoite	100654	P-3m1	11.5	4.432		23.995			408.294
Tetradymite	26720	R-3R	51.5	10.172			24.113		154.391
Tellurobismuthite	74348	R-3mH	1.9	4.397		30.512			510.975
Pyrrhotite	42491	C12/c1	26.1	11.935	6.864	12.834		117.236	934.840
Dolomite	66333	R-3H	8.1	4.679		16.573			314.297
Chalcopyrite	80095	I-42d	0.5	5.295		10.402			291.630
Quartz low	174	P3221S	0.4	4.929		5.361			112.811
Total			100.0						

Phase name	ICSD collection code	SG	Published values					
			a (Å)	b (Å)	c (Å)	alpha(°)	beta(°)	V (Å^3)
Tsumoite	100654	P-3m1	4.422		24.050			407.270
Tetradymite	26720	R-3R	10.330			24.170		162.410
Tellurobismuthite	74348	R-3mH	4.395		30.440			509.210
Pyrrhotite	42491	C12/c1	11.902	6.859	12.817		117.264	930.100
Dolomite	66333	R-3H	4.806		16.006			320.220
Chalcopyrite	80095	I-42d	5.277		10.441			290.750
Quartz low	174	P3221S	4.913		5.405			113.010

Discussion

Strunz defined the tetradymite group narrowly to encompass only Bi2(S+Se+Te)3 minerals, which include hexagonal or trigonal minerals featuring a tetradymite layer structure with an approximately cubic closest-packed arrangement [15]. Within this layer, the sequence of planes is Te-Bi-S-Bi-Te. The tetradymite group, as seen in tsumoite, includes the following main members:

Tetradymite: This is the principal tellurium mineral of the Dashuigou independent tellurium deposit, which comprises up to 95%. Hedleyite: trigonal crystal system, tin white, metallic lustre, opaque, measured hardness 2 on Mohs scale; perfect basal cleavage {0001}, common basal cleavage {0001}; common impurities including Se and S, often occuring as solid solution with tsumoite (Table 3).

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Table 6: The hkl vs two theta of the tsumoite

Tsumoite (ICDD 00-42-1447)						λ	Co tube 1.79
No.	h	k	l	m	d [Å]	th2 [°]	F^2
1	0	0	3	2	5.52443	18.63624	0.002
2	1	0	1	6	3.93660	26.26745	0.044
3	0	1	2	6	3.64054	28.44676	0.133
4	1	0	4	6	2.89716	35.96764	4.379
5	0	0	6	2	2.76221	37.78963	0.271
6	0	1	5	6	2.56574	40.80699	0.329
7	1	1	0	6	2.33976	44.95258	0.695
8	1	-2	-3	6	2.15449	49.06076	0.587
9	1	1	3	6	2.15449	49.06076	1.708
10	1	0	7	6	2.04430	51.89587	0.032
11	0	2	1	6	2.01131	52.81218	0.411
12	2	0	2	6	1.96830	54.05900	1.416
13	0	1	8	6	1.84461	58.01458	2.362
14	0	0	9	2	1.84148	58.12294	0.189
15	0	2	4	6	1.82027	58.86605	0.579
16	1	-2	-6	6	1.78534	60.13502	1.988
17	1	1	6	6	1.78534	60.13502	1.032
18	2	0	5	6	1.72884	62.31520	0.034
19	0	2	7	6	1.53947	71.04749	0.013
20	1	0	10	6	1.53401	71.33893	0.158
21	1	2	-1	6	1.52523	71.81287	0.412
22	2	1	1	6	1.52523	71.81287	0.281
23	1	-3	-2	6	1.50622	72.86383	1.261
24	1	2	2	6	1.50622	72.86383	0.465
25	2	0	8	6	1.44858	76.26714	0.645
26	1	-2	-9	6	1.44706	76.36179	0.603
27	1	1	9	6	1.44706	76.36179	0.300
28	1	2	-4	6	1.43670	77.01286	0.855
29	2	1	4	6	1.43670	77.01286	0.564
30	0	1	11	6	1.41222	78.60191	0.015
31	1	2	5	6	1.39045	80.07850	0.047
32	1	-3	-5	6	1.39045	80.07850	0.559
33	0	0	12	2	1.38111	80.73135	1.127

Tellurobismuthite: This mineral belongs to the trigonal crystal system, lead-gray, metallic lustre, opaque, streak pale lead-grey, hardness 1½ ~ 2 on Mohs scale (Table 3); common impurity S, usually associated with tetradymite and hard to distinguish from each other by the naked eye. Wehrlite or Pilsenite: trigonal crystal system, lead-gray, metallic lustre, opaque, hardness 1½ ~ 2½ on Mohs scale; common impurities including Ag, Pb, Fe and S; similar reflection color and polish as tetradymite but of higher hardness than the latter (Table 3).

There exists minimal reporting on tsumoite, as it is one of the world's rare minerals. Of course, there are reports of trace amounts of tsumoite being found in deposits such as copper-nickel [16 & 17]. For example Li et al. reported that one grain of was discovered for the first time in the ore from the Kelatongke Cu-Ni deposit in China, but no more detailed data is available about the discovery. Bao reported discovery of tsumoite in the Huangshandong Cu-Ni deposit in China, and called this "the second discovery of tsumoite in China". The two irregular grains of tsumoite, around 7.15 um in size, were discovered in drill core respectively at depths of 755.5 m and 472.0 m, of which the first was in chalcopyrite, and the second in pyrrhotite. Under the microscope, the tsumoite was bright white, weak anisotropic, interlocking with chalcopyrite, polishing hardness close to that of chalcopyrite. As compared to tsumoite from the Huangshandong Cu-Ni deposit, tsumoite from the Dashuigou deposit is poorer in tellurium [18-20].

Conclusions

Based on the preceding discussion, preliminary conclusions on tsumoite from the Dashuigou tellurium deposit can be drawn as follows:

As the second most abundant telluride following tetradymite in the Dashuigou independent tellurium deposit, tsumoite is found as irregular vermiform or fine veinlets at the interface between pyrrhotite, wall rock breccia containing dolomite, tetradymite, and pyrrhotite fractures. Tsumoite often occurs interlocked with tetradymite crystals and coexists with native gold, chalcopyrite, and other minerals. The coexistence of tsumoite with chalcopyrite suggests unmixing characteristics of solid solutions.Under a microscope, tsumoite exhibits a greasy yellowish-white color, anisotropic characteristics, and low hardness. Reflectance and micro-pressure hardness values are 36.2 (470 nm), 43.5 (546 nm), 44.8 (589 nm), 47.3 (650 nm), and 192 kg/mm2 (Hv25), respectively. Chemical compositions of tsumoite range from 35.58% to 37.54% Te (average 36.55%) and 61.56% to 62.20% Bi (average 61.84%). The calculated chemical formula is BiTe0.95~0.99, with an average of BiTe0.97, indicating slightly lower tellurium content than that found in tsumoite (BiTe1.01) from the Huangshandong Cu-Ni deposit in mainland China. Quantitative phase analysis (wt.%) XRD-Rietveld results and lattice parameters of tsumoite are a = 4.432 Å, c = 23.995 Å, and V = 408.294 Å3, respectively.

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Conflict of Interest:

None.

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