

Crystal chemistry and phase stability of wuyanzhiite, a new mineral dimorphous with chalcocite, from the Bofang Copper Mine, Hunan, China

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ABSTRACT

A new mineral species, wuyanzhiite, ideally Cu_2S (IMA 2017–081), which is dimorphous with chalcocite, was discovered in the Bofang sandstone-type copper deposit, Hengyang, Hunan, China. It occurs as granular aggregates or oriented ribbons, 10 to $>500\ \mu\text{m}$ in size, composed of nanometric to micrometric anhedral crystals. Associated minerals include chalcocite, djurleite, digenite, sphalerite, tennantite-(Zn), bornite, pyrite, and smithsonite, with minor presence of uraninite, arsenic, zeunerite, and kasolite. Wuyanzhiite is opaque with dark gray color, metallic luster, and black streak, brittle with uneven fracture, and has a Mohs hardness of 3 and a calculated density of $5.618\ \text{g/cm}^3$. Under reflected light, wuyanzhiite shows a gray blue color and becomes darker with increasing Fe content. The reflectance values (%) are 27.0–29.3 (470 nm), 23.8–26.6 (546 nm), 23.1–26.3 (589 nm), and 21.1–25.2 (650 nm). The empirical chemical formula from the average of 75 electron microprobe analyses is $(\text{Cu}_{1.801}^{+}\text{Cu}_{0.081}^{2+}\text{Fe}_{0.018}^{2+}\text{Ag}_{0.001})_{\Sigma 1.901}\text{S}_{1.000}$ assuming charge balance with Fe^{2+} . The chemical composition of wuyanzhiite exhibits a range of cation/S ratio from 1.993 to 1.710 and of Fe content from 0 to 2.88 wt% (0–0.074 apfu), with significant negative correlations between Cu (apfu), (Cu+Ag)/S and Fe (apfu), and a positive correlation between Cu^{2+} (apfu) and Fe (apfu). Wuyanzhiite is the tetragonal polymorph of Cu_2S with space group $P4_32_12$ and unit-cell parameters $a = 4.0042(4)\ \text{\AA}$, $c = 11.2555(13)\ \text{\AA}$, $V = 180.47(3)\ \text{\AA}^3$, and $Z = 4$. The structure of wuyanzhiite, refined to $R1 = 0.0480$ for 131 independent reflections [$I > 2\sigma(I)$], is characterized by approximate cubic close packing of S atoms along $[0\ \bar{1}\ 2]$ with an interlayer distance of $3.554\ \text{\AA}$. Cu atoms are located at the centers of nearly equilateral triangles of S atoms with Cu-S bond lengths ranging from 2.296 to $2.317\ \text{\AA}$, and the CuS_3 triangles are corner-connected to form a framework with each S atom shared by six CuS_3 triangles. The high-Fe content ($>0.7\ \text{wt\%}$) in wuyanzhiite may enhance its stability at ambient conditions. The name wuyanzhiite honors Yanzhi Wu (1931–2014) at Central South University, Changsha, China.

Keywords: Wuyanzhiite, chalcocite, copper sulfide, new mineral, crystal chemistry, mineral stability, Bofang, China

INTRODUCTION

The Cu-S system contains a complex suite of minerals and synthetic phases with various Cu/S ratios, including chalcocite (Cu_2S), djurleite ($\text{Cu}_{31}\text{S}_{16}$), digenite (Cu_9S_5), roxbyite (Cu_9S_5), geerite (Cu_8S_5), spionkopite ($\text{Cu}_{39}\text{S}_{28}$), anilite (Cu_7S_4), yarrowite (Cu_9S_8), covellite (CuS) (Goble 1985; Mumme et al. 1988), and synthetic CuS_2 phases (Bither et al. 1968; King and Prewitt 1979; Kjekshus et al. 1979). These Cu-S phases are not only economically significant as copper ores but are also of interest for their potential applications in solid-state ionics, photovoltaics, and superconductivity (e.g., Bither et al. 1968; Wang 2012; Suekuni and Takabatake 2016; Li et al. 2022; Hou et al. 2023). The monoclinic chalcocite is stable below $105\ ^\circ\text{C}$ and converts to hexagonal Cu_2S between 105 and $420\ ^\circ\text{C}$, and to

cubic Cu_2S above $420\ ^\circ\text{C}$ at room pressure (Roseboom 1966; Skinner 1966). Zimmer et al. (2018) showed that the monoclinic chalcocite undergoes two pressure-induced first-order phase transitions at ~ 3.1 and $\sim 7.1\ \text{GPa}$ to two other monoclinic HP1 and HP2 phases, respectively. Djurle et al. (1958) first synthesized metastable tetragonal $\text{Cu}_{1.96}\text{S}$ at $150\ ^\circ\text{C}$. Janosi (1964) prepared the same phase at $140\ ^\circ\text{C}$ and determined its crystal structure in space group $P4_32_12$ with the ideal formula Cu_2S . Zimmer et al. (2017) demonstrated that the tetragonal phase of Cu_2S , synthesized at $500\ \text{K}$ and $8\ \text{GPa}$, converted to an orthorhombic $Pna2_1$ Cu_2S phase at low temperatures around $-51\ ^\circ\text{C}$. Skinner (1970), Clark and Sillitoe (1971), and Gablina et al. (2004) showed that the tetragonal phase of Cu_2S is unstable at ambient conditions and will transform to monoclinic chalcocite within several months or a year. The natural occurrences of the tetragonal phase have been observed by Skinner et al. (1967), Clark and Sillitoe (1971), and Gablina et al. (2004). However, the intimate intergrowth of this phase with chalcocite, djurleite, and bornite, along with its instability in air in their samples, had

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prevented the acquisition of sufficient data for the definition of a new mineral species.

During an investigation on the mineralogy of the Bofang copper deposit in March 2017, we identified the tetragonal Cu_2S phase from the massive chalcocite ore and characterized its morphology, petrology, composition, and crystallography, which allowed us to propose it as a new mineral to the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA-CNMNC). Both the mineral and its name (“wuy” as the symbol) have been approved by IMA-CNMNC (IMA 2017–081). The new mineral was named in honor of the late Chinese ore geologist, Wu Yanzhi (1931–2014). Wu received his B.S. degree from Nanjing University in 1952 and later became one of the first teachers in the Department of Geology at the Central South Institute of Mines and Metallurgy (now Central South University). He made significant contributions to the understanding of ore genesis and to the exploration of nonferrous and precious metal deposits in China. His responsibility and proficiency in geoscience education were highly respected and remembered by colleagues at

Central South University and across China. The type material of wuyanzhiite was deposited in the Geological Museum of China under catalog number GMC M13712.

OCCURRENCE AND MINERAL ASSOCIATION

The Bofang Copper Mine is located at $26^{\circ}32'24.4''\text{N}$, $112^{\circ}26'53.5''\text{E}$, about 50 km south of Hengyang City, Hunan Province, China. The deposit is considered to be a sandstone type hosted in the Cretaceous sandstone or along the unconformities between the Cretaceous sandstone and the Upper Carboniferous limestone or the Lower Permian coal-bearing shale (Fig. 1). The Bofang Mine is a small-scale mine and has been under production since 1960 with a total reserve of about 200 000 tons of metal copper. It is famous for the massive chalcocite ores, with an average copper grade of about 35%, which are directly transported to the copper smelter without ore dressing. Wuyanzhiite was found in the specimens of massive chalcocite ores collected from #5 orebody at the –65 m level (Fig. 2). The associated minerals include chalcocite,

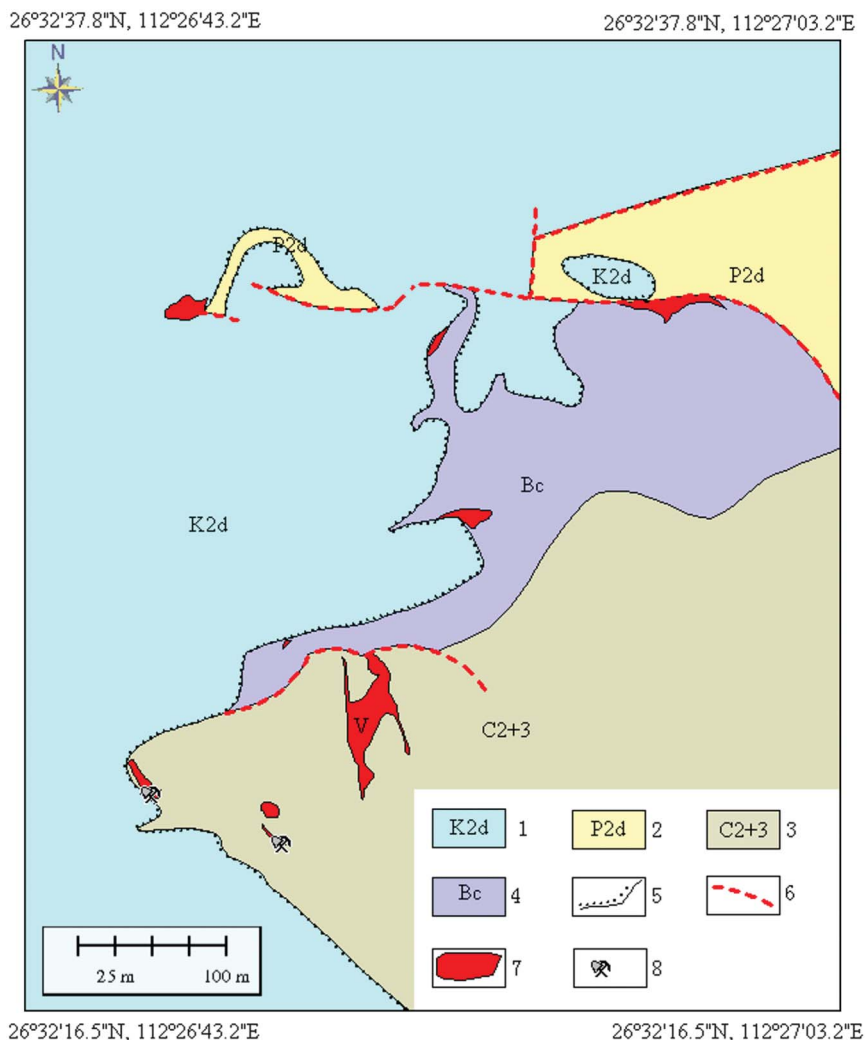


FIGURE 1. Geological map of the –65 m underground pit level of the Bofang copper mine and sampling locations of wuyanzhiite (after the internal data of the Mine). Legend: 1 = Sandstone of the Upper Cretaceous Daijiaping Group. 2 = Carbonaceous shale and sandstone of the Upper Permian Douling Group. 3 = Limestone of the Middle and Upper Carboniferous. 4 = Brecciated rocks. 5 = Disconformity. 6 = Supposed faults. 7 = Massive copper ore bodies. 8 = Sampling locations of wuyanzhiite.



FIGURE 2. Specimen of massive chalcocite (Cc ~85%) in association with djurleite (Dju ~8%), sphalerite (Sp, ~5%), wuyanzhiite (Wuy ~1%) and minor digenite (Dg), tennantite-(Zn) (Tnt), smithsonite (Smt), pyrite (Py), uraninite (Urn), and zeunerite (Zer).

djurleite, digenite, sphalerite, tennantite-(Zn), bornite, pyrite, and smithsonite with the presence of uraninite, arsenic, zeunerite, and kasolite (Fig. 3).

Wuyanzhiite, along with other copper and zinc sulfide and carbonate minerals, is considered to have been formed from secondary enrichment of copper at relatively high temperature (182–192 °C) and low salinity (1.2–4.7% NaCl equiv.) (Peng 1991; Deng et al. 2008; Yuan 2008).

MORPHOLOGICAL, PHYSICAL, AND OPTICAL PROPERTIES

Wuyanzhiite occurs as granular aggregates or oriented ribbons measuring 10 to >500 μm , composed of nanometric to micrometric anhedral crystals. It often forms intimate intergrowth with chalcocite, djurleite, digenite, tennantite-(Zn), and zeunerite (Fig. 3). Macroscopically, it is dark gray with metallic luster and black streak (Fig. 2). The mineral is brittle with uneven fracture, and the measured VHN_{50} hardness is 81–102 (average 94) corresponding to Mohs hardness around 3. The calculated density is 5.618 g/cm^3 based on the average empirical formula and unit-cell parameters obtained from single-crystal X-ray diffraction.

Under a reflected light, wuyanzhiite shows bireflectance with a pleochroism color from gray blue to slightly darker blue, which makes wuyanzhiite distinguishable from associated chalcocite and djurleite (Fig. 3). It is weakly anisotropic without internal reflections. The reflectance of wuyanzhiite decreases, and the color becomes bluer and darker with increasing Fe content. The reflectance values ($R_{\text{min}}/R_{\text{max}}$) measured in air with Tidas MSP 400 microphotometer attached to Leica DM2500p microscope using SiC standard are listed in Table 1, yielding a color index (relative to the C-illumination): $x = 0.2911$, $y = 0.2924$, $Y = 23.71\%$, $\lambda_d = 473 \text{ nm}$, $\text{Pe} = 0.097$ for R_{min} with higher Fe content (0.62 Fe apfu), and $x = 0.2970$, $y = 0.2974$, $Y = 26.66\%$, $\lambda_d = 469 \text{ nm}$, $\text{Pe} = 0.071$ for R_{max} with lower Fe content (0.13 Fe apfu).

TABLE 1. Reflectance data for wuyanzhiite (in %)

λ (nm)	R_{min}	R_{max}	λ (nm)	R_{min}	R_{max}
400	34.2	36.0	560	23.6	26.5
420	32.7	34.6	580	23.3	26.4
440	29.9	32.0	589 (COM)	23.1	26.3
460	27.8	30.1	600	22.9	26.2
470 (COM)	27.0	29.3	620	22.4	26.0
480	26.3	28.6	640	21.6	25.5
500	25.2	27.7	650 (COM)	21.1	25.2
520	24.4	27.0	660	20.5	24.8
540	23.9	26.7	680	19.9	23.7
546 (COM)	23.8	26.6	700	18.8	22.1

CHEMICAL COMPOSITION

The chemical composition of wuyanzhiite was determined using Shimadzu EPMA-1720 with an accelerating voltage of 15 kV, a beam current of 10 nA, and a beam size of 1 μm . Quantitative analyses were carried out in WDS mode using the standards (X-ray lines): CuFeS_2 ($\text{SK}\alpha$), Cu_2S ($\text{CuK}\alpha$), Ag metal ($\text{AgL}\alpha$), CuFeS_2 ($\text{FeK}\alpha$), and FeAsS ($\text{AsL}\alpha$). The ZAF4 correction program supplied with the instrument was used for the correction calculations. The detection limits for Cu, Fe, Ag, As, and S are around 0.01 wt%. Due to the difficulty in distinguishing wuyanzhiite from associated chalcocite and djurleite in backscattered electron images (Fig. 3c–3d), all analyses were carried out using optical images and checked by in situ X-ray microdiffraction. The average of 75 analyses gave Cu 77.87, Fe 0.66, Ag 0.10, S 20.87, As 0.01, total 99.50 wt% (Table 2), corresponding to an empirical formula $(\text{Cu}_{1.801}^+ \text{Cu}_{0.081}^{2+} \text{Fe}_{0.018}^{2+} \text{Ag}_{0.001})_{\Sigma 1.901} \text{S}_{1.000}$ based on $\text{S} + \text{As} = 1$, in which Cu^+ and Cu^{2+} are calculated according to charge balance. The simplified formula is $(\text{Cu}^+, \text{Ag}^+, \text{Cu}^{2+}, \text{Fe}^{2+})_2\text{S}$, and the ideal formula is Cu_2S , which requires 79.86 Cu and 20.14 S wt% (for more detail, please refer to the Online Materials¹ Table S1).

It is noted that the Fe content of wuyanzhiite varies in a wide range from 0 to 2.88 wt% (0 to 0.074 apfu), and the increase of Fe content is accompanied by a decrease of total Cu apfu from 1.941 to 1.675 and a decrease of $(\text{Cu} + \text{Ag})/\text{S}$ atomic ratio from 1.993 to 1.710 (Table 2; Figs. 4a–4b). A calculation of charge balance shows that Cu^{2+} is needed for charge balance, and its content (apfu) increases with increasing Fe (apfu) as shown in Figure 4d. For comparison, the compositions of associated chalcocite (39) and djurleite (14) in the Bofang Mine were also analyzed, and the mean results are presented in Table 2 (see Online Materials¹ Table S1 for more detail). It is evident that chalcocite and djurleite are poor in Fe content, and the Cu/S ratio of chalcocite (1.991) is close to the ideal value of 2 (Cu_2S), while djurleite (1.897) is lower than the ideal 1.9375 ($\text{Cu}_{31}\text{S}_{16}$), indicating the presence of more Cu^{2+} in the structure of djurleite.

X-RAY CRYSTALLOGRAPHY

X-ray powder diffraction data of wuyanzhiite were obtained in situ on the polished sections with Rigaku D/Max Rapid II microdiffractometer using a rotating Cu target X-ray generator at 40 kV, 250 mA, and 0.03, 0.05, and 0.1 mm collimators for the beam size of X-ray with the exposure time from 20 min to 5 h. The peak data are listed in Table 3, from which the tetragonal unit-cell parameters were refined using the program of Holland and Redfern (1997): $a = 4.0019(1) \text{ \AA}$; $c = 11.2691(4) \text{ \AA}$; $V = 180.477(8) \text{ \AA}^3$; $Z = 4$.

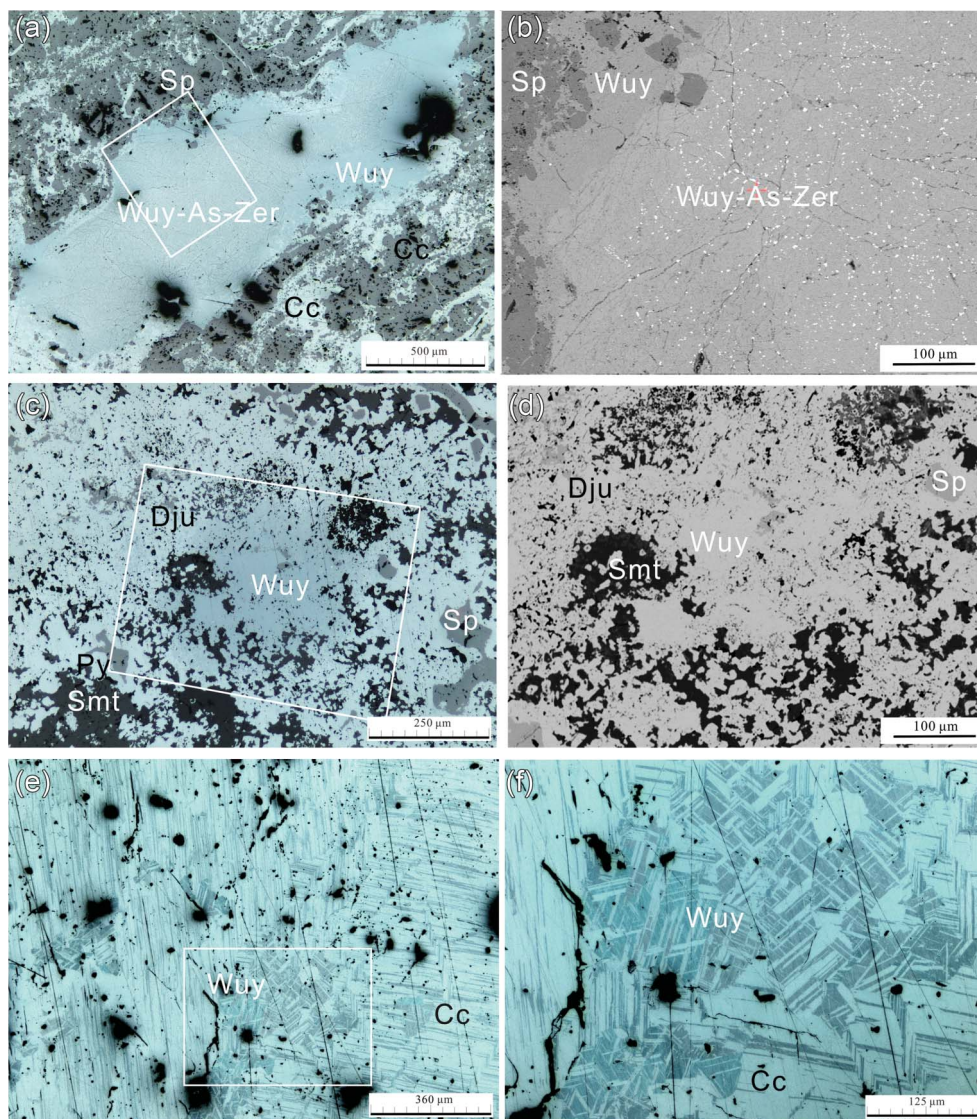


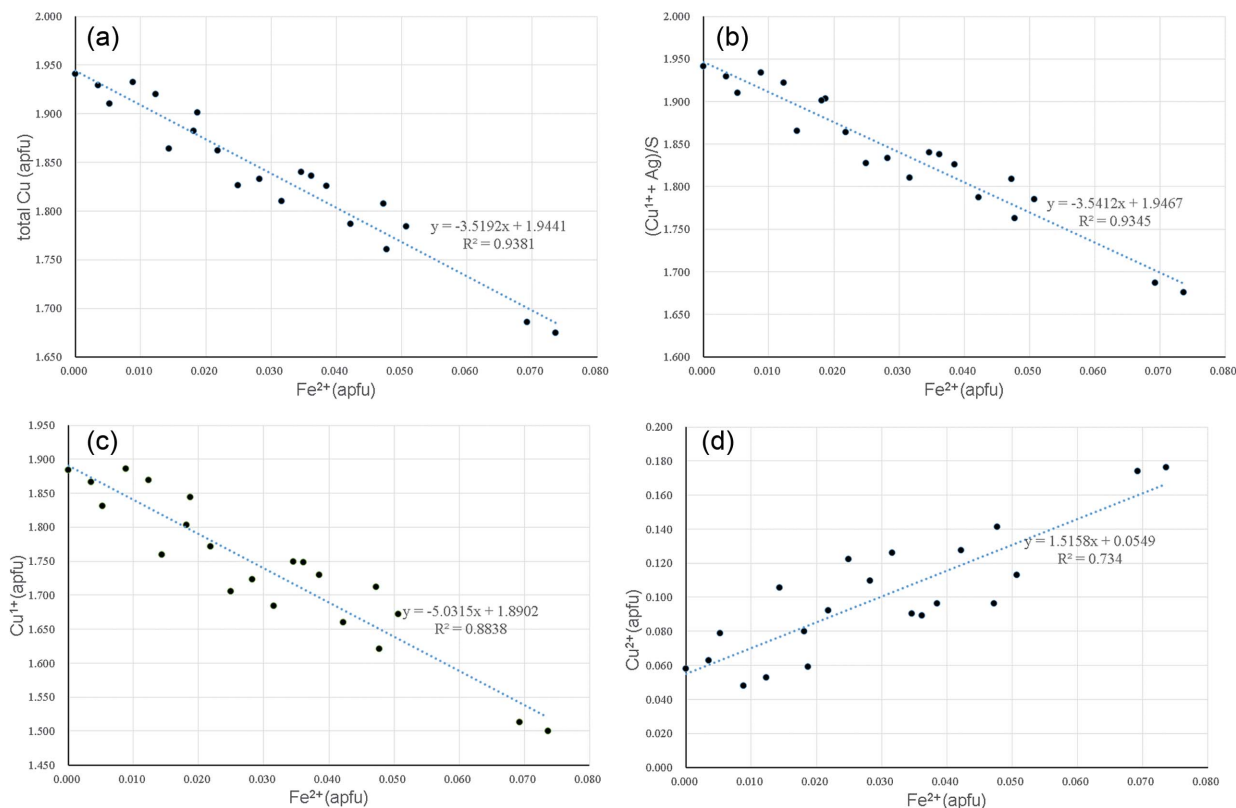
FIGURE 3. Photomicrographs (a, c, e, f) and backscattered electron images (b, d) showing the optical character and mineral paragenesis of wuyanishiite, photos taken from April 16 to May 6, 2017. Abbreviations: As = arsenic; Cc = chalcocite; Dju = djurleite; Smt = smithsonite; Sp = sphalerite; Wuy = wuyanishiite; Tnt = tennantite; Zer = zeunerite. (a) Wuyanishiite associated with sphalerite, chalcocite, arsenic, and zeunerite. (b) Enlarged framed area in (a), intimate intergrowth of wuyanishiite and arsenic with disseminated zeunerite, peripherally surrounded by pure wuyanishiite. (c) Wuyanishiite anhedronal grain and smithsonite disseminated in djurleite. (d) Enlarged framed area in (c), wuyanishiite and djurleite cannot be distinguished in BSE image. (e) Oriented ribbons of wuyanishiite in chalcocite. (f) Enlarged framed area in (e), close-up view of oriented ribbons of wuyanishiite in chalcocite.

A single-crystal X-ray diffraction experiment was carried out on a Rigaku Synergy 4-circle diffractometer using a micro-focused Cu anode tube at 50 kV, 1 mA, and 3–9 s exposure time/frame. Several fragments of wuyanishiite, 10 to 20 μm in size, were extracted from the polished section (Fig. 3e) for data collection. The Rigaku CrysAlisPro software package was used for data reduction, correction of Lorentz and polarization effects, and absorption correction using the multi-scan method. It was found that the diffraction data were from the contributions of more than three pseudomorph twinning crystals, each with about 15% overlapped reflections, making the whole diffraction like a pseudocubic symmetry with $a = 11.3020(6)$ Å as

described by Zimmer et al. (2017). The diffraction data were then separated for each crystal after treatment for overlapped reflections, which led to a lower data completeness from 80% to 87%. The crystal structure of wuyanishiite was solved and refined using SHELX (Sheldrick 2015a, 2015b) and Olex2 (Dolomanov et al. 2009). The possible space groups for the structure solution include $P4_32_12$, $P4_3$, and $P4_1$. The space group $P4_32_12$ is adopted for wuyanishiite as it yields a better $R1$, in agreement with the synthetic phases (Janosi 1964; Zimmer et al. 2017), in which Cu occupies the $8b$ site, and S is located at the $4a$ site. The occupancies of Cu, Fe, and Ag at the cation site were manually assigned according to average

TABLE 2. Representative data for the chemical composition of wuyanzhiite

Point No.	wt%					Total	apfu					Cu ²⁺	Cu ⁺	Cation/S
	Cu	Ag	Fe	S	As		Cu	Ag	Fe	S	As			
BF37a-wz10	78.64	0.08	0	20.44	0	99.16	1.941	0.001	0	1.000	0	0.058	1.883	1.942
BF37a-wz7	78.90	0.04	0.12	20.63	0	99.69	1.929	0.001	0.003	1.000	0	0.063	1.866	1.933
BF37a-wz16	78.55	0.00	0.19	20.74	0	99.48	1.911	0.000	0.005	1.000	0	0.079	1.832	1.916
BF06a-wyz25	77.90	0.14	0.31	20.33	0.01	98.70	1.932	0.002	0.009	1.000	0	0.048	1.884	1.943
BF06a-w20	78.59	0.12	0.44	20.65	0	99.80	1.921	0.002	0.012	1.000	0	0.053	1.867	1.935
BF30b-wz13	77.61	0.08	0.53	21.00	0	99.21	1.864	0.001	0.014	1.000	0	0.106	1.758	1.880
BF06a-wyz3	78.80	0.12	0.68	20.90	0.01	100.51	1.902	0.002	0.019	1.000	0	0.059	1.842	1.922
BF06a-wyz01	77.77	0.12	0.80	21.07	0	99.76	1.862	0.002	0.022	1.000	0	0.092	1.770	1.886
BF37a-wz13	76.91	0.08	0.92	21.24	0	99.14	1.827	0.001	0.025	1.000	0	0.122	1.705	1.853
BF30b-wz10	77.66	0.02	1.05	21.36	0.03	100.12	1.833	0	0.028	0.999	0.001	0.110	1.723	1.862
BF37a-wz14	76.78	0.04	1.18	21.40	0	99.40	1.810	0.001	0.032	1.000	0	0.126	1.684	1.842
BF06-w07	76.52	0.03	1.26	20.98	0	98.79	1.840	0.000	0.035	1.000	0	0.090	1.750	1.875
BF06a-w21	76.97	0.16	1.33	21.12	0.06	99.64	1.836	0.002	0.036	0.999	0.001	0.089	1.747	1.874
BF06a-w01	76.21	0.03	1.41	21.05	0	98.70	1.826	0.000	0.039	1.000	0	0.096	1.730	1.865
BF06a-w10	76.53	0.10	1.59	21.61	0	99.82	1.787	0.001	0.042	1.000	0	0.128	1.659	1.830
BF06a-w02	76.43	0.08	1.76	21.33	0	99.59	1.808	0.001	0.047	1.000	0	0.096	1.712	1.856
BF06-w17	75.41	0.14	1.80	21.58	0.05	98.98	1.761	0.002	0.048	0.999	0.001	0.142	1.620	1.811
BF06a-w03	76.29	0.08	1.90	21.57	0.01	99.85	1.784	0.001	0.051	1.000	0	0.113	1.671	1.836
BF06a-w24	74.07	0.12	2.67	22.16	0.02	99.03	1.686	0.002	0.069	1.000	0	0.174	1.512	1.757
BF06a-w04	74.64	0.08	2.88	22.48	0	100.08	1.675	0.001	0.074	1.000	0	0.176	1.499	1.750
Average (75)	77.87	0.10	0.66	20.87	0.01	99.50	1.882	0.001	0.018	1.000	0	0.080	1.802	1.901
Chalcocite (39)	79.01	0.07	0.04	20.46	0.01	99.58	1.988	0.002	0.001	0.999	0.001	0.007	1.981	1.991
Djurleite (14)	78.73	0.08	0.03	21.08	0.01	99.89	1.895	0.001	0.001	0.999	0.001	0.102	1.793	1.897

**FIGURE 4.** Variation relationships of Fe²⁺ (apfu) with (a) Cu (apfu), (b) Cu+Ag/S ratio, (c) Cu⁺ (apfu), and (d) Cu²⁺ (apfu).

compositional data from EPMA analyses. The final anisotropic full-matrix least-squares refinement of F^2 converged to an $R1$ of 0.0480 and a $wR2$ of 0.1089 for 131 independent reflections ($I > 2\sigma_1$). The refinement statistics and structure parameters are presented in Table 4 (and the CIF¹ file is deposited and available for additional detail).

Wuyanzhiite is isostructural with the synthetic tetragonal phase of Cu₂S (Janosi 1964; Zimmer et al. 2017). Its structure can be described as slightly distorted cubic close packing of S atoms along $[0 \bar{1} 2]$ with an interlayer distance of 3.554 Å and Cu atoms situated at the centers of nearly equilateral triangles of S atoms. Alternatively, the structure of wuyanzhiite may be

TABLE 3. Powder X-ray diffraction data (d in Å, I in %) of wuyanzhiite

l_{cal}	l_{obs}	d_{calc}	d_{obs}	h	k	l
9.6	5	3.770	3.775	0	1	1
19.2	20	3.262	3.266	0	1	2
26.9	24	2.829	2.833	1	1	0
100.0	100	2.744	2.746	1	1	1
0.1	2	2.528	2.530	1	1	2
85.0	98	2.303	2.304	0	1	4
28.3	28	2.260	2.262	1	1	3
39.2	62	2.000	1.998	1	1	4
14.2	29	1.970	1.967	0	1	5
22.6	26	1.885	1.887	0	2	2
10.7	17	1.766	1.767	0	2	3
20.9	28	1.705	1.704	1	2	2
13.4	14	1.615	1.617	1	2	-3
1.9	2	1.510	1.512	1	2	-4
4.1	4	1.496	1.492	0	1	7
12.4	18	1.401	1.401	1	2	5
7.8	11	1.328	1.330	0	1	8
3.9	3	1.324	1.326	2	2	3
2.6	5	1.265	1.263	1	1	8
4.2	5	1.257	1.258	1	3	1
7.8	7	1.234	1.234	1	3	2
5.3	8	1.197	1.196	1	2	7
0.6	2	1.154	1.153	1	3	-4
0.5	1	1.145	1.144	1	1	9
6.1	7	1.087	1.086	0	3	6
1.1	1	1.064	1.065	2	3	-3

Note: Strongest lines are given in bold.

viewed as S atoms forming layers of tetragonal symmetry parallel to (001), with the cations occupying the triangular interstices between the S layers (Fig. 5a). The average interlayer distance of the S layers is 2.814 Å ($1/4 c$). The CuS_3 triangle faces are oriented approximately parallel to (102), ($\bar{1} 0 2$), (012),

and ($0 \bar{1} 2$) with Cu-S bond lengths from 2.296 to 2.317 Å (average 2.309 Å) (Fig. 5b). The triangles are corner-connected to form a framework with each S atom being the joint of six CuS_3 triangles (Fig. 5c). Notably, there is no equilateral triangle in the S layer parallel to (001) to accommodate cations, as the S-S lengths vary greatly from 4.004 to 5.663 Å in the layer.

PHASE STABILITY AT AMBIENT CONDITIONS

The tetragonal Cu_2S phase was reported to decompose into chalcocite, djurleite, and digenite in several months to 3 years when exposed to air at ambient conditions (Skinner et al. 1967; Skinner 1970; Clark and Sillitoe 1971; Gablina et al. 2004). Skinner (1970) showed that the rate of conversion from tetragonal phase to monoclinic chalcocite was temperature-dependent, from about 1.1% per day at 25 °C to 0 at 97 °C. Machani et al. (2011) found that tetragonal Cu_2S could be stabilized with the addition of Fe^{3+} and Fe^{2+} during synthesis. Since excavating the specimens from the Bofang Mine in April 2017, we have carefully monitored changes in the samples over the past eight years. We also monitored a synthetic sample prepared earlier in 2012 from a Cu-Mo metallurgical process (Chen et al. 2013). It was found that the wuyanzhiite sample with higher Fe contents (0.8 wt% or more) did not show any visual change after repolishing (Figs. 6a–6c), whereas for a sample with the Fe contents varying from 0 to 1.88 wt%, the area with low Fe contents (below 0.3 wt%) might be converted to chalcocite and djurleite within several months, but the Fe-rich part (0.54–1.08 wt%) remained unchanged (Figs. 6d–6f). Some samples (Fe < 0.24 wt%) were almost

TABLE 4. Summary on structure refinement for wuyanzhiite

Crystal data							
Structural formula			Cu _{1.882} Fe _{0.018} Ag _{0.001} S ₁				
Formula weight			152.65 Da.				
Crystal size/mm ³			0.01 × 0.01 × 0.01				
Crystal system			Tetragonal				
Space group			P4 ₃ 2 ₁ 2				
Unit cell dimensions			a = 4.0042(4) Å, c = 11.2555(13) Å				
Volume			180.47(3) Å ³				
Z			4				
Density (calculated)			5.618 g/cm ³				
Data collection and refinement							
Instrument			Rigaku Synergy				
Radiation, wavelength, temperature			CuKα, 1.54184 Å, 293(2) K				
F(000)			284.0				
2θ range (°)			23.582 to 145.128				
Total reflections			796				
Unique ref (all)			140				
Unique ref [I > 2σ _I]			131				
R _{int} , R _σ			0.0503, 0.0249				
Range of h, k, l			−4 ≤ h ≤ 4; −4 ≤ k ≤ 4; −13 ≤ l ≤ 14				
R ₁ , wR ₂ [I > 2σ _I]			R ₁ = 0.0480, wR ₂ = 0.1089				
R ₁ , wR ₂ [all data]			R ₁ = 0.0528, wR ₂ = 0.1108				
Goodness-of-fit			1.260				
No. of parameters, restraints			15, 0				
Maximum and minimum residual peak (e Å ^{−3})			0.68/−1.00				
Flack parameter			0.1(9)				
Structure parameters							
Site	Wyckoff position	s.o.	x/a	y/b	z/c	U _{eq}	BVS ^a
Cu	8b	Cu _{0.941} Fe _{0.009} Ag _{0.0005} S _{1.00}	0.1401(7)	0.4927(6)	0.08622(18)	0.0490(10)	0.964
S	4a		0.4904(9)	0.5096(9)	0.25	0.0397(19)	1.930

Notes: $R_{\text{int}} = \sum |F_o^2 - F_c^2| / \sum F_o^2$, $\text{GoF} = S = \{ \sum [w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}$; $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ where a is 0.028 and b is 1.98; $P = [2F_c^2 + \text{Max}(F_o^2, 0)] / 3$.

^aBond valence sums are calculated using the parameters of Brown and Altermatt (1985).

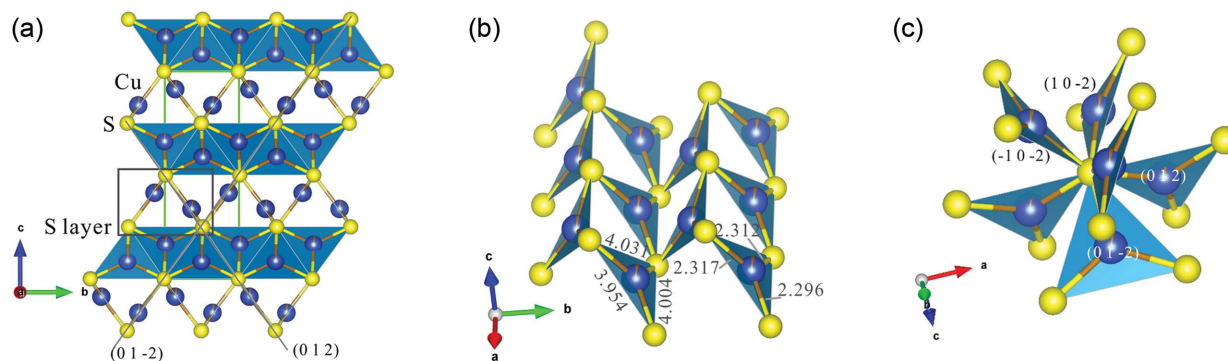


FIGURE 5. The crystal structure of wuyanishiite, plotted with Vesta (Momma and Izumi 2011). (a) The structure viewed along the a-axis, showing the hexagonal close-packed S layer and the arrangement of CuS₃ triangles; the unit cell is outlined by the solid green line. (b) Close view of the framed part in (a) to show the bonds of CuS₃ triangles. (c) Close-up view of a S atom surrounded by six CuS₃ triangles in 4 facial orientations.

completely converted to chalcocite and djurleite with very little wuyanishiite left (Figs. 6g–6i). In addition, we did not observe any apparent change in the synthetic tetragonal phase with Fe contents of 0.73–1.38% from August 2012 to May 2025 as checked by powder X-ray diffraction. Therefore, it appears that the stability of wuyanishiite strongly depends on Fe content. It can remain stable for a long time at Fe contents above 0.7 wt%, but might alter to chalcocite and djurleite within several months or a year at Fe contents below 0.3 wt%, as reported by Skinner (1970). However, the precise temporal change of wuyanishiite as a function of Fe content, temperature, and pressure still needs further investigation.

DISCUSSIONS AND IMPLICATIONS

Valence State Estimation of Fe

In the literature, the composition of synthetic tetragonal Cu₂S was shown to vary between Cu_{1.815}S and Cu₂S (e.g., Skinner et al. 1964; Serebryanaya 1966; Roseboom 1966). Gablina et al. (2004) reported Fe contents of 0.08–0.44 wt% for an intergrowth of chalcocite and tetragonal phase from the Rainbow hydrothermal ores. In our study, the ratio of cation/S of wuyanishiite spans a wider range, from 1.750 to 1.943, due to the incorporation of Fe²⁺ and Cu²⁺. The charge balance equation for Cu⁺(*c*1), Cu²⁺(*y*), and Fe²⁺(*x*) in the formula (Cu_{*c*1}⁺Cu_{*y*}²⁺Fe_{*x*}²⁺)S of wuyanishiite is: *c*1 + 2*y* + 2*x* = 2. In the absence of Cu²⁺ (*y* = 0), we have *c*1 = −2*x* + 2, but the regression equation from EPMA analyses (Fig. 4c) is *c*1 = −5.032*x* + 1.890. Accordingly, we have *y* = 1.516*x* + 0.055, as shown by the regression equation in Figure 4d. On the other hand, if we assume Fe³⁺ for charge balance calculation, all the data also reveal positive values for Cu²⁺ and a negative correlation between Fe³⁺(*x*) and Cu⁺(*c*1) (*R*² = 0.899, *c*1 = −3.670*x* + 1.880) and a positive correlation between Fe³⁺(*x*) and Cu²⁺(*y*) (*R*² = 0.226, *y* = 0.514*x* + 0.055). Therefore, it is also possible for Fe³⁺ to be present in wuyanishiite, and further work, using techniques sensitive to Fe²⁺ and Fe³⁺ such as Mössbauer spectroscopy, is needed to determine the valence of Fe.

Structural Classification of Cu-S Phases

Goble (1985) classified the crystal structures of the Cu-S system into three groups: (1) the approximate cubic close-packing

type (anilite, digenite, geerite); (2) the approximate hexagonal close-packing type (djurleite and chalcocite); and (3) the approximate hexagonal close-packing plus S-S pair bonding type (covellite, yarrowite, spionkopite) and further proposed a systematic variation of the close-packing distance as $D = 2.063 + 0.654(\text{Cu/S}) + 1.183(\text{Fe/S})$. In their crystal structures, linear CuS₂ dimer, CuS₃ triangles, CuS₄ tetrahedra are involved. In addition, the synthetic CuS₂ phases constitute the fourth type that is composed of CuS₆ octahedra with S-S bonding pair (e.g., King and Prewitt 1979; Kjekshus et al. 1979), which is not suitable for description by the close-packing model of S atoms. Wang (2012) proposed a solid-liquid hybrid model to describe the high-temperature phases of Cu₂S in which Cu ions diffuse like a liquid in the hexagonal lattice of S atoms. Apparently, wuyanishiite belongs to the cubic close-packed structure type, with only CuS₃ triangles. In the Bofang deposit, almost all the minerals in the Cu-S system, except for geerite, have been identified and characterized by EPMA and XRD, and the structures of chalcocite, djurleite, anilite and covellite were determined and refined to *R*1 = 0.0284–0.0660 by single-crystal X-ray diffraction (the CIF files are available on request from the author), which are, respectively, in accord with the original work of Evans (1971, 1979), Koto and Morimoto (1970), and Oftedal (1932). Their crystal-chemical data, along with some synthetic phases from the literature, are listed in Table 5, which indicates that, with decreasing the Cu/S ratio from 2 to 0.5, the coordination number *n* in CuS_{*n*} polyhedra increases from 3 to 6, the coordination number *n* in SCu_{*n*} polyhedra decreases from 6 to 3, and the close packing distance *D* decreases from around 3.30 Å to 2.72.

Copper sulfides in the Cu-S system have been widely studied both for their resource values and their potential applications in ion conductors, solar cell absorbers, switching devices, and even Cu-doped superconductors (e.g., Wang 2012; Li et al. 2022). The crystal chemistry and phase stability of various polymorphs of Cu₂S are essential for their applications and have attracted investigations on their phase transformations at various temperatures and pressures (e.g., Zimmer et al. 2017, 2018). It is shown that wuyanishiite, both natural and synthetic, tends to be stable at higher temperature and pressure (e.g., Skinner 1970; Zimmer et al. 2017), but unstable at ambient conditions (e.g., Gablina

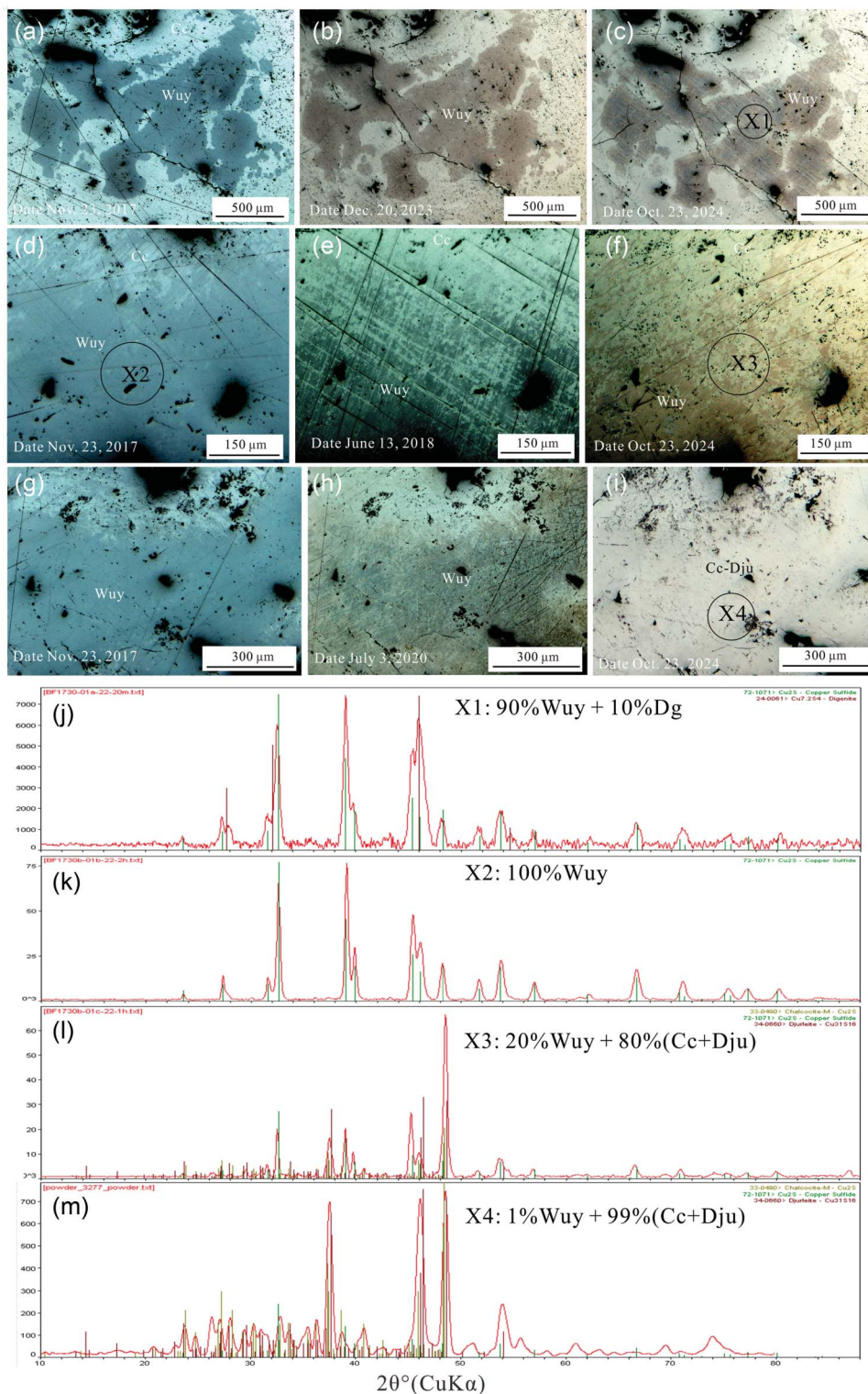


FIGURE 6. Photomicrographs and XRD patterns on different dates for wuyanishiite (a–c) and (j) for an intergrowth of wuyanishiite and minor digenite with Fe contents of 0.50–2.88 wt%. (d–f) and (k–l) for wuyanishiite with Fe contents of 0–1.08 wt%. (g–i) and (m) for wuyanishiite with Fe contents <0.2 wt%.

TABLE 5. Crystal chemical data for wuyanzhilite and the phases in the Cu-S system

Minerals	Ideal formula	Empirical formula	Space group	a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)	Z	Density (g/cm ³)	Bonds in CuS _n (Å)	Bonds in SCu _n (Å)	S close packing distance/(hkl) (Å)
Synthetic ^a (700 K, 5 GPa)	Cu ₂ S	Cu ₂ S	P4 ₃ 2 ₁ 2	4.0022	4.0022	11.276	90	180.615	4	5.853	<CuS ₃ > = 2.317	<SCu ₆ > = 2.291	Dccp = 3.281/(012)
Synthetic ^a (100 K, room P)	Cu ₂ S	Cu ₂ S	Pna2 ₁	5.385	5.702	5.811	90	178.428	4	5.925	<CuS ₃ > = 2.327	<SCu ₆ > = 2.327	Dccp = 3.254/(111)
Chalcocite	Cu ₂ S	Cu _{1.98} S	P2 ₁ /c	15.2357	11.8902	13.4955	116.242	2192.808	48	5.765	<CuS ₂ > = 2.211 <CuS ₃ > = 2.318 <CuS ₄ > = 2.309	<SCu ₆ > = 2.283 <SCu ₅ > = 2.305 <SCu ₆ > = 2.309	Dhcp = 3.381/(102) Dccp = 3.284/(012) Dhcp = 3.245/(100)
Wuyanzhilite	Cu₂S	Cu_{1.90}Fe_{0.20}S	P4₃2₁2	4.0042	4.0042	11.2555	90	180.466	4	5.618	<CuS ₃ > = 2.207 <CuS ₄ > = 2.257	<SCu ₅ > = 2.269 <SCu ₆ > = 2.329	
Djurleite	Cu ₃₁ S ₁₆	Cu _{30.35} S ₁₆	P2 ₁ /n	26.8986	15.7375	13.556	90	5738.481	8	5.652			
Digenite ^{b,h}	Cu ₉ S ₅	Cu _{8.56} Fe _{0.02} S ₅	R3̄m	3.9217	3.9217	48.008	90	639.430	3	5.496			Dccp = 3.216/(555)
Roxbyite ^{c,dh}	Cu ₉ S ₅	Cu _{8.60} Fe _{0.08} S ₅	C2/m	53.55	30.99	13.34	89.38	22136.63	102	5.442			Dhcp = 3.277/(100)
Anilite	Cu ₇ S ₄	Cu _{6.76} Fe _{0.05} S ₄	Pnma	7.8938	7.8418	11.0312	90	682.849	4	5.453	<CuS ₃ > = 2.292 <CuS ₄ > = 2.373	<SCu ₆ > = 2.308	Dccp = 3.252/(011)
Geerite ^e	Cu ₈ S ₅	Cu ₈ S ₅	R3̄m	3.83	3.83	46.84	90	595.039	3	5.598			Dccp = 3.128/(555)
Spionkopite ^{fh}	Cu ₃₈ S ₂₈	Cu _{40.06} Fe _{0.42} S ₂₈	P3m1	22.89	22.89	41.52	90	18839.94	16	4.928			Dccp = 2.964/(0014)
Yarrowite ^{fh}	Cu ₉ S ₈	Cu _{8.77} Fe _{0.06} S ₈	P3m1	3.802	3.802	67.06	90	839.496	3	4.849			Dccp = 2.796/(0014)
Covellite	CuS	Cu _{0.99} S	P6 ₃ /mmc	3.7917	3.7917	16.3444	90	203.501	6	4.650	<CuS ₃ > = 2.189 <CuS ₄ > = 2.310	<S ₂ > = 2.078 <SCu ₃ > = 2.304 <SCu ₅ > = 2.245 <S ₂ > = 2.050 <SCu ₃ > = 2.452	Dhcp = 2.724/(001)
Synthetic ^d (300 K, 60–65 kb)	Cu ₂ S	Cu ₂ S	Pd3̄	5.7891	5.7891	5.7891	90	194.014	4	4.371	<CuS ₆ > = 2.451		

^aZimmer et al. (2017).^bMorimoto and Kullerud (1963).^cMumme et al. (1988).^dMumme et al. (2012).^eGoble and Robinson (1980).^fGoble (1980).^gKing and Prewitt (1979).^hThe chemical data (empirical formula) and unit-cell parameters are from this work.

et al. 2004). Our crystal-chemical data for wuyanishiite from this study reveal that high Fe contents (>0.7 wt%) can increase its stability for over 13 years, providing a better way to understand the stability and applications of copper sulfides.

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