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CLEARCREEKITE, A NEW POLYMORPH OF $Hg^{1+}_3(CO_3)(OH)•2H_2O$, FROM THE CLEAR CREEK CLAIM, SAN BENITO COUNTY, CALIFORNIA

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ABSTRACT

Clearcreekite is a newly recognized polymorph of $Hg^{1+}_3(CO_3)(OH)•2H_2O$ (along with the previously described peterbaylissite). The mineral is monoclinic, space group $P2_1/c$ (14), with unit-cell parameters refined from powder data: a 6.760(4), b 9.580(4), c 10.931(4) Å, β 105.53(5)°, V 682.1(6) Å^3, a:b:c = 0.7056:1:1.1410, Z = 4. The strongest six reflections in the X-ray powder-diffraction pattern [d in Å(I)(hkl)] are: 7.09(70)(011), 5.32(40)(111), 4.62(90)(012), 2.831(100)(023), 2.767(100)(211,221), and 2.391(40)(040,204). The mineral is an extremely rare constituent in a small prospect pit near the long-abandoned Clear Creek mercury mine, New Idria district, San Benito County, California. The mineral is found as an isolated cluster of crystals in a shallow depression, associated with cinnabar and edoylerite, on a single specimen of brecciated silica–carbonate rock. Individual crystals do not exceed 0.17 mm in longest dimension and are subhedral, tabular, with major {001} and minor {010} forms. The mineral is transparent with a pale greenish yellow color and streak. Physical properties include: vitreous luster, uneven fracture, brittle, nonfluorescent, soft (grains punctured by an electron beam), calculated density 6.96 g/cm^3 (idealized formula). The mineral becomes dark brown-black and opaque when subjected to X-radiation, and the change is irreversible. Electron-microprobe analysis yielded 84.65 wt.% Hg_2O. The empirical formula, derived from results of a crystal-structure analysis and of an electron-microprobe analysis, is $Hg^{1+}_{2.92}(C_{1.01}O_{2.98})(OH)_{1.04}•2H_2O$, based on O = 6. The idealized formula requires Hg_2O 87.54, CO_2 6.16, H_2O 6.30, total 100.00 wt.%. The infrared-absorption spectrum confirms the presence of both CO_3 and H_2O. The mineral is named after the type locality.

Keywords: clearcreekite, new mineral species, polymorph, peterbaylissite, hydrated mercurous hydroxide–carbonate, X-ray data, electron-microprobe data, infrared-absorption data, Clear Creek claim, San Benito County, California.

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Sommaire

La clearcreekite est une forme polymorphique de $Hg^{1+}_3(CO_3)(OH)\bullet 2H_2O$ récemment reconnue (la peterbaylissite l'était déjà). Il s'agit d'un minéral monoclinique, groupe spatial $P2_1/c$ (14), ayant les paramètres réticulaires suivants, affinées à partir du spectre de diffraction obtenu sur poudre: *a* 6.760(4), *b* 9.580(4), *c* 10.931(4) Å, β 105.53(5)°, *V* 682.1(6) Å^3, *a*:*b*:*c* = 0.7056:1:1.1410, *Z* = 4. Les six raies les plus intenses du spectre de diffraction (méthode des poudres) [*d* en Å(*I*)(*hkl*)] sont: 7.09(70)(011), 5.32(40)(111), 4.62(90)(012), 2.831(100)(023), 2.767(100)(211,221), et 2.391(40)(040,204). Il s'agit d'un membre rarissime d'une association découverte dans un petit puit d'exploration près de la mine de mercure de Clear Creek, abondonnée depuis fort longtemps, dans le district de New Idria, comté de San Benito, en Californie. Le minéral se présente en amas isolés de cristaux dans un depression peu profonde, en association avec cinnabre et edoylerite, sur un seul échantillon de roche silicatée et carbonatée bréchifiée. Les critaux individuels ne dépassent pas 0.17 mm en longueur; ils sont sub-idiomorphes et tabulaires, avec les formes {001} (majeure) et {010} (mineure). C'est un minéral transparent, ayant une couleur et une rayure jaune verdâtre pâle. Les propriétés physiques incluent: éclat vitreux, fracture inégale, cassant, non fluorescent, relativement mou (grains transpercés par le faisceau d'électrons), densité calculée de 6.96 g/cm^3 (pour la formule idéale). Dans un faisceau de rayons X, le minéral devient brun foncé à noir et opaque, de façon irréversible. Une analyse à la microsonde électronique a donné 84.65% Hg_2O (poids). La formule empirique, dérivée des résultats d'une ébauche de la structure et d'analyses à la microsonde électronique, serait $Hg^{1+}_{2.92}(C_{1.01}O_{2.98})(OH)_{1.04}\bullet 2H_2O$, sur une base de six atomes d'oxygène. Cette formule idéalisée requiert Hg_2O 87.54, CO_2 6.16, H_2O 6.30, pour un total de 100.00% (poids). Le spectre d'absorption infra-rouge confirme la présence de CO_3 et de H_2O. Le nom du minéral rappelle la localité-type.

(Traduit par la Rédaction)

Mots-clés: clearcreekite, nouvelle espèce minérale, polymorphe, peterbaylissite, hydroxide–carbonate hydraté de mercure (mercureux), données de diffraction X, données de microsonde électronique, données d'absorption infra-rouge, indice de Clear Creek, comté de San Benito, Californie.

Introduction

The new mineral species described here, clearcreekite, was first identified in 1989 by one of us (RCE), both by X-ray powder diffraction and by X-ray single-crystal analysis. The rock specimen on which it occurs had been originally collected by amateur mineralogist Mr. Edward H. Oyler from a small prospect pit near the long-abandoned Clear Creek mercury mine, New Idria district, San Benito County, California (lat. 36°22'59"N, long. 120°43'58"W). The specimen was initially examined and retained by Mr. Oyler as it contains crystals of edoylerite (Erd *et al.* 1993, Burns 1999) associated with cinnabar. Clearcreekite megascopically resembles, both in general habit and color, terlinguaite, which had previously been identified at this locality, and thus was not positively identified as a potential new mineral species until subjected to routine X-ray powder-diffraction study. Despite assiduous searches and numerous X-ray identifications, only one specimen containing crystals of clearcreekite has so far been found.

The mineral is named *clearcreekite* after the type locality, the Clear Creek mercury mine, New Idria district, San Benito County, California. The mineral species and its name have been approved by the Commission on New Minerals and Mineral Names, IMA. The holotype specimen, microprobe mount, two single-crystal mounts, and a small vial containing less than 1 μm of pure material are preserved within the Systematic Reference Series of the National Mineral Collection at the Geological Survey of Canada, Ottawa, under catalogue number NMCC 68074.

Occurrence and Associated Minerals

Clearcreekite is an extremely rare constituent at the Clear Creek claim. Only one clearcreekite-bearing area, a small millimeter-sized shallow depression on one side of the discovery specimen, has been identified to date. From within this depression, two isolated subhedral crystals were successfully extracted for further study. All mineralogical studies, including the crystal structure, were carried out on portions of these two crystals. Clearcreekite is found near cinnabar, but not in direct contact with it. Edoylerite has also been megascopically identified on the same side of the specimen. The host rock is a brecciated silica–carbonate rock composed principally of ferroan magnesite and quartz. Other mercury-bearing minerals identified by X-ray powder-diffraction analyses from the Clear Creek claim include edgarbaileyite (Roberts *et al.* 1990a, Angel *et al.* 1990), szymańskiite (Roberts *et al.* 1990b, Szymański & Roberts 1990), wattersite (Roberts *et al.* 1991, Groat *et al.* 1995), deanesmithite (Roberts *et al.* 1993, Szymański & Groat 1997), hanawaltite (Roberts *et al.* 1996, Grice 1999), peterbaylissite (Roberts *et al.* 1995, Groat *et al.*, in prep.), calomel, montroydite, native mercury, eglestonite, terlinguaite, schuetteite, mosesite, gianellaite, metacinnabar, donharrisite and nine unnamed mercury-bearing phases currently under investigation. A description of the geology of the Clear Creek mercury mine is given by Eckel & Myers (1946); other references dealing with the geology, geochemistry, and mineralogy of the area surrounding Clear Creek can be found in the paper dealing with edoylerite (Erd *et al.* 1993). Clear-

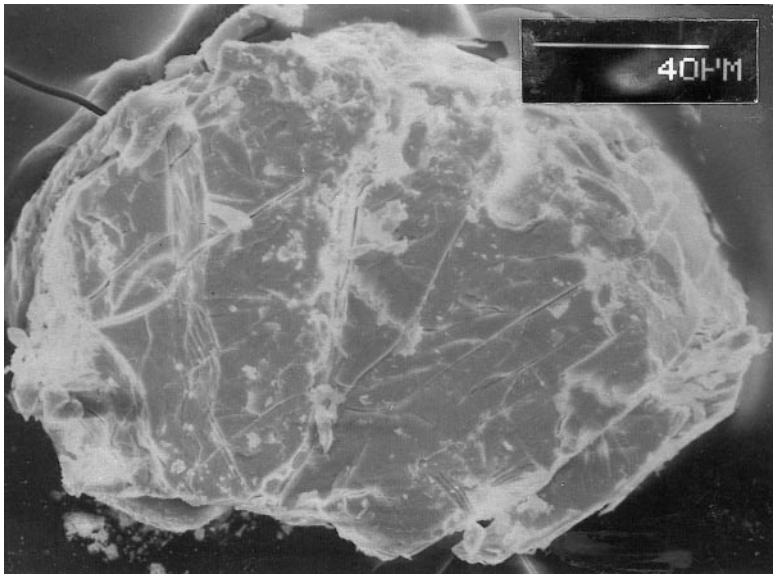

FIG. 1. Crystal of clearcreekite showing subhedral tabular habit. Scale bar: 40 μm.

creekite probably formed as a result of the alteration of a pre-existing mercury-bearing mineral, such as cinnabar.

PHYSICAL PROPERTIES

Clearcreekite occurs as a small cluster of crystals on the surface of the sample. Individual crystals do not exceed 0.17 mm in longest dimension, are subhedral, tabular with major {001} and minor {010} forms. A scanning-electron photomicrograph of one of the extracted crystals is presented in Figure 1. The mineral is transparent, pale greenish yellow, with a pale greenish yellow streak. It possesses a vitreous luster, an uneven fracture, is brittle, and is nonfluorescent under both long- and short-wave ultraviolet radiation. The cleavage is {001}, good. The crystals are too small for an accurate determination of hardness (although the mineral might be soft since the electron beam of a scanning-electron microprobe can perforate a crystal), and there is insufficient material available for a determination of density using the Berman balance. Clearcreekite becomes colorless and transparent in concentrated HCl, but otherwise is unaffected and does not seem to effervesce. However, what does markedly affect this mineral is X-radiation: under both Cu and Mo X-radiation, the typically greenish yellow grains turn an opaque dark brown-black color. This color change is irreversible and obviously inhibits any attempt at accurate optical reflectance studies. Any measurements of reflectance obtained on "altered" material would not be representative of the mineral, and would give values that are erroneous (A.J. Criddle, pers. commun. 1996). For this reason, reflectance studies have not been attempted. The calculated average index of refraction ($\bar{n}$) for clearcreekite varies from 2.06 to 2.12 depending on the k value of Hg_2O that is used in the Gladstone–Dale equation. These average values indicate that all indices of refraction are too high to be measured in normal index of refraction oils.

X-RAY CRYSTALLOGRAPHY

Two crystal fragments, one mounted with b^* and the other mounted with c^* parallel to the dial axis, were examined by single-crystal precession methods employing Zr-filtered Mo radiation. The following levels were photographed: $hk0 \rightarrow hk3$, $0kl \rightarrow 2kl$, $h0l \rightarrow h3l$, and $b^* \wedge 201^*$. Clearcreekite is monoclinic; the systematic absences ($h0l$ with $l \neq 2n$, and $0k0$ with $k \neq 2n$) dictate that the space group is uniquely defined as $P2_1/c$ (14). The $hk0$ precession film shows pseudo $k \neq 2n$ symmetry with k-odd reflections very weak. The calculated unit-cell parameters derived from measurement of zero-level precession films are: a 6.765, b 9.59, c 10.91 Å, β 105.67°. The symmetry, cell parameters and space group have been confirmed by the results of a crystal-structure analysis (Groat *et al.*, in prep.).

The X-ray powder-diffraction data are presented in Table 1. The unit-cell parameters were refined using 14 powder reflections representing d values between 3.541 and 1.756 Å for which unambiguous indexing was pos-

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR CLEARCREEKITE

$I_{est.}$	dÅ$_{(meas.)}$	dÅ$_{(calc.)}$	*hkl*	$I_{est.}$	dÅ$_{(meas.)}$	dÅ$_{(calc.)}$	*hkl*
70	7.09	7.09	011	3	2.598	2.604	$\bar{1}$14
30	5.40	5.39	110	10	2.539	2.539	014
40	5.32	5.30	$\bar{1}$11	30	2.486	2.488	202
90	4.62	4.62	012	40	2.391	2.395	040
20	4.41	4.42	111			2.383	$\bar{2}$04
5	4.28	4.27	$\bar{1}$12	15	2.337	2.335	041
3	3.63	3.64	102	3	2.298	2.307	024
10	3.541	3.543	022	3	2.190	2.189	$\bar{3}$11
3	3.389	3.407	112	20	2.147	2.147	231
		3.379	$\bar{1}$22	20	2.101	2.101	$\bar{2}$33
10	3.293	3.294	$\bar{1}$13	25	2.056	2.057	015
10	3.084	3.083	210	3	1.982	1.986	$\bar{1}$25
30	3.058	3.056	031	5b	1.845	1.847	241
10	3.018	3.015	$\bar{2}$12	5	1.816	1.817	$\bar{2}$43
5	2.866	2.867	130	10b	1.792	1.800	052
100	2.831	2.832	023			1.791	214
100	2.767	2.776	211	20	1.756	1.755	006
		2.760	$\bar{2}$21			1.725	242
20b	2.687	2.693	220	25	1.725	1.725	$\bar{2}$16
		2.687	131	30	1.692	1.716	$\bar{2}$35
		2.682	113			1.689	$\bar{2}$44
		2.678	$\bar{2}$13			1.688	$\bar{4}$02
5	2.648	2.647	$\bar{2}$22				

114.6 mm Debye-Scherrer powder camera
Cu radiation, Ni filter (Å CuKα – 1.54178 Å)
intensities estimated visually
b broad line
Not corrected for shrinkage and no internal standard
Indexed on a – 6.760, b = 9.580, c = 10.931 Å, β 105.53°

sible, based on visual inspection of single-crystal precession films. The refined unit-cell parameters are: *a* 6.760(4), *b* 9.580(4), *c* 10.931(4) Å, β 105.53(5)°, *V* 682.1(6) Å^3, *a*:*b*:*c* = 0.7056:1:1.1410. The powder-diffraction data are unique and bear no resemblance to those of any other inorganic phase listed in the Powder Diffraction File. The crystal-structure analysis (Groat *et al.*, in prep.) shows that clearcreekite has a polymorphic relationship with peterbaylissite (Roberts *et al.* 1995); details comparing and contrasting the two structures will be presented in a forthcoming paper. With Z = 4, the calculated density for the idealized formula, $Hg^{1+}{}_3(CO_3)(OH)\cdot 2H_2O$, is 6.96 g/cm^3.

Chemical Composition

A portion of one of the clearcreekite crystals was analyzed with a Cameca SX–50 electron microprobe at the Department of Earth and Ocean Sciences, University of British Columbia, utilizing an operating voltage of 15 kV, a beam current of 10 nA, a beam 20 μm in diameter and a 20-second count time. The grain decomposes very quickly under the electron beam and is very sensitive to beam damage. Hg, C and O were the only elements detected in a wavelength-dispersion scan. The nature of the material precluded quantitative analyses for C and O. The compound HgTe was used as a microprobe standard for Hg. Data reduction was performed with the "PAP" φ(ρz) method of Pouchou & Pichoir (1985). The crystal structure was known prior to the final interpretation of the analytical data. One analysis gave 81.41 wt.% Hg, which was then recast to 84.65 wt.% Hg_2O. Quantitative values for CO_2 [6.16 wt.%] and H_2O [6.30 wt.%] were derived from the results of the crystal-structure analysis (Groat *et al.*, in prep.). Using these results and the Hg_2O value derived from the electron-microprobe analysis, the chemical formula, based on O = 6, is $Hg^{1+}{}_{2.92}(C_{1.01}O_{2.98})(OH)_{1.04}\cdot 2H_2O$ or, ideally, $Hg^{1+}{}_3(CO_3)(OH)\cdot 2H_2O$. The idealized formula requires Hg_2O 87.54, CO_2 6.16, H_2O 6.30, total 100.00 wt.%. Clearcreekite has a polymorphic relationship with peterbaylissite, a fact that would not have been evident without knowledge of the crystal structure. This is yet another example of the use of crystal-structure analysis in order to determine the precise chemical formula of a complex mineral species (Hawthorne & Grice 1990).

Infrared Spectroscopy

The infrared spectrum of clearcreekite was obtained using the same equipment and procedures as those used to collect the infrared spectrum of peterbaylissite (Roberts *et al.* 1995). We note that the transmittance spectrum of clearcreekite (Fig. 2) was collected on a crystal fragment that did not exceed 30 μm in size before crushing. The advantages of this type of instrumentation to complement existing methods for the characterization of new mineral species are obvious.

The spectrum of clearcreekite shows the presence of structural H_2O by a medium-intensity band at 1627 cm^{-1} due to H–O–H flexing. The strong absorption band, centered at 3370 cm^{-1}, is due to O–H stretching in H_2O molecules and (OH) groups. Bending of Hg–OH bands produces the 969 cm^{-1} band. Internal modes for the carbonate group account for several other strong to medium-weak absorptions (ν_2 at 828, ν_3 at 1488, ν_4 at 726 cm^{-1}). The strong band at 1314 cm^{-1} cannot be assigned with certainty, but may be due to hydrogen bonding between carbonate and hydroxyl.

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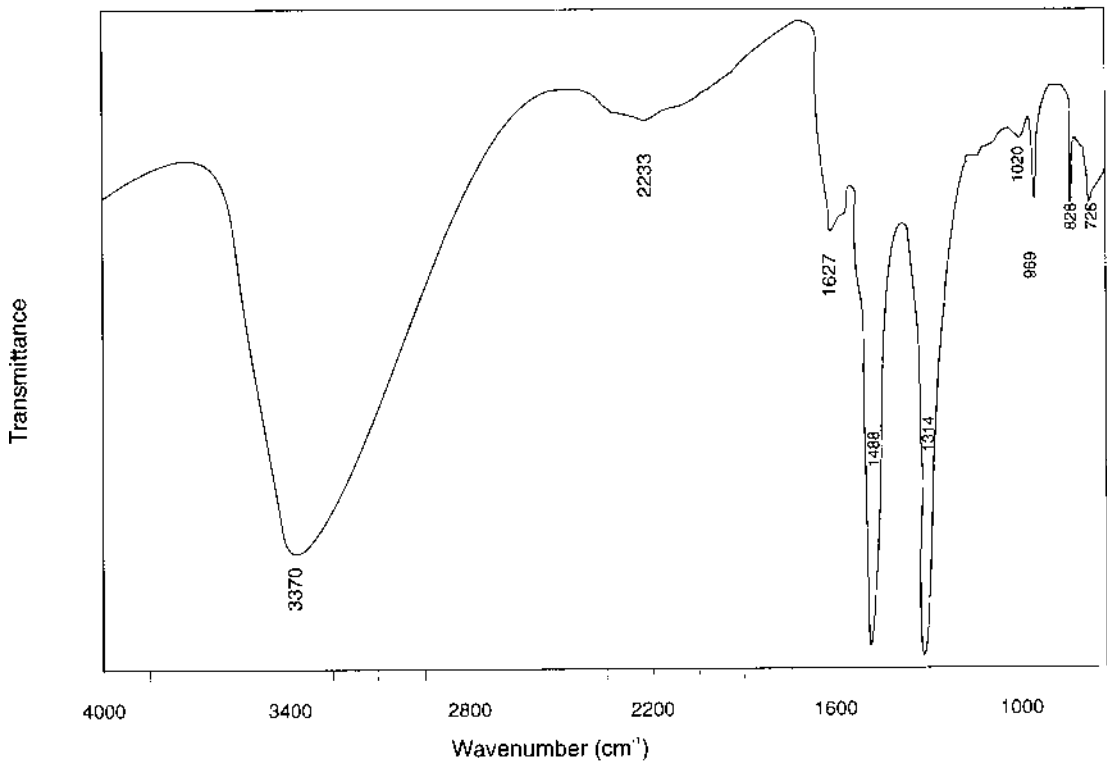

FIG. 2. Infrared-transmission spectrum for clearcreekite.

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