WATTERSITE

Hg⁺¹Hg⁺²Cr⁺⁶O₆ A New Mineral from the Clear Creek Claim San Benito County, California

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ABSTRACT

Wattersite, idealized as Hg₄⁺¹Hg⁺²Cr⁺⁶O₆, is monoclinic, space group C2/c(15), with refined unit-cell parameters a = 11.250(5), $b = 11.630(7), c = 6.595(5) \text{ Å}, \beta = 98.16(4)^{\circ}, V = 854(2) \text{ Å}^{3},$ a:b:c = 0.9673:1:0.5671, Z = 4. The strongest eight lines in the Xray powder pattern are [d(I) (hkl)]: 8.06 (80) (110); 5.58 (50) (200); $3.60(50)(\overline{2}21); 3.300(60)(\overline{3}11); 3.260(60)(002); 2.948(50)(311);$ 2.920 (50) (112,040); 2.655 (100) (202,041). The mineral is a rare constituent in a small prospect pit near the long-abandoned Clear Creek mercury mine, New Idria district, San Benito County, California. It is most closely associated with cinnabar and native mercury in a host rock composed predominantly of quartz and chalcedony. Wattersite typically occurs as thin shell-like aggregates in vugs and, less commonly, as small, less than 0.1 mm in size, discrete crystals or crystal aggregates on fracture surfaces. Individual crystals are prismatic and are elongate [001]. Forms observed are: {110}, {010}, {310}, {130}, $\{021\}, \{100\}, \{101\}, \{\overline{4}03\}, \{011\}, \{342\}, \{311\}, \{001\}, \{111\}, \{742\},$ {112}, and {312}. Crystals show simple contact twinning on {100} and the twin axis is [001]. The mineral is dark reddish brown, inclining to black in masses, and possesses a dark brick-red streak. Physical properties include: submetallic luster; opaque (masses) to translucent (thin edges of crystals); nonfluorescent; brittle; conchoidal fracture; hardness less than 5; calculated density 8.91 g/cm³ (for empirical formula). In polished section, wattersite is moderately bireflectant and pleochroic. In plane-polarized light it is a bright, slightly greenish white to a darker lilac-gray with deep, bright red internal reflections. Measured reflectance values are tabulated, in air and in oil, for both individuals of a twinned grain. Electron microprobe analyses yielded Hg₂O = 72.1, HgO = 18.7, CrO₃ = 8.7, total = 99.5 weight %, corresponding to Hg⁺¹_{3.98}Hg⁺²_{0.99}Cr⁺⁶_{1.01}O₆, based on O = 6. The original HgO = 93.6 weight % value was partitioned in a ratio of 4 Hg₂O : 1 HgO after the crystal structure was determined. The mineral is named for Mr. Lu Watters (1911–1989), a well-known California mineral collector, jazz trumpeter, chef and environmentalist.

INTRODUCTION

The new mineral species described here, wattersite, was first identified both by X-ray powder diffraction and by X-ray single-crystal analysis in 1972 by one of us (RCE). The mineral had been collected by Edward H. Oyler from a small prospect pit near the long-abandoned Clear Creek mercury mine, New Idria district, San Benito County,

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California. At that time only a few crystals of the mineral had been found, insufficient to permit a more detailed mineralogical study. The powder data could not be correlated with any known inorganic phase listed in the Powder Diffraction File. In 1987, Mr. Oyler brought RCE some additional specimens of wattersite-bearing material from the Clear Creek area. Enough material was then available for a comprehensive mineralogical study and full characterization; the results are reported here.

The mineral is named *wattersite* after Lu Watters (1911–1989), a well-known California mineral collector, jazz trumpeter, chef and environmentalist. Mr. Watters knew about the new mineral and had approved the mineral name prior to his death. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, IMA. The type material is preserved within the Systematic Reference Series of the National Mineral Collection at the Geological Survey of Canada, Ottawa, under catalog number NMC 65141.

OCCURRENCE and CRYSTAL MORPHOLOGY

Wattersite has been identified in four specimens collected from a small prospect pit near the long-abandoned Clear Creek mercury mine, New Idria district, San Benito County, California (latitude 36°22'59"N, longitude 120°45'58"W). The mineral is rare and is most closely associated with cinnabar and native mercury. The silica-carbonate host rock is predominantly quartz and chalcedony with accessory opal, ferroan magnesite, goethite, ferroan magnesiochromite, montmorillonite, huntite, gypsum, dolomite and chlorite. Mercurybearing minerals identified by X-ray diffraction analysis include edoylerite (Hg₃⁺²Cr⁺⁶O₄S₂; Erd et al., in preparation, IMA approved), edgarbaileyite (Roberts et al., 1990a; Angel et al., 1990), szymańskiite (Roberts et al., 1990b; Szymański and Roberts, 1990), metacinnabar, eglestonite, calomel, terlinguaite, mosesite, gianellaite, montroydite and four unnamed mercury-bearing phases that are currently under investigation. A description of the geology of the Clear Creek mercury mine is given by Eckel and Myers (1946).

Wattersite has been identified in two different varietal forms: as thin shell-like aggregates in vugs; and, less commonly, as small, generally less than 0.1 mm in size, discrete crystals or crystal aggregates on fracture surfaces. The largest known crystal, which measures 2 mm in length, is shown in Figure 1. Individual crystals are prismatic and are elongate [001]. Masses appear to be granular. The observed forms, measured by a combination of optical goniometric and X-ray single-crystal studies, are: large $\{110\}$, $\{010\}$; medium $\{310\}$, $\{130\}$; small to medium $\{021\}$; small $\{100\}$, $\{101\}$, $\{403\}$, $\{011\}$, $\{342\}$; very small $\{311\}$; tiny $\{001\}$, $\{111\}$, $\{742\}$, $\{112\}$, $\{312\}$. Twinning is ubiquitous and is found as simple contact twinning on $\{100\}$. The twin axis is [001].

PHYSICAL PROPERTIES

Individual wattersite crystals are dark reddish brown, but masses tend to look black. The streak is dark brick-red. Aggregates of crystals are opaque but individual crystals are translucent on thin edges. The mineral is brittle, possesses a conchoidal fracture and a submetallic luster, and is nonfluorescent under both longwave and shortwave ultraviolet light. The density could not be measured due to specimen size limitations and dearth of material; the calculated density, based on the empirical formula, is 8.91 g/cm³. Neither cleavage nor parting was observed megascopically. The hardness is less than 5 (the mineral does not scratch glass), but a more precise value has not been determined.

X-RAY DIFFRACTION

Precession single-crystal studies, employing Zr-filtered Mo radiation, showed that wattersite is monoclinic, with measured and calculated unit-cell parameters: a = 11.24, b = 11.65, c = 6.581 Å,



Figure 1. Wattersite crystal (at arrow) in host rock. Crystal is 2 mm in longest dimension. Blue marking adjacent to the crystal is due to a felt pen.

 $\beta = 98.17^{\circ}$. The following levels were photographed: $h0l \rightarrow h3l$, $hk0 \rightarrow hk2$, and $021^*\Lambda a^*$. Twinning by 180° rotation about a^* was noted in the h0l plane. The space-group extinction conditions are compatible with the space groups C2/c (15) or Cc (9), and the diffraction aspect is C^*/c . The correct space group is C2/c (15) based on the crystal structure determined by one of us (YL). Details regarding the structure will be published elsewhere, but it should be noted that the structure refinement clearly shows one Hg⁺² atom in octahedral coordination, four Hg⁺¹ atoms with typical Hg-Hg bonds, and one Cr⁺⁶ atom in tetrahedral coordination.

The X-ray powder diffraction data are presented in Table 1. The unit cell parameters were refined using 17 powder reflections representing d-values between 3.60 and 1.651 Å for which unambiguous indexing was possible, based on visual inspection of precession single-crystal films. The refined unit-cell parameters are: a = 11.250(5), b = 11.630(7), c = 6.595(5) Å, $\beta = 98.16(4)^\circ$, V = 854(2) Å³, a:b:c = 0.9673:1:0.5671. The powder data are unique and bear no resemblance to any other inorganic phase listed in the Powder Diffraction File. Wattersite is the second reported mercury chromate (the first was edoylerite).

OPTICAL PROPERTIES

Reflectance measurements for wattersite were made relative to a Zeiss SiC reflectance standard, no. 472, using X40 objectives, the effective Numerical Apertures of which had been adjusted to 0.26. Zeiss immersion oil, $N_D = 1.515$, was used at an ambient temperature of 20°C. Further details of the instrumentation and measurement procedures employed are given in Criddle *et al.* (1983). The wattersite specimen, which consists of a fractured grain, 180 by 180 microns in size, and displays simple twinning, was lightly buffed with MgO immediately before measurement.

In plane-polarized light it is moderately bireflectant and pleochroic, with R_i a darker lilac-gray by comparison with the bright, slightly



Figure 2. Reflectance spectra measured in air and in oil ($N_D = 1.515$) for two grains (twins) of wattersite.

Table 1. X-ray powder diffraction data for wattersite.												
I	d(Å)meas.	$d(\mathring{A})calc$.	hkl	I_o	d(Å)meas	s. d(Å)calc.	hkl					
80	8.06	8.04	110	5	2.173	∫ 2.171	042					
50	5.58	5.57	200			1 2.170	151					
40	5.35	5.34	111	10	0 107	∫ 2.131	151					
10	4.82	4.83	111	10	2.127	1 2.126	4 22					
5	4.36	4.34	021	-	1 000	f 2.002	223					
5	3.68	3.66	130	130		1 1.992	511					
50	3.60	3.59	221			1.980	441					
10	3.54	3.54	310	5	1.974	f 1.976	313					
60	3.300	3.302	311			1 1.971	350					
60	3.260	3.264	002			1.961	242					
20	3.014	3.008	202	5	1.944	∫ 1.947	512					
50	2.948	2.947	311			l 1.938	060					
50	2 0 2 0	2.922	112	15	1.925	1.927	351					
30	2.920	2.908	040	105	1 854	f 1.856	600					
10	2.841	2.846	022	100	1.054	l 1.849	351					
5	2.785	2.784	400	25	1 833	∫ 1.833	133					
40	2 677	2.681	330	25	1.055	l 1.831	260					
40	2.077	2.672	$\overline{2}22$	20	1.796	1.796	442					
100	2 655	2.656	202			1.768	620					
100	2.055	2.656	041	5b	1.765	1.768	621					
30	2 577	2.579	312			1.760	4 23					
50	2.511	2.577	240			1.760	532					
30	2 512	2.575	331			1 .751	313					
50	2.512	2.511	420	20	1.746	◀ 1.747	352					
40	2 452	2.453	$\bar{2}41$	-		1.742	043					
	2.432	2.451	4 21	5b	1.710	1.710	512					
3	2.383	2.382	132	10	1.668	1.667	062					
10	2.346	2.345	241	20	1.651	1.651	622					
20	2 280	2.284	402	20	1.633	1.634	352					
20	2.200	2.277	150			1.632	114					
3	2.248	2.249	421			1.632	004					
		2.185	332			1.630	204					

-114.6 mm Debye-Scherrer powder camera

-Co radiation Fe filter (λ CoK $\alpha = 1.79021$ Å)

-Pattern obtained at CANMET by Mr. Paul Carrière

-Intensities estimated visually

-b = broad line

-Indexed with a = 11.250, b = 11.630, c = 6.595Å,

 $\beta = 98.16^{\circ}$

greenish, white of R_2 . Deep and bright red internal reflections, which are seen at low magnifications in plane-polarized light, are strengthened between crossed polars. The mineral displays straight (orthogonal) extinction, and is strongly anisotropic with distinctive and brilliant rotation tints: purple, dark blue, "bottle"-green/blue, turquoiseblue to a dull greenish blue. Reflectance spectra for the two twins of wattersite are shown in Figure 2, and minimum (R_1) and maximum (R_2) reflectance and color values are given in Table 2.

The bireflectance and reflectance pleochroism for the two grains (twins) of wattersite are confirmed by the reflectance spectra (Fig. 2, Table 2): the dispersion of R_1 shows a slight increase from 400 nm to a peak at 420 nm for grain 1 and 440 nm for grain 2, and then a gentle reduction in reflectance to 700 nm for both grains. This vibration direction appears lilac-gray by comparison with much more strongly dispersed and higher reflecting R_2 vibration which, peaking at about 520 nm, is perceived as slightly greenish white. For both grains there is a change in the sign of the bireflectance at 460 nm in air, and at

Table 2. Reflectance values for two grains (twins) of wattersite: for ${}^{im}R$, $N_p = 1.515$.

Grain:	1			2		1		2					
λnm	R_1	R_2	R_1	R_2	${}^{im}R_1$	${}^{im}R_2$	${}^{im}R_1$	$^{im}R_2$					
400	23.75	18.8	19.6	16.0	10.2	8.17	8.33	6.46					
10	24.1	19.7	20.6	16.9	10.5	8.59	8.70	6.99					
20	24.3	20.5	21.6	18.1	10.4	9.00	9.17	7.70					
30	24.2	21.3	22.1	19.3	10.3	9.45	9.34	8.39					
40	23.8	21.7	22.3	20.4	9.98	9.82	9.25	8.98					
450	23.3	22.3	22.15	21.2	9.56	10.1	9.06	9.53					
60	22.85	22.85	21.9	22.0	9.19	10.4	8.78	10.0					
70 *	22.4	23.5	21.7	22.9	8.88	10.9	8.60	10.6					
80	22.0	24.3	21.5	23.9	8.57	11.4	8.40	11.3					
90	21.7	25.3	21.2	24.9	8.29	12.0	8.20	12.0					
500	21.3	26.2	21.0	25.9	8.07	12.6	8.02	12.6					
10	21.0	26.8	20.7	26.5	7.84	12.95	7.83	13.0					
20	20.6	27.1	20.4	26.7	7.63	13.0	7.64	13.0					
30	20.3	26.9	20.2	26.5	7.41	12.7	7.45	12.6					
40	20.0	26.5	19.9	26.0	7.20	12.2	7.25	12.1					
550	19.8	25.8	19.6	25.3	7.01	11.6	7.09	11.4					
60	19.5	25.1	19.35	24.5	6.82	10.95	6.92	10.7					
70	19.3	24.45	19.1	23.7	6.68	10.4	6.76	10.15					
80	19.1	23.85	18.9	23.1	6.54	9.93	6.61	9.60					
90	18.9	23.3	18.7	22.5	6.40	9.49	6.47	9.14					
600	18.8	22.8	18.5	21.9	6.34	9.16	6.34	8.76					
10	18.6	22.4	18.3	21.5	6.25	8.82	6.22	8.39					
20	18.5	22.1	18.1	21.0	6.16	8.57	6.12	8.08					
30	18.4	21.7	18.0	20.7	6.10	8.34	6.03	7.82					
40	18.4	21.5	17.8	20.35	6.05	8.14	5.93	7.61					
650	18.3	21.2	17.7	20.1	5.99	8.00	5.85	7.39					
60	18.15	21.0	17.6	19.8	5.98	7.90	5.80	7.26					
70	18.1	20.9	17.5	19.6	5.97	7.82	5.77	7.16					
80	18.1	20.8	17.4	19.4	5.97	7.75	5.74	7.10					
90	18.1	20.7	17.3	19.2	5.96	7.70	5.71	7.06					
700	18.1	20.6	17.2	19.1	5.96	7.67	5.65	6.97					
Color	Color values (relative to CIE illuminant C)												
x	0.293	0.305	0.295	0.305	0.277	0.291	0.281	0.290					
у	0.298	0.334	0.304	0.339	0.280	0.334	0.289	0.341					
Y%	19.8	24.8	19.5	24.2	7.02	10.9	7.03	10.7					
λ.	476	533	480	536	476	503	479	507					

 $\lambda_d P_e\%$

8.6

3.8

7.0

4.8

16.2

6.2

13.7

6.6

440–450 *nm* in oil. There is also a change in the sign of the birefringence at 490–500 *nm*. The dispersion of the refractive indices follow the same trends as the *R* spectra, except that n_2 peaks at 2.97 at 550 *nm* rather than 520*nm*. The refractive indices at 590 *nm* for grain 1 are $(n_1$, then n_2): 2.52 and 2.86, and for grain 2 are: 2.44 and 2.70. Absorption peaks are found at 490–500 *nm* for R_2 (absorption coefficients > 1), and the absorption for this vibration direction is greater in the red than the blue, whereas the absorption is greater at the blue end of the spectrum for R_1 .

CHEMISTRY

Wattersite was analyzed chemically by means of a CAMEBAX electron microprobe, using a 20-kV operating voltage, a 30-nA beam current, a 5-second count rate, and a 10-micron beam diameter. The standards employed were natural cinnabar (for Hg) and synthetic Cr metal (for Cr). A wavelength-dispersive microprobe scan indicated the absence of any other elements with atomic number greater than 9 except those reported here. The average of seven analyses gave HgO = 93.6(2), CrO₃ = 8.7(3), total = 102.3 weight %. After the crystal structure was determined, the HgO value was converted to Hg and then recalculated to Hg₂O and Hg) in a ratio of 4:1. This gives Hg₂O = 72.1, HgO = 18.7, CrO₃ = 8.7, total = 99.5 weight %. With O = 6, the empirical formula is Hg⁺¹_{1.98}Hg⁻²_{0.92}Cr⁺⁶_{0.6}, or ideally, Hg⁺¹₄Hg⁺²Cr⁺⁶O₆ with X = 4. This idealized formula requires Hg₂O = 72.49, HgO = 18.82, CrO₃ = 8.69, total = 100.00 weight %.

The mineral heated in a closed tube gives off elemental Hg and leaves a residue of green Cr_2O_3 (the synthetic equivalent of eskolaite). Wattersite is easily attacked by cold dilute HCl to form a white precipitate of calomel.

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REFERENCES

- ANGEL, R. J., CRESSEY, G., and CRIDDLE, A. (1990) Edgarbaileyite, Hg₆Si₂O₇: the crystal structure of the first mercury silicate. *American Mineralogist*, **75**, 1192–1196.
- CRIDDLE, A. J., STANLEY, C. J., CHISHOLM, J. E., and FEJER,
 E. E. (1983) Henryite, a new copper-silver-telluride from Bisbee,
 Arizona. Bulletin de Minéralogie, 106, 511-517.
- ECKEL, E. B., and MYERS, W. B. (1946) Quicksilver deposits of the New Idria district, San Benito and Fresno Counties, California. *California Journal of Mines and Geology*, **42**, 81–124.
- ROBERTS, A. C., BONARDI, M., ERD, R. C., CRIDDLE, A. J., STANLEY, C. J., CRESSEY, G., ANGEL, R. J., and LA-FLAMME, J. H. G. (1990a) Edgarbaileyite the first known silicate of mercury, from California and Texas. *Mineralogical Record*, 21, 215–220.
- ROBERTS, A. C., ERCIT, T. S., ERD, R. C., and OSCARSON,
 R. L. (1990b) Szymańskiite, Hg₁₆⁺¹(Ni,Mg)₆(CO₃)₁₂(OH)₁₂(H₃O)₈⁺¹
 ³H₂O, a new mineral species from the Clear Creek claim, San Benito County, California. *Canadian Mineralogist*, 28, 703–707.
- SZYMAŃSKI, J. T., and ROBERTS, A. C. (1990) The crystal structure of szymańskiite, a partly disordered (Hg Hg)⁺², (Ni, Mg)⁺² hydronium-carbonate-hydroxite-hydrate. *Canadian Mineralogist*, 28, 709–718.



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