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KENHSUITE, γ-$Hg_3S_2Cl_2$, A NEW MINERAL SPECIES FROM THE McDERMITT MERCURY DEPOSIT, HUMBOLDT COUNTY, NEVADA

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ABSTRACT

Kenhsuite, γ-$Hg_3S_2Cl_2$, a new mineral species, occurs with cinnabar and mercury sulfo-halide minerals at the McDermitt mercury mine, Humboldt County, Nevada, where it is associated with the alpha form, corderoite, α-$Hg_3S_2Cl_2$. Kenhsuite crystals, 1 × 10 µm long, are dispersed along fractures in altered tuffaceous lacustrine rocks. Kenhsuite is orthorhombic, with possible space-groups *Ammm*, *A2mm*, *Am2m*, *Amm2*, or *A222*; *a* 9.332(5), *b* 16.82(2), *c* 9.108(5) Å, *V* 1429.63 Å^3, *a:b:c* = 0.5548:1.0:0.5415, and Z = 8. The strongest four peaks in the X-ray powder-diffraction pattern [*d* in Å(*I*)(*hkl*)] are 2.58(100)(242), 3.65(90)(122), 3.11(51)(300), and 2.60(49)(331). Color and streak are canary yellow. The mineral blackens on exposure to sunlight. Kenhsuite is transparent, with a glassy luster; it has a Mohs hardness of 2–3 and a conchoidal and hackly fracture. It fluoresces red and red-orange under 366 nm ultraviolet radiation. The measured density is 6.83 (5) g/cm^3, and the calculated density, 6.87 g/cm^3. Kenhsuite is biaxial (+), with $2V_z$ greater than 70°, and index of refraction 2.25 ± 0.01. It has pleochroic colors that are weak pale yellow to greenish yellow. In reflected light, kenhsuite has medium to low reflectance, estimated at about 15%, and is white with abundant bright canary yellow to palest yellow-white internal reflections. Its polishing hardness is about the same as cinnabar (soft, 2–2.5). Kenhsuite formed later than cinnabar and corderoite, and possibly, in part simultaneously with corderoite. The mineral is named after Dr. Kenneth Jinghwa Hsu, Professor Emeritus, Swiss Federal Institute of Technology, Zurich, Switzerland.

Keywords: kenhsuite, corderoite, mercury, sulfochloride, polymorphism, McDermitt, Nevada.

SOMMAIRE

La kenhsuite, γ-$Hg_3S_2Cl_2$, nouvelle espèce minérale, a été découverte avec cinabre et des sulfo-halogénures à la mine de mercure de McDermitt, dans le comté de Humboldt, au Nevada; elle y est associée aussi avec la cordéroïte, α-$Hg_3S_2Cl_2$. Les cristaux de kenhsuite, mesurant 1 × 10 µm, sont dispersés le long de fractures dans des tufs lacustres altérés. Il s'agit d'un minéral orthorhombique, cristallisant dans un des groupes spatiaux suivants: *Ammm*, *A2mm*, *Am2m*, *Amm2*, ou *A222*; *a* 9.332(5), *b* 16.82(2), *c* 9.108(5) Å, *V* 1429.63 Å^3, *a:b:c* = 0.5548:1.0:0.5415, et Z = 8. Les quatre raies les plus intenses du spectre de diffraction X (méthode des poudres) [*d* en Å(*I*)(*hkl*)] sont 2.58(100)(242), 3.65(90)(122), 3.11(51)(300), et 2.60(49)(331). La couleur du minéral et sa rayure sont jaune serin; il se ternit au soleil. La kenhsuite est transparente, avec un éclat vitreux, et une fracture conchoïdale et âpre. Sa dureté de Mohs est entre 2 et 3. Elle fait preuve d'une fluorescence rouge à rouge-orange en réponse à la lumière ultra-violette (λ 366 nm). Sa densité est 6.83 (5) (mesurée) et 6.87 (calculée). La kenhsuite est biaxe négative, avec $2V_z$ supérieur à 70°, et un indice de réfraction égal à 2.25 ± 0.01. Elle montre un faible pléochroïsme, du jaune très pâle au jaune verdâtre. En lumière réfléchie, la kenhsuite possède une réflectance modérée à faible, que nous estimons être environ 15%; elle est blanche avec plusieurs reflets internes allant du jaune serin brillant au jaune très pâle. Au polissage, elle a à peu près la même dureté que le cinabre (mou, 2–2.5). La kenhsuite s'est formée tardivement par rapport au cinabre et à la cordéroïte, et peut-être même temps qu'une partie de cette dernière. Le minéral honore Kenneth Jinghwa Hsu, Professeur émérite, Institut Suisse Fédéral de Technologie à Zurich.

(Traduit par la Rédaction)

Mots-clés: kenhsuite, cordéroïte, mercure, sulfochlorure, polymorphisme, McDermitt, Nevada.

INTRODUCTION

Kenhsuite, the first naturally occurring example of γ-$Hg_3S_2Cl_2$, occurs in small quantities in the open pit of the inactive McDermitt mercury deposit in north-central Nevada, about 10 km southwest of the town of McDermitt, at the Oregon State line. Several other non-operating mercury mines are to be found in the district, including the Cordero, Crofoot, Lenway, and Ruja underground mines and the Opalite surface workings (Yates 1942, Bailey & Phoenix 1944, Curry 1960, Fisk 1968). Kenhsuite was found in one area in the open pit, associated with cinnabar (HgS) and the alpha polymorphic form, corderoite (α-$Hg_3S_2Cl_2$: Foord *et al.* 1974).

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Kenhsuite is named for Dr. Kenneth Jinghwa Hsu (b. 1929), Professor Emeritus, Swiss Federal Institute of Technology (E.T.H.)., Zurich, Switzerland, in recognition of numerous contributions to many fields in the earth sciences. Kenhsuite is pronounced "ken" as in kennel, "hsu" as shoe, "ite" as in white. The mineral and mineral name were approved by the Commission on New Minerals and New Mineral Names of the International Mineralogical Association. Representative samples of kenhsuite are housed in the Smithsonian Institution [museum catalogue number NMNH 171405 (type specimen) and 171406], Washington, D.C., and the W.M. Keck Museum of the Mackay School of Mines, University of Nevada, Reno, Nevada.

OCCURRENCE

Kenhsuite is found in hydrothermally altered rhyolitic, tuffaceous lacustrine rocks in the Miocene McDermitt caldera complex, which is 80 km in diameter (McKee 1976, Speer 1977, Roper 1976, Rytuba 1976, Rytuba *et al.* 1979, Rytuba & Conrad 1981, Rytuba & Glanzman 1979, Rytuba & McKee 1984, McCormack 1996). Regionally, the rocks have become altered to diagenetic alkaline zeolite minerals and, locally, to hydrothermal montmorillonite, kaolinite, adularia, opal, and cristobalite (Glanzman & Rytuba 1979, Hetherington 1983, Hetherington & Cheney 1985, Giraud 1986, McCormack 1986, McCormack *et al.* 1991). Kenhsuite was found at one location near the center of the open pit, in montmorillonite and associated with cinnabar and corderoite (Fig. 1). Rare mercury-bearing minerals that also occur at McDermitt include radtkeite (Hg_3S_2ClI), calomel (Hg_2Cl_2), kleinite [$Hg_2N(Cl,SO_4){\bullet}nH_2O$], eglestonite ($Hg_4Cl_2O$), native mercury (Hg), and possibly mosesite [$Hg_2N(SO_4,MoO_4,Cl){\bullet}H_2O$] (Foord *et al.* 1974, McCormack 1986). Extremely fine grains of kenhsuite, with coarser cinnabar and corderoite, are dispersed in clay adjacent to fractures in argillized tuffaceous sedimentary rocks. Fibrous and bladed crystals 1 × 10 μm in length are typical (Figs. 2, 3).

McCormack (1986) showed that pyrite and stibnite were deposited earlier than cinnabar, which preceded the mercury sulfo-halide minerals. Corderoite, which accounts for approximately 25% of the mercury ore, formed by the reaction of sulfur-deficient chloride solutions with cinnabar, by means of a volume-for-volume replacement (McCormack 1986). Kenhsuite commonly is in contact with both cinnabar and corderoite. Some kenhsuite also occurs as isolated masses and individual crystals on fracture surfaces and cavities, near cinnabar and corderoite; this necessitates transfer of components by diffusion or transport in fluids. Simultaneous deposition of some kenhsuite with corderoite cannot be ruled out.

PHYSICAL AND OPTICAL PROPERTIES

Fine threadlike fibers (1 × 10 μm) and elongate prismatic tablets and blades (1 × 7 x 25 μm) of kenhsuite occur in associated clays and silica, and could not be separated by settling from suspensions in fluids. However, it was possible to prepare nearly pure fractions of kenhsuite by taking advantage of chemical and surface properties. Silicate matrix minerals react more rapidly with HF acid than sulfides, and could be selectively dissolved, leaving a sulfide-rich fraction that is highly concentrated in kenhsuite. In addition, nearly pure samples of kenhsuite were prepared by flotation. Kenhsuite, suspended in acetone–water solutions through which air is passed, is attracted to bubble surfaces, from which it is readily collected. No effects on its properties were detected from exposure to HF acid or water–acetone solutions.

Properties of both natural and synthetic kenhsuite agree. The X-ray powder-diffraction pattern of the mineral matches that of the synthetic materials, except for differing intensities of lines owing to preferred orientations (Table 1). The color and streak of kenhsuite are canary yellow on freshly broken surfaces. The mineral is photosensitive, and blackens within a few minutes on exposure to direct sunlight. The mineral fluoresces in shades of red to red-orange under long-wave (λ 366 nm) ultraviolet light. The intensity of the fluorescence weakens for samples exposed to sunlight. Kenhsuite crystals are glassy and transparent. The hardness of the synthetic material is 2–3 on the Mohs scale. The mineral is brittle, with a hackly and conchoidal fracture. An excellent cleavage is parallel to (100). The mineral was not suitable, and synthetic materials were not produced in great enough quantity, to allow accurate determinations of density. The density of synthetic γ-$Hg_3S_2Cl_2$ according to Ďurovič (1968) is 6.83(5) g/cm³; this is close to 6.87 g/cm³, calculated for the mineral from our unit-cell constants and the simplified chemical formula.

Optical properties of the synthetic material, determined in plane-polarized light, are: biaxial positive (+); $2V > 70°$; sign of elongation negative (–) or length fast; parallel extinction; dispersion $r >> v$. Color is greenish yellow. Weak pleochroic colors, observable in thick sections, are pale yellow to greenish yellow. The maximum observed index of refraction is 2.25(1), determined by Becke line comparison of multiple-grain fragments with S–Se melts (Merwin & Larsen 1912). No reaction with the S–Se media was observed.

In reflected light, in air, the mineral is white, with reflectivity less than that of corderoite and much less than that of cinnabar, visually estimated at approximately 15%. Bireflectance and anisotropism were not observed. The abundant internal reflections are bright canary yellow to pale yellow-white. The polishing hardness of kenhsuite is less than that of cinnabar.

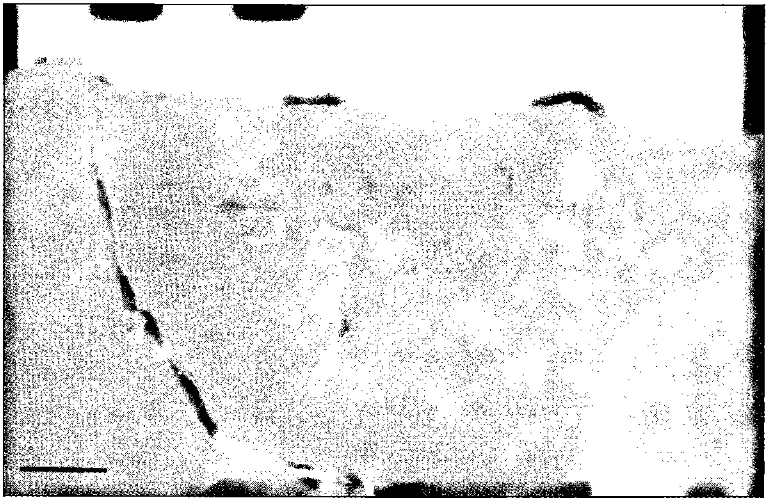

FIG. 1. Canary yellow kenhsuite, as dispersions in argillized groundmass minerals, and as coatings on cinnabar grain (red). White rectangular grains of corderoite containing a core of cinnabar occur at the left of kenhsuite-coated cinnabar grain. Reflected light, uncrossed polars, bar scale in lower left: 0.10 mm.

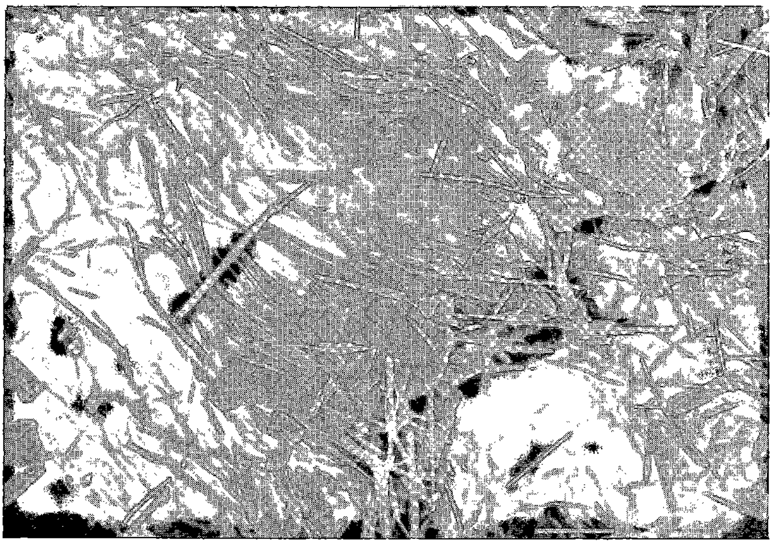

FIG. 2. Fibrous crystals and coarser tablets of kenhsuite, adjacent to equant grain of corderoite in upper right. SEM photo, scale bar represents 10 μm.

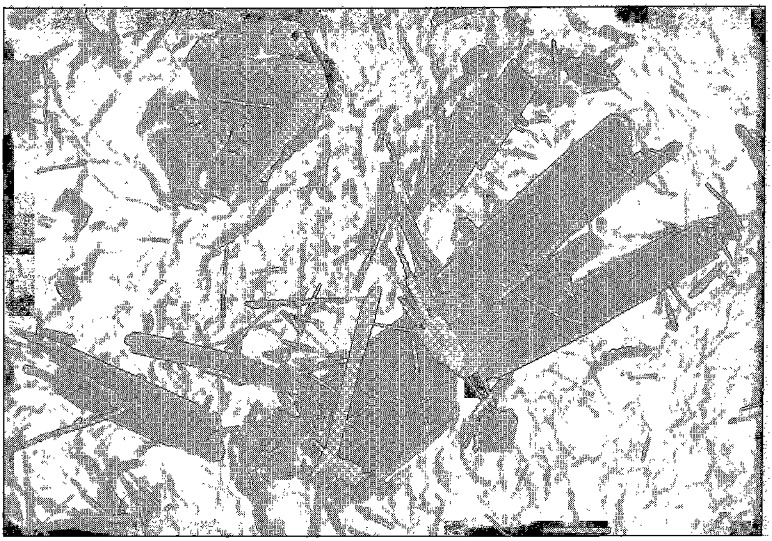

FIG. 3. Tabular grain of kenhsuite and equant grain of corderoite in upper left. Note kenhsuite fibers on corderoite surface. SEM photo, scale bar represents 10 μm.

SYNTHESIS

Kenhsuite has been synthesized by Puff *et al.* (1966) and by Carlson (1967). Carlson (1967) produced granular α-$Hg_3S_2Cl_2$ and crystals of γ-$Hg_3S_2Cl_2$ by reacting HgS with HCl gas in closed tubes with a thermal gradient. We produced a few mm-sized glassy crystals of γ-$Hg_3S_2Cl_2$ along with fine crystals of another polymorphic form, cubic β-$Hg_3S_2Cl_2$ (not a known mineral), by reacting stoichiometric mixtures of HgS and $HgCl_2$ (2:1) in sealed evacuated glass tubes at 400°C. Crystals of γ-$Hg_3S_2Cl_2$ formed on the upper and slightly cooler portions of tubes, separate from the β-polymorphic form, which made up most of the synthetic product. Crystals of γ-$Hg_3S_2Cl_2$ and HgS, Hg_2Cl_2, $HgCl_2$, and α-$Hg_3S_2Cl_2$ were found to grow in evacuated glass tubes in which natural materials (powdered gangue and sulfide minerals) were heated in a thermal gradient from 350 to 25°C.

CRYSTALLOGRAPHY

Properties of kenhsuite match those of synthetic γ-$Hg_3S_2Cl_2$ produced by us and others. Puff *et al.* (1966) described his synthetic phase as orthorhombic, space-group choices *Cmmm*, *C*222, *Cm*2*m* or *Cmm*2, with *a* 9.09, *b* 16.84, *c* 9.34 Å, *Z* = 8. Cell constants for the mineral were calculated by refinement of our powder-diffraction data by assigning the crystal system to orthorhombic and using the cell constants of Puff *et al.* (1966) as initial input. Systematic extinctions of *hkl*, indexed for a primitive cell from refined unit-cell constants, were used in the selection of possible space-groups.

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR KENHSUITE AND SYNTHETIC γ-$Hg_3S_2Cl_2$

kenhsuite				γ-$Hg_3S_2Cl_2$	
d_{meas}	*I*	*hkl*	d_{calc}	d_{meas}	*I*
9.33	11	100	9.332	9.33	17
		011	8.009	8.00	1
6.30	26	120	6.247	6.26	5
		111	6.078	6.06	2
		031	4.774	4.77	5
4.66	10	200	4.667	4.67	17
		002	4.554	4.54	4
		131	4.250	4.23	7
4.09	10	102	4.093	4.08	9
		211	4.032	4.02	4
3.84	20	140	3.833	3.84	7
3.65	90	122	3.680	3.68	18
3.35	7	231	3.337	3.34	12
		202	3.259	3.26	2
3.11	51	300	3.111	3.12	100
		222	3.039	3.03	5
2.97	23	013	2.988	2.98	3
2.93	9	142	2.933	2.94	17
2.83	36	113	2.846	2.84	3
2.69	11	160	2.684	2.69	7
2.60	49	331	2.606	2.59	27
2.58	100	242	2.576	2.57	38
2.52	5	213	2.516	2.51	2
2.45	6	322	2.457	2.47	5
		062	2.387	2.39	1
2.33	41	400	2.333	2.34	73
2.27	6	004	2.277	2.27	9
2.23	15	411	2.240	2.25	6
2.17	2	313	2.155	2.16	1
2.11	31	080	2.102	2.10	9
2.09	8			2.08	3
2.02	5			2.02	7
1.997	17				
				1.959	1
1.907	5			1.910	3
				1.872	5
1.868	8				
1.853	14				
				1.839	8
				1.804	1
				1.752	5
				1.739	9
				1.714	5
1.634	23			1.630	9
1.603	6				
				1.596	9
				1.559	4

Powder-diffraction data; Cu*K*α (λ 1.54178 Å); quartz internal standard; intensities measured. Data in the last two columns pertain to synthetic γ-$Hg_3S_2Cl_2$.

PDF data on card 20–738 (γ-$Hg_3S_2Cl_2$) pertain to somewhat disordered crystals synthesized by Carlson (1967), who recognized superstructure in some of his crystals. Ďurovič (1968) determined the atomic structure of these crystals. He described them as disordered and belonging to the OD family $A(2)mm$, $\{(b_{1/2})2_{1/2}2\}$, $\{(b_{1/2})2_{1/2}2\}$, (category III*a*). The crystals possess a common unit-cell, which Ďurovič listed as: orthorhombic; *A2mm*; *a* 9.328(5), *b* 16.82(1), *c* 9.081(6) Å, *V* 1424.78 Å^3 and $Z = 8$. Ďurovič chose a different crystallographic orientation from that of Puff *et al.* (1966), and followed the convention $c < a < b$.

No additional single-crystal work was done for this study owing to the existing structural work by Ďurovič (1968) and the match between kenhsuite and γ-$Hg_3S_2Cl_2$. We accepted Ďurovič's orientation. Crystallographic data for kenhsuite are: orthorhombic, space-group choices *Ammm*, *A2mm*, *Am2m*, *Amm2* or *A222*, *a* 9.332(5), *b* 16.82(2), *c* 9.108(5) Å, *V* 1429.63 Å^3, $a{:}b{:}c$ 0.5548:1.0:0.5415, $Z = 8$.

Values of *hkl*, for *d*-values down to 2.10 Å, listed in Table 1, were calculated using unit-cell constants derived for natural kenhsuite.

Our patterns, when compared to those of Carlson (PDF 20–738), show single peaks where his pattern shows several closely spaced doublets of equal intensity. Ďurovič (1968) concluded that this doubling of peaks reflected deviations of crystallographic angles as much as 0.5° from the expected 90° angle. Carlson's crystals were found to be slightly disordered, but otherwise match properties of the mineral and our synthetic products.

COMPOSITIONS AND PHASE RELATIONS

Chemical analyses were obtained with a JEOL T300 scanning electron microscope equipped with a Kevex energy-dispersion X-ray spectrometer, and with Ag_2S (S), $PbCl_2$ (Cl), HgI_2 (Hg, I) as standards. Mean analytical results and ranges based on 12 analyses of eight grains of kenhsuite are: Hg 81.2 (79.2–86.2), S 9.4 (7.1–10.4), Cl 9.4 (6.6–10.3). The empirical formula based on 3.0 Hg atoms and the average composition in mol.% is $Hg_3S_{2.17}Cl_{1.97}$. The simplified formula is $Hg_3S_2Cl_2$, which requires Hg 81.67, S 8.70, and Cl 9.62, Σ 99.99 wt.%.

Textures of kenhsuite and corderoite (Fig. 1) imply that they may have grown simultaneously, in part, either in equilibrium or in disequilibrium, controlled by kinetics of crystallization. The growth of metastable phases in the presence of stable phases agrees with our synthesis experiments and concepts of irreversible processes (Prigogine & Stengers 1984, Ortoleva 1994).

Kenhsuite is one of several minerals in the three-component system $Hg_3S_2Cl_2 - Hg_3S_2Br_2 - Hg_3S_2I_2$ that have related structures. Other minerals are: lavrentievite [monoclinic $Hg_3S_2(Cl,Br)_2$] and arzakite (monoclinic $Hg_3S_2(Br,Cl)_2$: Vasil'ev *et al.* (1984)], radtkeite [orthorhombic Hg_3S_2ClI: McCormack *et al.* (1991)], and grechischevite [tetragonal $Hg_3S_2(Cl,Br,I)_2$: Vasil'ev *et al.* (1989)].

The three polymorphic forms of $Hg_3S_2Cl_2$ described by Puff *et al.* (1966) are: α-$Hg_3S_2Cl_2$ (corderoite), body-centered cubic, with *a* 8.968 Å, $Z = 4$, β-$Hg_3S_2Cl_2$ (no known mineral counterpart), primitive cubic with *a* 17.93 Å, $Z = 32$, and γ-$Hg_3S_2Cl_2$ (kenhsuite), orthorhombic, considered possibly to be metastable. The mineral kenhsuite lacks disorder. Whether it formed metastably at McDermitt relative to corderoite is not known.

Crystal structures are known for the following: corderoite, α-$Hg_3S_2Cl_2$: Puff & Küster (1962), Aurivillius (1967), and Frueh & Gray (1968); kenhsuite, γ-$Hg_3S_2Cl_2$: Ďurovič (1968), and synthetic $Hg_3S_2I_2$: Blachnik *et al.* (1986). Atomic structures consist of covalently bonded $Hg_3S_2^{2+}$ groups linked by ionic bonds to halide ions [Puff & Küster (1962): α-$Hg_3S_2Cl_2$, and Ďurovič (1968): γ-$Hg_3S_2Cl_2$]. Ďurovič (1968) noted that the weak bonds linking $Hg_3S_2^{2+}$ to Cl are reflected by the excellent (100) cleavage of kenhsuite, which is parallel to planes occupied by the Cl ions.

Experimental studies on compositions, growth conditions, and crystallography of solid phases in this three-component system are reported by McCormack (1997).

ACKNOWLEDGEMENTS

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