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A MONOCLINIC, PSEUDO-ORTHORHOMBIC Au–Hg MINERAL OF POTENTIAL ECONOMIC SIGNIFICANCE IN PLEISTOCENE SNAKE RIVER ALLUVIAL DEPOSITS OF SOUTHEASTERN IDAHO

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ABSTRACT

A mineral with the approximate composition of $Au_{94}Hg_6$ – $Au_{88}Hg_{12}$ (atomic %) has been identified in Pleistocene Snake River alluvial deposits in southeastern Idaho. The gold–mercury mineral occurs as very small grains or as polycrystalline masses composed of subhedral to nearly euhedral attached crystals. Small aggregates of these crystals are mostly less than 1 μg in mass; the individual grains are mostly less than 5 μm in maximum dimension, although acicular grains 10 μm across and about 150 μm long have been observed. Vibratory cold–polishing techniques with 0.05-μm alumina abrasive for polished sections revealed a porous internal texture for most subhedral crystals after 48–72 hours of treatment. Thus, optical character (isotropic or anisotropic) could not be determined by reflected-light microscopy, and pore-free areas were too small for measurement of reflectance. Several hundred of the tiny particles of the mineral, concentrated by flotation, appear to be nearly the same color as native gold, but they are more brass-colored under the stereoscopic microscope at 80×. Elements other than gold and mercury were not detected by electron-microprobe analysis. X-ray-diffraction lines rather than individual reflections (spots), on powder camera X-ray films of unrotated spindles of single grains that morphologically appear to be single crystals, indicate that individual subhedral or euhedral crystals are composed of domains in random orientation. Thus, no material was found suitable for single-crystal X-ray-diffraction studies. The available X-ray data are best indexed according to a monoclinic cell: *a* 4.729(2), *b* 5.243(8), *c* 4.546(2) Å, β 90.90(6)°.

Keywords: Au–Hg mineral, polycrystalline masses, composition, X-ray powder patterns, alluvium, Snake River, Idaho.

SOMMAIRE

Nous avons identifié un minéral ayant comme composition approximative $Au_{94}Hg_6$ – $Au_{88}Hg_{12}$ (proportions atomiques) dans les alluvions pleïstocènes de la rivière Snake, dans le sud-est de l'Idaho. Ce minéral forme de très petits grains ou des masses polycristallines faites de cristaux rattachés sub-idiomorphes ou presque idiomorphes. De petits agrégats de tels cristaux pèsent généralement moins d'un microgramme. Les cristaux individuels sont généralement moins de 5 μm de taille, quoique certains cristaux aciculaires atteignent 10 μm en largeur et environ 150 μm en longueur. Des sections polies préparées par vibration à froid avec une pâte d'alumine à granulométrie de 0.05 μm révèlent une texture interne poreuse dans la plupart des cristaux sub-idiomorphes après 48–72 heures de polissage. C'est pourquoi le caractère optique (isotrope ou anisotrope) n'a pu être établi en lumière réfléchie, les surfaces sans pores étant trop petites pour mesures de la réflectance. Plusieurs centaines de particules, concentrées par flottation, ressemblent à l'or, mais possèdent une couleur plus proche de celle du laiton sous le microscope stéréoscopique à 80×. Aucun élément autre que l'or et le mercure n'a été décelé par analyse à la microsonde électronique. Nous observons des raies de diffraction X, plutôt que des taches individuelles, sur des clichés de diffraction de grains stationnaires qui semblent être des cristaux uniques. Ce fait montre qu'il s'agit de domaines en orientation aléatoire à l'intérieur d'un cristal idiomorphe. C'est donc dire qu'aucun matériau propice à une étude par diffraction X sur monocristal n'a été trouvé. Les données de diffraction X semblent répondre à une maille monoclinique, *a* 4.729(2), *b* 5.243(8), *c* 4.546(2) Å, β 90.90(6)°.

(Traduit par la Rédaction)

Mots-clés: minéral de Au–Hg, masses polycristallines, composition, clichés de diffraction X, alluvions, rivière Snake, Idaho.

INTRODUCTION

During 1985–1987, we investigated low-grade deposits of placer gold in Holocene and Pleistocene gravel and sand along the Snake River (Desborough *et al.* 1988a, b, 1989). These studies identified two distinct types of gold that are of placer origin, *i.e.*, both were transported in a fluviatile environment. One of these types is the "can-lid"-shaped grains, which have long been recognized in the region. These grains appear to have been transported long distances (from conglomerates in Wyoming) according to Iddings *et al.* (1899). A second type of placer gold was recently recognized (Desborough *et al.* 1986, 1988a) in the area downstream

from Blackfoot, Idaho. This type is associated with silver and gold tellurides and with gold – silver – mercury. Free mercury, as tiny spheres, has been recovered from gravels explored by drilling to depths of about 12 m in areas on the Fort Hall Indian Reservation. These areas had never been previously disturbed by mining or exploration prior to our study. We concluded from the wide vertical distribution of mercury in the gravels that this free mercury originated from the same lode source as the second type of placer gold, which is associated with mercurian minerals such as coloradoite and cubic gold – silver – mercury. Petzite, stuetzite, hessite, and native tellurium are associated with the mercurian minerals (Desborough *et al.* 1988b).

A third type of gold, recently recognized in these deposits (Desborough *et al.* 1988a), is a gold–mercury mineral that occurs in grains and grain aggregates that are so small and of such low density that they are effectively recovered only by flotation methods. Although these gold–mercury grains occur in the placer environment with the other two types of placer gold, we believe that they are not of detrital origin but grew *in situ*.

Because of the potentially significant economic contribution of these gold–mercury grains to the otherwise low-grade placer-gold deposits, the mineral warrants description at this time, even though its description does not meet the requirements for definition of a new mineral species according to the rules of the Commission on New Minerals and Mineral Names, International Mineralogical Association.

Gold–Mercury Minerals

A literature search revealed that over the last 20 years, a large number of alloys or minerals that contain gold and mercury have been described, based largely upon electron-microprobe analysis (Table 1). Except for the three analyses of gold containing 0.7–1.4 wt.% mercury, but no silver (Harris 1989, p. 72), no natural alloy of gold and mercury, without silver, has been recognized prior to our study. All cases of a natural alloy of gold and mercury reported so far contain minor or major amounts of silver (Table 1). Note added in proof: A mercurian gold phase has been found by J.W. Drexler (Department of Geology, University of Colorado, Boulder, Colorado). It has the approximate composition $Au_{80}Hg_{20}$, is fine grained, and unstable under the electron-microprobe beam. It occurs at one locality in the Boulder tungsten – gold telluride district, Colorado (J.W. Drexler, oral. com., 1992).

Five minerals containing only silver and mercury are known: mercurian silver (Ag,Hg), called amalgam or kongsbergite by some investigators, luanheite (Ag_3Hg), moschellandsbergite (Ag_2Hg_3), schachnerite ($Ag_{1.1}Hg_{0.9}$) and paraschachnerite (Ag_3Hg_2). The only two documented minerals containing gold, mercury, and silver are gold–silver–mercury alloy and weishanite, $(Au,Ag)_3Hg_2$. In addition to the data shown in Table 1 concerning natural occurrences of gold – silver – mercury, DiLabio *et al.* (1988, Table 1) gave results of 75 electron-microprobe analyses of natural gold – silver – mercury grains (either flakes or spheres) from eleven localities in eight countries.

TABLE 1. COMPOSITION AND NAMES OF NATURAL GOLD-SILVER-MERCURY MINERALS

Composition		Location	Symmetry or Name	Reference
$Au_5Ag_{10}Hg$	M	Karabash, Ural Mts., U.S.S.R.	Not given	Novgorodova & Tsepin (1976)
Au with $Ag_{9.2-23.8}$ $Hg_{3.5-14.7}$	W	Kazakhstan, U.S.S.R.	Mercurian gold, cubic	Naz'mova & Spiridonov (1979)
$Au_{79-88.6}$ $Ag_{3.9-17}$ $Hg_{0.3-15.5}$	W	Kamchatka and Yakutia, U.S.S.R.	Not given	Ozerova *et al.* (1980)
$Ag_{74.2}$ $Au_{16.4}$ $Hg_{9.4}$	M	Rajpura-Duriba, India	Not given	Basu *et al.* (1981)
$Hg_{1.2-4.6}$ in Au-Ag alloys	M?	Witwatersrand, South Africa	Not given	Erasmus *et al.* (1982)
$Hg_{1.2-4.6}$ in Au-Ag alloys	W	Barberton, South Africa	Not given	Hallbauer & von Gehlen (1983)
$Hg_{0.27-3.0}$ in Au-Ag alloys	W	Witwatersrand, South Africa	Not given	von Gehlen (1983)
Hg_x in Au-Ag alloys	W	Svoboda, Bohemian Massif Czechoslovakia	Not given	Novak & Malec (1984)
$Hg_{1.2-5.9}$ in Au-Ag alloys	W	Witwatersrand, South Africa	Not given	Oberthur & Saager (1986)
Hg_{3-16} in Au-Ag alloys	M	Langsele and Altik, northern Sweden	Isotropic	Nysten (1986)
$Hg_{53.2}$ $Au_{38.6}$ $Ag_{8.2}$	M	China	"Gamma-gold amalgam"	Keqiao *et al.* (1981)
$Hg_{0.7-1.4}$ in Au	W	Hemlo, Ontario	Not given	Harris (1989)
$Hg_{0-7.7}$ in Au-Ag alloys	W	Tsugu gold-vein deposit, Japan	Not given	Shikazono & Shimizu (1988)
Hg_{20-28} in Au-Ag alloys	M	Snake River, Idaho, U.S.A.	Isotropic	Desborough *et al.* (1988b)
$Au_{58.9}$ $Ag_{3.2}$ $Hg_{39.9}$	M	Henan Province, China	Weishanite, hexagonal, anisotropic	Yuheng *et al.* (1984)

M = mole or atomic percent; W = weight percent.

Our study seems to be the first documentation of a gold–mercury mineral without silver. The mineral is apparently monoclinic (pseudo-orthorhombic), according to the X-ray-diffraction data.

The phase relations of the gold–mercury binary system have been well known to metallurgists and crystal chemists for more than half a century (Hansen & Anderko 1958, Fig. 122). However, no natural mineral phases have been reported to correspond to any of the gold–mercury phases reported in the binary diagram below temperatures of about 300°C. Therefore, all of the phases reported in the binary diagram may be only metastable.

The implications of the above observations, deduced from the literature, are that pure gold and mercury, at temperatures below about 300°C, do not react with each other to form a stable (geologically stable) binary phase. No gold–mercury minerals have been reported from

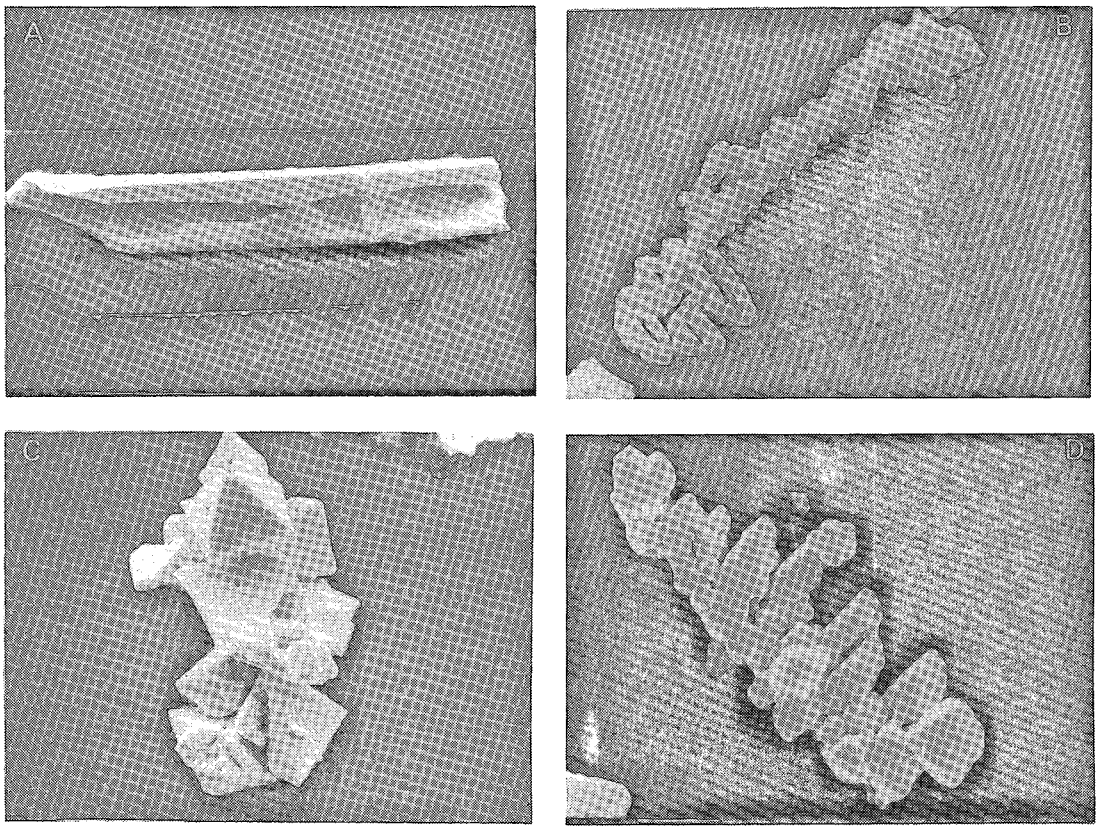

FIG. 1. Scanning electron photomicrographs of a variety of morphologies of the gold–mercury mineral, Snake River alluvium. Scale bar represents 20 (A, B) and 10 μm (C, D).

hydrothermal or metamorphic mineral occurrences. If the information in the literature is reliable, then mercury apparently does not react rapidly with pure gold at relatively low temperatures (*e.g.*, less than 200°C). Therefore, pure gold probably cannot be recovered by low-temperature "reaction" with mercury, *i.e.*, by "amalgamation" methods of recovery. On the other hand, it is well known that amalgamation methods are highly reliable for recovery of native gold, as long as silver is present in the native gold.

The gold–mercury mineral examined in the present study was heated at 370°C for 22.5 hours in a furnace in air. There was no change in the X-ray-diffraction pattern after heating. If the gold–mercury binary diagram were correct, the mineral of the present study should have become isotropic (cubic), and have taken the structure of native gold (goldamalgam) after this heat treatment. Numerous grains of the mineral (the same grains treated above) were heated at 500°C for 22 hours in air; X-ray-diffraction analysis of this material showed the powder pattern of pure gold.

TABLE 2. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF THE GOLD–MERCURY MINERAL, SNAKE RIVER ALLUVIUM

Weight Percent			Normalized Atomic Percent	
Au	Hg	Total	Au	Hg
		Grain GS H5 [11]		
86.79(1.14)	8.83(0.63)	95.61(1.32)	90.94(0.60)	9.07
		Grain BL 3-12 [5]		
90.54(1.69)	6.04(0.30)	96.59(1.63)	93.85(0.33)	6.15
		Grain BL 3-13 [2]		
84.14(0.44)	10.48(0.14)	94.62(0.30)	89.11(0.19)	10.89
		Grain BL 3-16 [3]		
83.87(0.70)	11.55(0.10)	95.42(0.61)	88.09(0.18)	11.91
		Grain BL 3-15 [2]		
82.56(1.61)	10.13(0.05)	92.70(1.66)	89.25(0.14)	10.75
		Grain BL 5-58 [5]		
81.84(1.34)	11.10(0.72)	92.94(0.95)	88.25(0.08)	11.75
		Grain BL 6-73 [2]		
84.34(0.01)	11.50(0.15)	95.84(0.16)	88.20(0.14)	11.80
		Grain BL 8-131 [12]		
88.68(0.86)	9.23(0.46)	97.91(0.19)	90.73(0.44)	9.27
		Grain BL 72 [1]		
84.84	7.52	92.36	91.99	8.01

Ag, Cu, and Sb were sought but were not found at the detection levels of about 0.05-0.07 weight percent.

20 kV, Lines used: Au-Mα, Ag-Lα, Cu-Kα, Hg-Mβ, Sb-Lα; Standards: Au, HgS, Au-Ag, Au-Ag-Cu, Sb_2S_3.

Mean and (standard deviation) are given for number of analyses [11].

TABLE 3. d-VALUES AND CELL DIMENSIONS OF THE GOLD–MERCURY MINERAL FROM SNAKE RIVER ALLUVIUM AND COMPARISON WITH PURE GOLD

Int. (obs.)	d (Å) (obs.)	hkl	d (Å) (calc.)	Int.	d (Å)	hkl
100	2.362	200	2.362	100	2.355	111
8	2.285	120	2.289			
50	2.054	$\bar{1}02$	2.056			
				52	2.039	200
80	2.030	102	2.032			
9	1.636	130	1.6354			
27	1.4461	$\bar{1}03$	1.4458			
				32	1.442	220
26	1.4342	103	1.4335			
8	1.2635	$\bar{3}12$	1.2635	36	1.230	311
(This scan terminated at d = 1.263 Å)						
				12	1.1774	222
				6	1.0196	400
				23	0.9358	331
				22	0.9120	420
				23	0.8325	422

Au-Hg mineral	Gold
a = 4.723(4) (Å)	a = 4.0786 (Å)
b = 5.230(4)	
c = 4.535(2)	
β = 90.84(6)°	

TABLE 4. POWDER DATA AND CELL DIMENSIONS FOR ACICULAR APPEARING CRYSTAL OF THE GOLD-MERCURY MINERAL

		Film 3 Monoclinic a = 4.729(2) (Å) b = 5.243(8) c = 4.546(2) β = 90.90(6)°		Film 3 Pseudo-orthorhombic a = 4.728(3) (Å) b = 5.248(5) c = 4.543(4) β = 90.00°	
Int. (obs.)	hkl	d (Å) (obs.)	d (Å) (calc.)	hkl	d (Å) (obs.)	d (Å) (calc.)
med.	020	2.622	2.622	020	2.622	2.624
v. str.	200	2.368	2.364	200	2.368	2.364
v. wk.	002	2.277	2.273	002	2.277	2.273
med.	$\bar{1}02$	2.059B*	2.061	102	2.059B*	2.047
v. wk.	122	1.597	1.608	122	1.597	1.614
wk.	$\bar{1}03$	1.445	1.4496			
				103	1.445	1.4422
wk.	103	1.436	1.4364			
med.	213	1.237	1.2313	213	1.237	1.2391
med.	400	1.182	1.1822	400	1.182	1.1820
med.	$\bar{5}12$	0.8661B	0.86604	512	0.8661B	0.86111
	$\bar{3}43$		0.84309			
v. str.		0.8393B		343	0.8393B	0.83928
	343		0.83534			

The same lines are indexed as monoclinic and orthorhombic, respectively, using the method of least-squares refinement.
114.6-mm diameter camera, no rotation of crystal. Long axis of apparent crystal perpendicular to axis of X-ray beam.
* B indicates that X-ray line appears unusually broad compared to adjacent X-ray lines.

Electron-Microprobe Data

Initial results of quantitative microprobe analyses (for Au, Hg, and Ag) of about 50 diamond-polished grains of the gold–mercury mineral were thought to be suspect because of unexplainable low totals of about 91–98%; no silver was detectable. Major gold and minor mercury were detected using both quantitative wavelength-dispersion analysis and simultaneous qualitative energy-dispersion analysis. A wavelength-dispersion scan for oxygen was done using hematite as an oxygen standard; no oxygen was detected.

After 48–72 hours of cold polishing with 0.05-μm alumina abrasive, microscopically porous textures were observed in all gold–mercury crystals. Electron-microprobe analysis of these grains likewise gave totals that were significantly lower than 100% (<98%). We attribute the low totals to the porosity, clearly visible at high magnification under a reflected-light microscope. Because of these problems, we have "normalized" the gold and mercury ratios, but the original data (in wt.%) also are given in Table 2. The quantitative electron-microprobe data show some range in the gold–mercury proportions (Table 2) for the 43 analyses of nine grains. Data in Table 2 show that the atomic ratio of gold to mercury ranges from about 7:1 to 16:1; the most common ratio of gold to mercury is 10:1.

Morphology of Grains

The morphological variety displayed by grains of the gold–mercury mineral, including octahedral forms as well as a skeletal form (Fig. 1), and monoclinic, prismatic forms that are hollow and acicular or solid and stubby (Fig. 2), is interesting. The preservation of these delicate shapes precludes mechanical transport. Also, all grains in the low-magnification photomicrograph (Fig. 2, upper left) appear to consist of the gold–mercury mineral, based on semiquantitative energy-dispersion X-ray analysis using the scanning electron microscope.

X-Ray-Diffraction Studies

Initial examination of X-ray powder patterns (114.6-mm Gandolfi camera) of several grains aggregated on a spindle appeared to show the strongest lines of native gold, with other lines that were attributed to contaminating minerals. However, a concentrate of hundreds of grains, obtained by more than 20 hours of settling grains through a pipette containing 20% methanol plus water, permitted an accumulation on a collodion substrate. This concentrate was analyzed with a Phillips automated diffractometer using copper radiation at a scan rate of about 4° 2θ per hour. Results of this scan (Table 3, left side) compared to the X-ray data for pure gold demonstrate why we first thought that the gold–mercury mineral was gold, based on the lines observed in the initial powder-camera patterns.

The clearly resolved set of double peaks, indexed as $\bar{1}02$ and 102, and $\bar{1}03$ and 103, in Table 3, appear only as very broad lines on the powder-camera pattern (Table 4). In the absence of the diffractometer data, the film data could easily be misconstrued to represent reflections of an orthorhombic mineral, as shown on Table 4. The powder-camera film data in Table 4 were obtained from

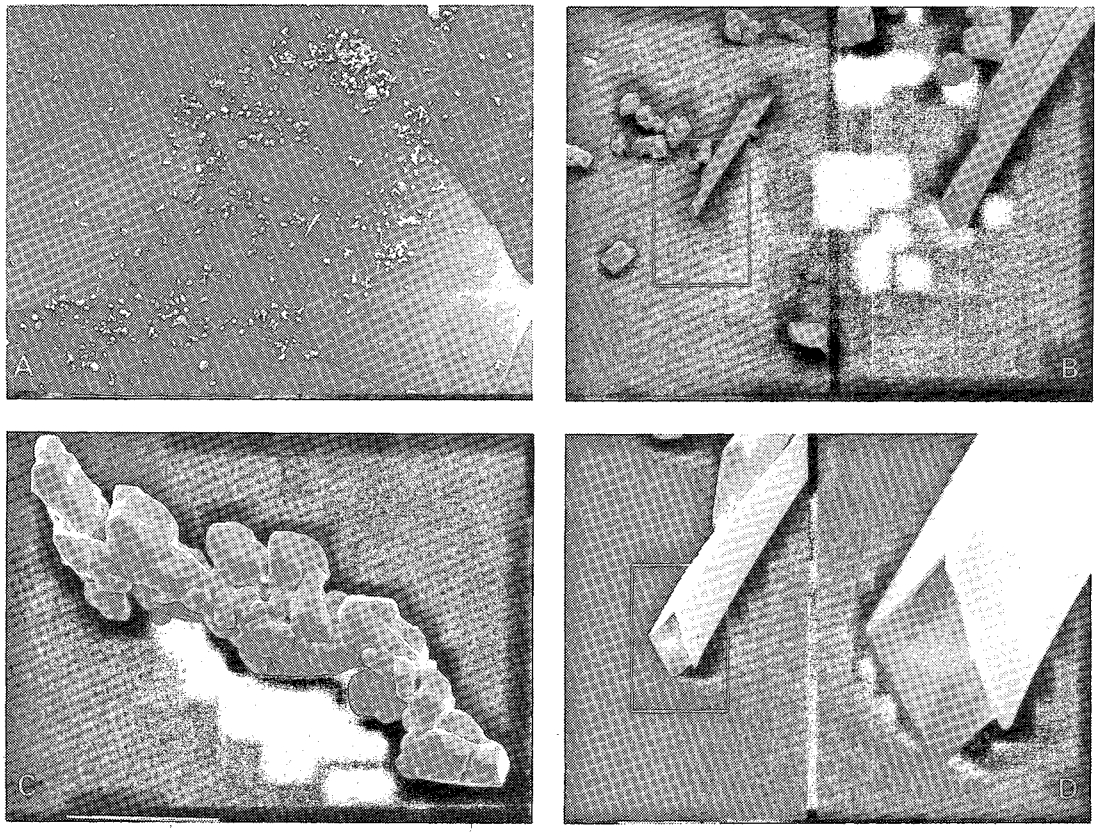

FIG. 2. Scanning electron photomicrographs of a gold–mercury mineral, Snake River alluvium. A. Low-magnification photograph showing numerous grains. The acicular elongate crystal right of center is shown enlarged in B and D. The lower left photograph (C) shows an aggregate of crystals. Scale bar represents 1 mm (A), 100 μm (left side of B), and 20 μm (C, left side of D).

an acicular "crystal" without rotation of the spindle on which it was mounted. Four films were produced from this polycrystalline "crystal" similar to the elongate one shown in the scanning-electron microscope photomicrographs (Fig. 2).

In the absence of single crystals for study by X-ray diffraction, we have indexed the powder patterns to indicate that the gold–mercury mineral is monoclinic with dimensions as given in Tables 3 and 4. Monoclinic indexing is in agreement with the monoclinic habit of the acicular "crystals" shown in Figure 2. The available X-ray data are best indexed according to a monoclinic cell: a 4.729(2), b 5.243(8), c 4.546(2) Å, β 90.90(6)°.

DISCUSSION

This gold–mercury mineral has apparently eluded prior detection chiefly because of the small grain-size, the small mass of individual particles, the unusual composition that prohibits recovery of the particles by amalgamation, and an X-ray-diffraction powder pattern that is superficially similar to but significantly different from that of native gold. We tentatively believe that this monoclinic gold–mercury mineral may be a natural stable phase that formed from the inversion of a crystalline natural metastable phase. It may have originally been a hydrous gold–mercury mineral that became unstable, after initial formation in an aqueous environment, either due to elevated temperature or to dehydration, or to both. This hypothesis would explain the well-crystallized external forms, the porous nature of the crystals that is apparent in polished sections, and the X-ray-diffraction patterns that indicate a microcrystalline nature of atomic ordering into a mineral having lower symmetry than the original metastable mineral.

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