

Dedicated to the memory of Dr A. J. Criddle, Natural History Museum, London, who died in May 2002

## Aurivilliusite, $\text{Hg}^{2+}\text{Hg}^{1+}\text{OI}$ , a new mineral species from the Clear Creek claim, San Benito County, California, USA

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### ABSTRACT

Aurivilliusite, ideally  $\text{Hg}^{2+}\text{Hg}^{1+}\text{OI}$ , is monoclinic,  $C2/c$ , with unit-cell parameters refined from X-ray powder data:  $a = 17.580(6)$ ,  $b = 6.979(1)$ ,  $c = 6.693(3)$  Å,  $\beta = 101.71(4)^\circ$ ,  $V = 804.0(5)$  Å<sup>3</sup>,  $a:b:c = 2.5190:1:0.9590$ ,  $Z = 8$ . The strongest six lines of the X-ray powder-diffraction pattern [ $d$  in Å ( $I$ )( $hkl$ )] are: 8.547(70)(200), 3.275(100)(002), 2.993(80)( $\bar{2}21$ ), 2.873(80)(600), 2.404(50b)( $\bar{6}02$ , 421,  $\bar{2}22$ ) and 1.878(50)( $\bar{2}23$ ). This extremely rare mineral was collected from a small prospect pit near the long-abandoned Clear Creek mercury mine, New Idria district, San Benito County, California, USA. It is intimately intermixed with another new undefined Hg-O-I phase ('CCUK-15'), and is also closely associated with native mercury, cinnabar and edgarbaileyite in a host rock principally composed of quartz and magnesite. Aurivilliusite occurs in a cm-wide quartz vein predominantly as irregular-shaped thin patches 'splattered' on the quartz surface; patches vary in size from 10–20 µm up to 0.5 mm. The only known subhedral platy brightly reflecting crystal fragment, with major {100} form and distinct {100} cleavage, did not exceed 0.2 mm in longest dimension. The mineral is dark grey-black with a dark red-brown streak. Physical properties include: metallic lustre; opaque; non-fluorescent; brittle; uneven fracture; calculated density 8.96 g/cm<sup>3</sup> (empirical formula), 8.99 g/cm<sup>3</sup> (ideal formula). In polished section in plane-polarized reflected light, aurivilliusite resembles cinnabar, is extremely light sensitive, shows twinning and no internal reflections, and exhibits an unusual 'red light' coalescing phenomena. Averaged and corrected results of electron-microprobe analyses yielded HgO 40.10, Hg<sub>2</sub>O 38.62, I 22.76, Br 0.22, Cl 0.06, sum 101.76, less O = I + Br + Cl –1.46, total 100.30 wt.%, corresponding to  $\text{Hg}_{1.00}^{2+}\text{Hg}_{1.00}^{1+}\text{O}_{1.01}(\text{I}_{0.97}\text{Br}_{0.01}\text{Cl}_{0.01})_{\Sigma 0.99}$ , based on O + I + Br + Cl = 2 atoms per formula unit (a.p.f.u.). The original value for Hg, 74.27 wt.%, was partitioned in a HgO:Hg<sub>2</sub>O ratio of 1:1 after the discovery of the crystal-structure paper dealing with the synthetic equivalent of aurivilliusite. The mineral name is in honour of the late Dr Karin Aurivillius (1920–1982), chemist-crystallographer at the University of Lund, Sweden, for her significant contributions to the crystal chemistry of Hg-bearing inorganic compounds. Aurivilliusite is related chemically to terlinguaite,  $\text{Hg}^{2+}\text{Hg}^{1+}\text{OCl}$ , but has a different structure and X-ray characteristics.

**KEYWORDS:** aurivilliusite, new mineral species, mercurous mercuric oxide iodide, X-ray data, electron-microprobe data, Clear Creek mine, San Benito County, California.

### Introduction

AURIVILLIUSITE, ideally  $\text{Hg}^{2+}\text{Hg}^{1+}\text{OI}$ , is a newly recognized mineral species first encountered

during megascopic examination, scanning electron energy-dispersion study and routine X-ray powder-diffraction characterization of a suite of Hg-bearing oxy-halide phases which have iodine as the dominant anion. These minerals were originally collected by one of us (GED) in the mid-1990s from a small prospect pit within the dumps surrounding the long-abandoned Clear

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Creek mercury mine, New Idria district, San Benito County, California, USA (lat. 36°22'59"N, long. 120°43'58"W). This mineral is the third of six new mercury oxy-halides which we hope to characterize fully in the near future. It has been given the designation 'CCUK-17' by Dunning *et al.* (2004), who provide a complete description of the history, geology, mineralogy and geochemistry of the Clear Creek claim. The mineral must be considered very rare; despite assiduous searches and numerous X-ray powder determinations, only four small aurivilliusite-bearing specimens have so far been found.

The mineral is named aurivilliusite in honor of the late Dr Karin Aurivillius (1920–1982), chemist-crystallographer at the University of Lund, Sweden. During her academic career, she was involved in the synthesis and crystal-structure determination of >30 Hg-bearing inorganic compounds, many of which are mercury oxy-halides; including the synthetic-equivalent of this natural phase. A short obituary was published in the *Journal of Applied Crystallography*, **15**, 469 (1982). The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, IMA (2002-22). Holotype material, consisting of one micromount specimen (15 × 9 × 3 mm), two polished sections and several X-ray powder mounts, is housed in the Systematic Reference Series of the National Mineral Collection at the Geological Survey of Canada, Ottawa, Ontario, Canada, under catalogue number NMC 68087.

### Occurrence and associated minerals

Aurivilliusite is an extremely rare constituent at the Clear Creek claim; we estimate that <10 µg of material is available for study. It occurs in a cm-wide vein of colourless to white quartz which, in turn, cuts across silicified serpentine. The host rock is principally composed of quartz and magnesite. Aurivilliusite is intimately intermixed with another new mercury oxy-halide ['CCUK-15', Dunning *et al.* (2004), for which a provisional formula derived from quantitative electron-microprobe analyses is:  $\text{Hg}_{10}^{1+}\text{Hg}_3^{2+}\text{O}_6\text{I}_2(\text{Cl},\text{Br})_2$ ] from which it is megascopically indistinguishable. Additional associated minerals are globules of native mercury, cinnabar and edgarbaileyite. It should be noted that aurivilliusite, in addition to 'CCUK-15', is also very similar in colour and overall appearance to tedhadleyite,  $\text{Hg}^{2+}\text{Hg}_{10}^{1+}\text{O}_4\text{I}_2(\text{Cl},\text{Br})_2$ , (Roberts *et al.*, 2002) and

vasilyevite (Roberts *et al.*, 2003) which are found in other micromount specimens collected from the same quartz vein. The isolated occurrence of aurivilliusite and these other related mercury oxy-halides prevents us from establishing an exact paragenesis of formation. All that can be said at this time is that there was a period of high activity of I (with lower Cl and Br) in the fluid phase. I-rich mercury oxy-halides will tend to form further to the right than Cl-rich mercury oxy-halides on the Eh-ph diagram since they are more basic and a little lower in Eh. Additional Hg-bearing minerals identified from the Clear Creek claim are listed in Roberts *et al.* (2001) and references therein and, as previously mentioned, Dunning *et al.* (2004) provide a complete description of the history, geology, mineralogy and geochemistry of the Clear Creek claim.

### Physical properties

The mineral occurs as irregular thin patches which appear to have been 'splattered' on the quartz fracture surface (Fig. 1). These patches range in size from 10–20 µm up to ~0.5 mm in longest dimension. The only crystal fragment found was a subhedral platy brightly reflecting cleavage fragment with {100} major and which did not exceed 0.2 mm in longest dimension; it was subsequently used for the precession single-crystal study. Megascopically, as well as chemically, the mineral is very similar to 'CCUK-15', vasilyevite (Roberts *et al.*, 2003) and tedhadleyite (Roberts *et al.*, 2002). Aurivilliusite is dark grey-black with a dark red-brown streak. It is opaque with a metallic lustre, brittle, has an uneven fracture, and is non-fluorescent under both long- and short-wave ultraviolet light. There is a distinct {100} cleavage on the solitary crystal fragment. The Mohs hardness is unknown, but it is easily scratched with a needle. The density could not be measured due to a lack of pure material; the calculated density, on the basis of the empirical formula and unit-cell parameters refined from powder data, is 8.96 g/cm<sup>3</sup>. The ideal formula and the same refined unit-cell parameters give a calculated density of 8.99 g/cm<sup>3</sup>. Twinning was not megascopically obvious, though a single-crystal precession study showed that the platy fragment was not single; it is, however, definitely present as determined by qualitative reflectance study. In general, aurivilliusite most closely resembles a metallic sulphide or sulphosal in appearance.

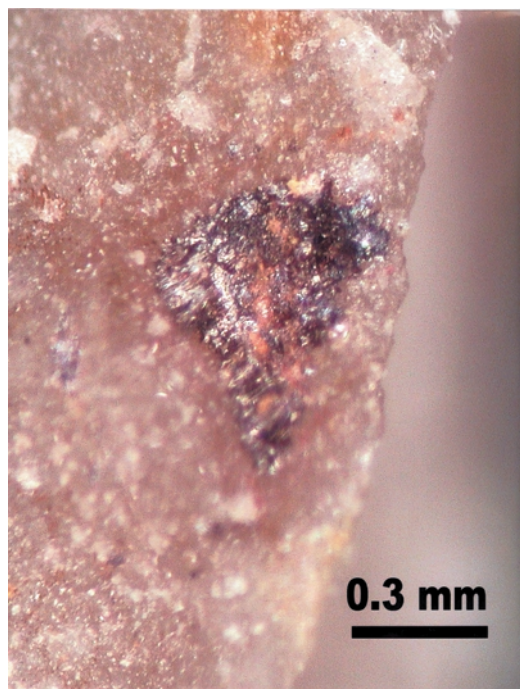


FIG. 1. Aurivilliusite-bearing 'splattered' patch on quartz. The brownish-red powder within the patch is where material was extracted for powder XRD identification.

### X-ray studies

Two cleavage fragments of aurivilliusite were examined by single-crystal precession methods employing Zr-filtered Mo X-radiation. One was mounted such that  $a^*$ , and the other such that  $c^*$ , is parallel to the dial axis. The following levels were collected:  $0kl \rightarrow 3kl$ ,  $h0l \rightarrow h2l$ ,  $hk0 \rightarrow hk2$ ,  $011^*a^*$  and  $021^*a^*$ . Precession films indicate monoclinic symmetry, with measured and calculated unit-cell parameters  $a = 17.77$ ,  $b = 7.034$ ,  $c = 6.762$  Å,  $\beta = 101.83^\circ$ . Systematic absences ( $hkl$  with  $h+k \neq 2n$  and  $h0l$  with  $h \neq 2n$  and  $l \neq 2n$ ) dictate that the space-group choices are  $C2/c$  (15) or  $Cc$  (9) (diffraction aspect  $C^*/c$ ). The correct space group is  $C2/c$  as determined from the crystal structure of the synthetic inorganic equivalent (see below). The refined unit-cell parameters,  $a = 17.580(6)$ ,  $b = 6.979(1)$ ,  $c = 6.693(3)$  Å,  $\beta = 101.71(4)^\circ$ ,  $V = 804.0(5)$  Å<sup>3</sup>,  $a:b:c = 2.5190:1:0.9590$ , and  $Z = 8$ , are based on the  $d$  values of 13 X-ray powder lines between 3.275 and 1.541 Å for which unambiguous indexing was possible. All reflections down to

1.52 Å were examined visually on the precession films. A fully indexed powder pattern is presented in Table 1. Neither cleavage fragment used for the precession study is suitable for crystal-structure analysis; both are multiple crystals with one dominant individual. One fragment was powdered to produce the diffraction data listed in Table 1 and the other fragment was lost during an attempted crystal-structure determination on a CCD-equipped four-circle diffractometer. Fortunately, the synthetic inorganic-equivalent crystal structure of aurivilliusite is known (Stålhandske *et al.*, 1985) and the structure is built up of infinite zigzag  $-\text{Hg}^{2+}-\text{O}-\text{Hg}^{2+}$ -chains, running in the [010] direction, which are condensed by  $\text{Hg}^{1+}-\text{Hg}^{1+}$  groups to form folded layers. These layers are further connected by weak  $\text{Hg}^{2+}-\text{O}$  bonds to form a three-dimensional structure. The I atoms are situated within cavities in the layers and are weakly bonded to  $\text{Hg}^{2+}$ . A calculated powder pattern (PDF 76-003) derived from this synthetic structure (ICSD #033275) is very similar to that produced for the natural material.

### Chemistry

Several very small anhedral fragments of relatively pure aurivilliusite were mounted in epoxy and analysed with a Cameca SX-50 electron microprobe, with an operating voltage of 20 kV, a beam current of 5 nA, a 5 s count time, and a variable spot size. The following standards were used: cinnabar (Hg), iodargyrite (I), synthetic KBr (Br) and halite (Cl). An energy-dispersion spectrum indicated the absence of elements with atomic numbers greater than 9 other than those reported here. The mineral (as is typical of other mercury oxy-halides) is very unstable under the electron beam; the longer it is subjected to electrons, the higher the Hg value tends to be above the ideal value. In addition, the mineral does not take a good polish. The average of five determinations (and ranges) gave Hg 74.27 (73.55–75.31), I 22.76 (20.87–24.13), Br 0.22 (0.06–0.28) and Cl 0.06 (0–0.11). The precision of these values is probably average at best due to the aforementioned instability under the electron beam. The Hg value was converted to HgO and Hg<sub>2</sub>O in a 1:1 ratio based upon the known structure of the synthetic analogue (Stålhandske *et al.*, 1985). This gives HgO 40.10, Hg<sub>2</sub>O 38.62, I 22.76, Br 0.22, Cl 0.06, sum 101.76, less O = I + Br + Cl – 1.46, total 100.30 wt.%. With O + I +

TABLE 1. X-ray powder-diffraction data for aurivilliusite.

$I_{\text{est.}}$	$d_{(\text{meas.})}$ (Å)	$d_{(\text{calc.})}$ (Å)	$hkl$	$I_{\text{est.}}$	$d_{(\text{meas.})}$ (Å)	$d_{(\text{calc.})}$ (Å)	$hkl$
70	8.547	8.607	200	3	2.227	2.233	$\bar{4}22$
20	6.475	6.468	110	3	2.154	2.156	330
30	4.796	4.79	$\bar{1}11$			2.152	800
15	4.467	4.437	111	5	2.116	2.119	$\bar{1}13$
5b	3.453	3.489	020	* 10	2.065	2.066	711
		3.43	311	20	1.97	1.97	602
* 100	3.275	3.277	002			1.969	422
* 10	3.082	3.08	021	* 50	1.878	1.878	$\bar{2}23$
* 80	2.993	2.992	$\bar{2}21$	* 15	1.848	1.849	$\bar{8}21$
* 80	2.873	2.869	600	* 20	1.745	1.745	040
* 20b	2.82	2.816	221	* 30	1.686	1.686	041
* 10	2.712	2.71	420	10	1.642	1.647	513
* 30	2.625	2.626	$\bar{4}21$			1.646	404
		2.415	$\bar{6}02$	5	1.603	1.604	423
50b	2.404	2.399	421	15	1.563	1.568	$\bar{1}021$
		2.395	$\bar{2}22$			1.566	$\bar{6}04$
15	2.319	2.331	$\bar{7}11$	* 20	1.541	1.541	$\bar{8}23$
		2.319	710				

114.6 mm Debye-Scherrer powder camera; Cu radiation, Ni filter ( $\lambda$  Cu- $K\alpha$  = 1.54178 Å)

Intensities estimated visually; b = broad line

Not corrected for shrinkage and no internal standard; \* = lines used for unit-cell refinement

Indexed with  $a = 17.580$ ,  $b = 6.979$ ,  $c = 6.693$  Å,  $\beta = 101.71^\circ$

Br + Cl = 2 a.p.f.u., the empirical formula is  $\text{Hg}_{1.00}^{2+}\text{Hg}_{1.00}^{1+}\text{O}_{1.01}(\text{I}_{0.97}\text{Br}_{0.01}\text{Cl}_{0.01})_{\Sigma 0.99}$ . The ideal end-member formula,  $\text{Hg}^{2+}\text{Hg}^{1+}\text{OI}$ , requires HgO 39.81,  $\text{Hg}_2\text{O}$  38.34, I 23.32, sum 101.47, less O = I - 1.47, total 100.00 wt.%.

Chemically, aurivilliusite is the I analogue of terlinguaite,  $\text{Hg}^{2+}\text{Hg}^{1+}\text{OCl}$ , with the same space group. However, the unit-cell parameters, crystal structures and resulting powder-diffraction patterns are distinctly different, as is the general appearance of the two minerals.

### Qualitative reflectance optics

In polished section under plane-polarized reflected light, aurivilliusite is similar in qualitative optical characteristics to that of cinnabar. It is, however, extremely light sensitive with very evident twinning and no internal reflections. In addition, as one observes it under the microscope, minute 'red lights' switch on; initially, they are randomly dispersed across the reflectance surface but then, as more 'red lights' switch on, they coalesce. This 'red light' phenomenon is unique amongst opaque minerals and should henceforth be known as the 'Criddle effect' after our late

colleague and coauthor, Dr Alan J. Criddle, who first recognized and described it. The calculated average index of refraction is either 2.35 or 2.38, depending on the  $k$  value used for  $\text{Hg}_2\text{O}$ .

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