Parnauite and goudeyite, two new copper arsenate minerals from the Majuba Hill Mine, Pershing County, Nevada

WILLIAM S. WISE

Department of Geological Sciences, University of California
Santa Barbara, California 93106

Abstract

Parnauite and goudeyite were found with other secondary copper minerals in the middle adit level of the Majuba Hill Mine, Pershing County, Nevada.

Parnauite occurs as pale-blue fans and rosettes of lath-like crystals up to 1 mm in length, as green scales and crusts, and drusy surface coatings. A combination of electron microprobe analyses and microanalyses for H_2O and CO_2 give the following composition: CuO 58.10, Al_2O_3 0.42, P_2O_5 2.56, As_2O_5 13.69, CO_2 0.7, SO_3 6.33, H_2O 17.7 percent, sum 99.50. The empirical cell contents are $Cu_{8.8}Al_{0.1}(AsO_4)_{1.48}(PO_4)_{0.43}(SO_4)_{0.94}(CO_3)_{0.19}(OH)_{10} \cdot 6.8H_2O$, with an ideal formula of $Cu_9(AsO_4)_2(SO_4)(OH)_{10} \cdot 7H_2O$. The crystals are blades, flattened on {010} and elongated parallel to c. The mineral is orthorhombic with a probable space group of $P2_122$. The cell dimensions are $a = 14.98(1)$, $b = 14.223(8)$, and $c = 6.018(8)$Å; $Z = 2$, D (meas) =3.09. The strongest lines of the X-ray power pattern (30 given) are 14.30 (100)(010); 10.38 (24)(110); 7.14 (10)(020); 6.42 (8)(120); 4.52 (60)(130); 4.00 (21)(230); 2.849 (19)(050); 2.798 (8)(150). The refractive indices are $\alpha = 1.650$, $\beta = 1.704$, $\gamma = 1.712$, $2V_\alpha = 60°$, and no observable dispersion of the optic axes. The optic plane is parallel to {100}, $X = b$, $Y = a$, and $Z = c$; X pale green, Y yellow-green, and Z blue-green with $Z > Y > X$. The mineral dissolves readily in dilute HCl with the evolution of CO_2 bubbles. The name honors John L. Parnau, a mineral collector of Sunnyvale, California, who was the first to find the mineral.

Goudeyite is the Al analog of agardite and is therefore a new member of the mixite group. It occurs as yellow-green hair-like crystals, encrusting fractures and as cross-fiber veinlets. Microprobe analyses with separate determinations for H_2O give the following composition: CaO 1.37, CuO 46.77, Al_2O_3 4.00, Y_2O_3 3.40, P_2O_5 4.55, As_2O_5 27.85, H_2O 11.0 percent, sum 98.94. This corresponds to $Ca_{0.24}Cu_{5.80}Al_{0.77}Y_{0.29}(AsO_4)_{2.40}(PO_4)_{0.63}(OH)_{6.17} \cdot 2.95H_2O$ and an ideal formula $Cu_6Al(AsO_4)_3(OH)_6 \cdot 3H_2O$. The crystals are hexagonal prisms up to 0.5 mm in length and 2 μm in diameter. The X-ray powder pattern was indexed by analogy with agardite, giving the cell dimensions $a = 13.472(1)$ and $c = 5.902(4)$Å; $Z = 2$, D (meas) = 3.50. The strongest lines of the X-ray powder pattern (30 given) are 11.63 (100)(100); 4.41 (43)(210); 3.53 (15)(211); 3.367 (20)(220); 3.235 (46)(310); 2.920 (50)(400); 2.677 (42)(320); 2.546 (40)(410). The refractive indices are $\omega = 1.704$ and $\epsilon = 1.765$; ω is pale yellow-green and ϵ is green with $\epsilon > \omega$. The mineral dissolves slowly in dilute HCl. The name honors Hatfield Goudey, a mining geologist and mineral collector of San Mateo, California.

Both minerals generally occur alone on limonite-stained fracture surfaces, but other secondary minerals within several meters include olivenite, clinoclase, cornwallite, strashimirite, scorodite, pharmacosiderite, arthurite, metazeunerite, chrysocolla, spangolite, chalcophyllite, malachite, azurite, chalcanthite, and bronchantite.

Introduction

The Majuba Hill Mine (northern Pershing County, Nevada) is located in a subvolcanic complex of rhyolitic porphyries and breccias intruded during mid-Tertiary time. The geology of the deposit has been described by Smith and Gianella (1942), Trites and Thurston (1958), and MacKenzie and Bookstrom (1976). The mine produced only 25,000 tons of copper ore and 350 tons of tin ore but is widely known for the rich suite of secondary copper and iron arse-

nate minerals. A comprehensive study of these secondary minerals revealed two new copper arsenate minerals.

These minerals are named parnauite and goudeyite after John L. Parnau, a mineral collector of Sunnyvale, California, and Hatfield Goudey, a mining geologist and mineral collector of San Mateo, California. Over the past 40 years both men have made substantial but unpublished contributions to the mineralogy of the Majuba Hill deposit. The names were approved by the Commission on new Minerals and Mineral Names, IMA, prior to publication. The names are pronounced par-NO-ite and GOW-dee-ite. Type material of parnauite (a few hundred milligrams) and goudeyite (a few tens of milligrams) have been deposited in the mineral collection at the University of California, Santa Barbara (specimens #8090 and #8091, respectively). Cotype material has been deposited in the National Museum of Natural History, Smithsonian Institution, Washington, D. C.

Occurrence

The Majuba Hill Mine exploited a relatively small copper ore body on three adit levels, spaced about 200 feet (60 m) apart in elevation. Most of the ore was removed from various stopes mined from the middle adit (see plate 9, Trites and Thurston, 1958). The largest of these stopes is commonly known as the Copper Stope and is labelled on Trites and Thurston's plan and elevation drawings of the workings.

Most of the primary ore minerals—chalcopyrite, arsenopyrite, pyrrhotite, pyrite, and cassiterite—originated with three of the seven intrusive pulses and were concentrated along several fault zones (MacKenzie and Bookstrom, 1976). Oxidation occurred along these same fault zones, and secondary minerals were deposited in most fractures between the surface and the middle adit, a depth of about 250 feet (75 m).

The new minerals were collected from the workings of the middle adit. Parnauite was collected from the walls and ceiling of crosscut 212 near the Copper Stope (see plate 9, Trites and Thurston, 1958). Goudeyite came from a small stope about 100 feet (30 m) north of the entrance to the Copper Stope. Common secondary minerals in and near the Copper Stope are olivenite, clinoclase, cornwallite, strashimirite, scorodite, pharmacosiderite, arthurite, metazeunerite, chalcanthite, and chrysocolla. Less common minerals are spangolite, chalcophyllite, malachite, azurite, and brochantite.

Parnauite

Physical properties and habit

The habit of parnauite greatly resembles that commonly exhibited by tyrolite. Where individual crystals occur, they are lath-like in groups forming fans or rosettes (Fig. 1). Parnauite in this habit is pale blue and is closely associated with chrysocolla. Green to blue-green scales and crusts are more common. Several specimens have been found with yellow-green parnauite in a radiating structure on a drusy surface.

The lath-like crystals are typically less than 1 mm long, 0.5 mm wide, and only 1 to 5 μm thick. The growths forming scales and crusts have indistinct crystals but yield the purest samples, which were used to provide material for the chemical analyses and density determinations.

The compact crusts are estimated to have a Mohs' hardness near 2, and a density of 3.09 ($\pm$0.04) gm/cm^3, as measured with a Berman balance on fragments of 10 mg in toluene at 22°C. Optically parnauite is biaxial negative with $2V_{\alpha} = 60°$ ($\pm$5°) and no discernable dispersion. The refractive indices are $\alpha = 1.680$, $\beta = 1.704$, $\gamma = 1.712$ (each $\pm$0.003). The optic plane is parallel to {100}, and $X = b$, $Y = a$, and $Z = c$. In this respect parnauite can be distinguished from tyrolite, which is length-fast when the bladed crystals are lying on the large b face. Moreover, $2V_{\alpha}$ (tyrolite) = 36°. Parnauite is weakly pleochroic with X pale green, Y yellow-green, and Z blue-green; $Z > Y > X$.
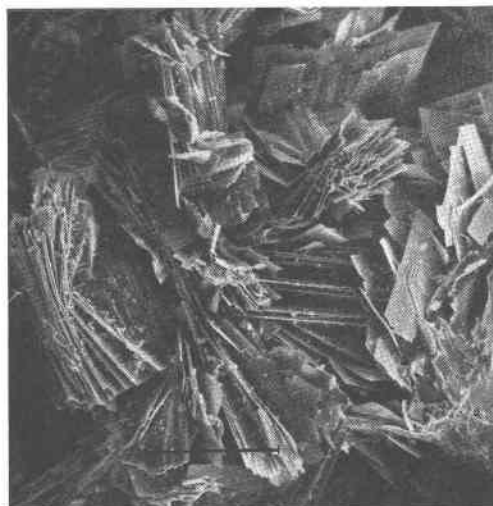

Fig. 1. Scanning electron photomicrograph of the bladed habit of parnauite. Length of bar is 250 μm; the width of the blades is less than 5 μm.

Crystallography and X-ray diffraction data

The cell dimensions were determined from crystals in the lath-like habit by means of an $h0l$ precession photograph, a c-axis rotation photograph, and an $hk0$ Weissenberg photograph, allowing at least two independent determinations of each cell edge. The cell dimensions from a least-squares refinement of the X-ray powder diffraction pattern (Table 1), standardized with annealed synthetic CaF_2 ($a = 5.459A$), using $CuK\alpha$ radiation ($\lambda = 1.5418A$), are: $a = 14.98(1)$, $b = 14.223(8)$, $c = 6.018(8)A$.

The diffraction symmetry is *mmm,* indicating orthorhombic symmetry. Indexing the Weissenberg photographs reveals no limitations in the hkl reflections, although all l odd reflections are very weak. In the $h00$ reflections, $h = 2n$. The photographs do not give clear evidence of extinctions in the $h0l$ and $0kl$ sets. These relations, nevertheless, suggest the space group $P2_122$.

The lath-like crystals are elongated parallel to c and flattened parallel to {010}.

Table 1. X-ray powder diffraction data for parnauite

hkl	d_{calc}	d_{obs}	I_{obs}
010	14.22	14.3	100
110	10.31	10.38	24
020	7.11	7.14	10
120	6.42	6.42	8
101	5.58	5.61	2
220	5.16	5.16	1
030	4.74		
310	4.71	4.73	2
130	4.52	4.52	60
230	4.00	4.00	21
040	3.56	3.55	6
140	3.46	3.46	6
330	3.44	3.44	7
240	3.21	3.21	4
510	2.93	2.93	4
340	2.90	2.90	3
050	2.845	2.849	19
150	2.795	2.798	8
520	2.761	2.757	3
250	2.659	2.663	3
302	2.577	2.577	7
312	2.536	2.537	6
530	2.532	2.529	7
402	2.346		
160	2.341	2.344	2
412	2.314	2.315	1
450	2.265		
332	2.264	2.264	5
360	2.141	2.141	2
640	2.043	2.04	1
460	2.003	2.01	2
270	1.961	1.96	1

plus 8 definable peaks, but with intensities less than 1 to d = 1.54

Chemical composition

Several clusters or scales from each of the three different habits were embedded in epoxy, ground to expose the centers, and coated with approximately 200A of carbon. Analyses were carried out on ten spots with an ARL electron microprobe, using an accelerating voltage of 15 kV for all elements and a sample current of 8 nanoamps. The spot size was made as large as the samples would allow (up to 20 μm). Standards include olivenite for Cu and As, chalcophyllite for Al and S, and apatite for P. Interelement effects were corrected with a modified version of the computer program EMPADR 7 (Rucklidge and Gasparrini, 1969).

Water and CO_2 analyses were obtained from a Hewlett-Packard C-H-N analyzer, using samples of 2 to 3 mg. Artinite was used as a standard, and the reported values are probably accurate to within 5 percent. Thermal gravimetric analysis of the water loss on a 5 mg sample showed a steady weight loss up to 250°C. A sharp loss occurred at 350°C. The early loss is interpreted to involve the structural water, and the latter was expulsion of the hydroxyl water.

A summary of the analyses is presented in Table 2. Although phosphate is present in all samples of parnauite analyzed, it does not appear to be an essential constituent, because all the arsenate minerals at Majuba Hill, including olivenite and clinoclase, contain about 20 percent phosphate. Sulfate with carbonate is

Table 2. Composition of parnauite

	(1)	(2)	(3)	(4)
CuO	58.10	58.69	58.95	57.65
Al_2O_3	0.42	1.11	0.46	--
P_2O_5	2.56	2.39	2.58	--
As_2O_5	13.69	14.50	13.06	18.51
SO_3	6.33	5.31	6.45	6.45
CO_2	0.7	--	--	--
H_2O	17.7	--	--	17.39
Total	99.50	82.00	81.50	100.00

(1) Green crusts and scales, (2) blue-green blades in rosettes, (3) yellow-green drusy surface coating, (4) ideal $Cu_9(AsO_4)_2(SO_4)(OH)_{10} \cdot 7H_2O$.

Empirical cell contents:

$Cu_{8.76}Al_{.10}(AsO_4)_{1.43}(PO_4)_{.43}(SO_4)_{.94}(CO_3)_{.19}(OH)_{7.98}$

$6.81\ H_2O.$

interpreted to be a separate, but essential, constituent—very similar to tyrolite. The complete lack of Ca in parnauite is the most significant difference in comparison with tyrolite.

Goudeyite

Physical properties and habit

Goudeyite occurs as hair-like crystals in tufted groups, encrusting fracture coatings, and cross-fiber veinlets. Individual crystals are simple hexagonal prisms, elongated parallel to the c axis. Scanning electron micrographs (Fig. 2) show the average crystal diameter of about $2 \mu m$. The lengths do not exceed 0.5 mm. Goudeyite is yellow-green where compact and lighter in dispersed tufts. The compact masses have a hardness between 3 and 4, and a density of 3.50 ($\pm$0.03) gm/cm³ as measured with a Berman balance on fragments of 8 mg in toluene at 22°C.

Goudeyite is uniaxial positive with $\omega = 1.704$ and $\epsilon = 1.765$ (each $\pm$0.002) in white light; dichroic, ω is pale yellow-green and ϵ is green with $\epsilon > \omega$. Table 3 is a comparison of the properties of goudeyite with mixite and agardite.

Crystallography and X-ray diffraction data

Single crystals are far too small for single-crystal X-ray diffraction study. However, the X-ray powder diffraction pattern is easily indexed by analogy with agardite (Dietrich et al., 1969). A least-squares refinement of the cell dimensions yields $a = 13.472(1)$ and $c = 5.902(4)$A. See Table 4 for the indexed powder pattern. Since the X-ray powder patterns of goudey-
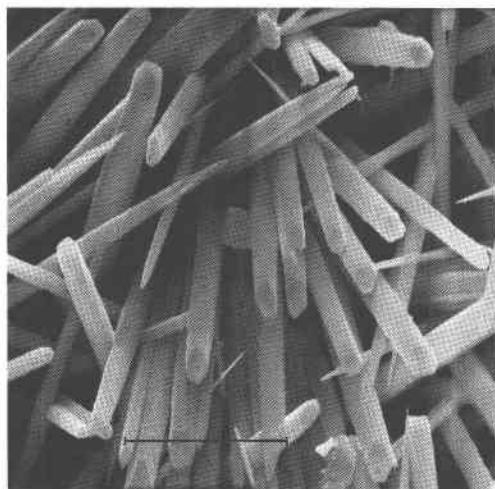
Table 3. Comparison of the properties of the mixite group

	Goudeyite	Agardite	Mixite
ω	1.704	1.701	1.743
ϵ	1.765	1.782	1.830
D (gm/cm³)	3.50	3.60	3.80
a (A)	13.47	13.55	13.84
c (A)	5.96	5.87	5.96
Color	yellow-green	blue-green	emerald-green blue-green

ite and mixite are identical, and mixite has the space group symmetry $P6_3/m$ or $P6_3$, goudeyite appears to have the same symmetry.

Chemical composition

Goudeyite was analyzed by the same electron microprobe methods described earlier but with the following standards: conichalcite for Ca, olivenite for Cu and As, apatite for P, gadolinite for Y, and K–feldspar for Al. H₂O was determined by weight loss

Table 4. X-ray powder diffraction data for goudeyite

hkl	d_{calc}	d_{obs}	I_{obs}
1 0 0	11.67	11.63	100
210	4.41	4.41	43
201	4.15	4.15	3
300	3.89	3.89	7
211	3.53	3.53	15
220	3.368	3.367	20
310	3.236	3.235	46
400	2.917	2.920	50
311	2.837	2.840	5
320	2.676	2.677	42
401	2.614	2.618	1
410	2.546	2.546	46
212	2.452	2.449	12
420	2.205	2.205	4
501	2.170	2.174	1
510	2.095	2.096	13
421	2.065	2.068	3
322	1.982	1.98	1
600	1.945	1.945	1
430	1.918	1.920	6
520	1.868	1.87	1
431	1.824	1.825	2
521	1.781	1.782	4
422	1.766	1.766	4
512	1.709	1.709	2
440	1.684	1.684	4
530	1.667	1.667	4
602	1.624	1.625	3
531	1.604	1.605	4
522	1.578	1.580	1

plus 15 definable peaks but with intensities less than 1 to d = 1.2

Fig. 2. Scanning electron photomicrograph of goudeyite. Length of bar is 10 μm.

Table 5. Composition of goudeyite

	(1)	(2)
CaO	1.37	--
CuO	46.77	48.65
Al_2O_3	4.00	5.20
Y_2O_3	3.40	--
P_2O_5	4.55	--
As_2O_5	27.85	35.14
H_2O	11.0	11.01
Total	98.94	100.00

*(1) Average of five electron microprobe analyses
H_2O by weight loss in heating a single 5 mgm sample
to 600°C.*

(2)   Ideal $Cu_6Al(AsO_4)_2(OH)_6 \cdot 3H_2O$.

Empirical cell contents:

$$Cu_{5.80}Ca_{.24}Al_{.77}Y_{.29}(AsO_4)_{2.40}(PO_4)_{.63}(OH)_{6.17} \cdot 2.95H_2O$$

upon heating a 5 mg sample to 600°C. An average of five analyses are given in Table 5 along with the empirical cell contents.

It is clear from the data in Tables 3, 4, and 5 that goudeyite is a new member of the mixite group, which appears to have the general formula $Cu_6R(AsO_4)_3(OH)_6 \cdot 3H_2O$, where R can be Al, Y (and rare earths), and Bi. The extent to which phosphate can substitute for arsenate in this series is not revealed by the Majuba Hill samples, because the arsenate/phosphate ratio is consistently 4/1 in the samples analysed.

Dietrich *et al.* (1969) showed in a study of 31 samples from eleven localities in Europe and the United States that all known "chlorotile" specimens were either mixite or agardite. Chemical tests showed either the presence of Bi or rare-earth elements with Y. Walenta (1970) described various members of the chlorotile–mixite group from the Black Forest and the Erzgebirge and found samples containing rare earths as well as Bi. Only one mixite sample contained significant amounts of Al. None of his samples had an *a* dimension less than the 13.55A value of agardite (Table 3).

References

Dietrich, J.-E., M. Orliac and F. Permingeat (1969) L'agardite, une nouvelle espèce minérale, et de problème du chlorotile. *Bull. Soc. fr. Mineral. Cristallogr., 92,* 420–434.

MacKenzie, W. B. and A. A. Bookstrom (1976) Geology of the Majuba Hill area, Pershing County, Nevada. *Nevada Bur. Mines Geol. Bull. 86.*

Rucklidge, J. and E. L. Gasparrini (1969) *EMPADR VII, a Computer Program for Processing Electron Microprobe Analytical Data.* Department of Geology, University of Toronto.

Smith, W. C. and V. P. Gianella (1942) Tin deposit at Majuba Hill, Pershing County, Nevada. *U. S. Geol. Surv. Bull., 931-C,* 39–55.

Trites, A. F. and R. H. Thurston (1958) Geology of Majuba Hill, Pershing County, Nevada. *U. S. Geol. Surv. Bull., 1046-I,* 183–203.

Walenta, K. (1970) Mineralien der Chlorotil–Mixitgruppe mit seltenen Erden von Fundorten im Schwarzwald. *Chemie der Erde, 29,* 36–47.