

**A CRYPTICALLY ZONED AMALGAM ($\text{Au}_{1.5-1.9}\text{Ag}_{1.1-1.4}$) $\Sigma_{2.8-3.0}\text{Hg}_{1.0-1.2}$
FROM A PLACER DEPOSIT IN THE TULAMEEN – SIMILKAMEEN RIVER SYSTEM,
BRITISH COLUMBIA, CANADA: NATURAL OR MAN-MADE?**

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ABSTRACT

We describe an unusual pattern of zoning in an amalgam of Au and Ag; it occurs as peripheral zones in a 0.3×0.15 mm grain in a placer deposit associated with the Tulameen – Similkameen river system, British Columbia. This amalgam formed at the expense of primary Au–Ag alloy, which is present as relics in the core: $\text{Au}_{54-55}\text{Ag}_{45-46}$ (Hg-free; not zoned). Abundances of Au gradually increase outward and complement decreasing levels of Ag in the amalgam. Values of Au/Ag increase from 1.1–1.2 in the core to 1.8 at the margin of the grain. The observed range of compositions, $(\text{Au}_{1.50-1.87}\text{Ag}_{1.06-1.40})\Sigma_{2.81-3.00}\text{Hg}_{1.00-1.19}$, is limited. Two possibilities are discussed to explain the formation of the zoned amalgam. (1) This phase could be natural, formed by reaction between primary Au–Ag alloy and a late melt or oxidizing fluid, which may have remobilized and transported Hg as a result of destabilization and oxidation of cinnabar. If so, the observed zonation would reflect an increasing activity of Au species (and decreasing activity of Ag) during crystallization. (2) This phase may have formed under supergene conditions, as a result of anthropogenic introduction of Hg into placer gravels during historic mining operations in this region; we favor this hypothesis. Zoning in the amalgam may have been controlled principally by electrochemical factors related to the process of “self-electrorefining”. Gold is more “noble” than silver, so that ions of Au probably migrated and were preferentially deposited closer to the margin of the grain. This mechanism is similar to that responsible for the “secondary” rim rich in Au (poor in Ag) in placer grains of Au–Ag alloy, as reported from other localities worldwide.

Keywords: zoning, Au, Ag, Hg, amalgam, weishanite, luanheite, placer deposits, British Columbia, Canada.

SOMMAIRE

Nous décrivons une zonation inhabituelle dans la périphérie d'un grain d'amalgame de Au et Ag mesurant 0.3×0.15 mm, découvert dans un placer associé au drainage des rivières Tulameen – Similkameen, en Colombie-Britannique. Cet amalgame s'est formé aux dépens d'un alliage Au–Ag primaire, encore présent sous forme de reliques dans le coeur du grain: $\text{Au}_{54-55}\text{Ag}_{45-46}$ (dépourvu de Hg et non zoné). La concentration en Au augmente graduellement vers la bordure à mesure que le taux d'argent diminue. Les valeurs de Au/Ag augmentent de 1.1–1.2 dans le noyau jusqu'à 1.8 à la bordure du grain. L'intervalle de compositions observé, $(\text{Au}_{1.50-1.87}\text{Ag}_{1.06-1.40})\Sigma_{2.81-3.00}\text{Hg}_{1.00-1.19}$, est limité. Nous évaluons deux hypothèses pour expliquer la formation du grain d'amalgame zoné. (1) Cette phase pourrait être entièrement naturelle, formée par réaction entre un alliage Au–Ag primaire et un bain fondu tardif ou bien une phase fluide oxydante, qui pourrait avoir remobilisé et transporté le mercure suite à la déstabilisation et l'oxydation du cinabre. Si c'est le cas, la zonation observée témoignerait d'une activité croissante de l'or et d'une diminution de l'activité de Ag au cours de la cristallisation. (2) Cette phase pourrait s'être formée sous conditions supergènes, suite à l'introduction anthropogénique de Hg dans le milieu des graviers du placer au cours des opérations minières historiques dans cette région. La zonation dans ce grain d'amalgame pourrait résulter principalement de facteurs électrochimiques liés à un processus “d'autoraffinage électrolytique”. L'or étant plus “noble” que l'argent, les ions Au auraient migré pour être déposés de

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préférence près de la bordure du grain. Ce mécanisme, que nous favorisons, ressemble à celui qui a causé la formation d'un liseré riche en Au et pauvre en Ag dans les grains d'alliage Au–Ag trouvés dans les placers un peu partout dans le monde.

(Traduit par la Rédaction)

Mots-clés: zonation, Au, Ag, Hg, amalgame, weishanite, luanheïte, gisement de type placer, Colombie-Britannique, Canada.

INTRODUCTION

Gold-bearing placers in which Au and Ag are associated with the platinum-group elements have been important producers of noble metals in British Columbia (*e.g.*, Nixon *et al.* 1990, Levson & Giles 1993, Levson & Morison 1995). In this paper, we describe the occurrence and compositional zoning in an unusual amalgam of Au and Ag, formed at the expense of primary Au–Ag alloy and recovered from a placer deposit in the Tulameen – Similkameen river system. We discuss two possible mechanisms of formation, natural and anthropogenic, to account for the development of zoning in this amalgam, which has a stoichiometric composition corresponding closely to the formula (Au,Ag)₃Hg. Its structure remains undetermined; thus a possibility exists that this phase, which is rich in Ag (1.1 < Au/Ag < 1.8), may represent an Au-dominant analogue (unnamed) of luanheite (Ag₃Hg). The zoning observed in this amalgam deserves special attention; the abundance of Au gradually increases toward the rim, antipathetically with Ag. This zonation mimics that of “secondary” rims rich in Au (poor in Ag) reported in placer grains of Au–Ag alloy from various localities (*e.g.*, Desborough 1970, Groen *et al.* 1990, Knight *et al.* 1999, McCready *et al.* 2003). In addition, our study contributes to the characterization of a broad variety of compositional zoning in ore minerals and compounds (*e.g.*, Craig & Solberg 1999).

SAMPLE DESCRIPTION AND ANALYTICAL PROCEDURE

The grain of Au–Ag amalgam, found in a heavy-mineral concentrate in sample VLE–2001–95a, was collected from the Similkameen River in southern British Columbia, approximately 15 km above its confluence with the Tulameen River near the town of Princeton. The sample was obtained from the uppermost meter of a modern river bar overlying bedrock, downstream of a steep, narrow channel. River gravels in the placer area are typically one to two meters deep, and are locally overlain by fine sands and muds. These gravels contain variably rounded pebble- to cobble-size clasts set in a sandy matrix, and are commonly iron-stained and poorly stratified. The placer sample comprises a black to dark brown, well-sorted, non-magnetic, fine sand composed of abundant mafic minerals, including olivine, garnet, magnetite, pyrite, chalcocopyrite, chromite, and accessory Au–Ag and Pt–Fe–(Cu) alloys. Interestingly, grains of Au–Ag alloy weighing up to

about 0.25 g and Pt–Fe alloy up to 0.1 g also occur in this placer.

The sample of placer concentrate was processed by Overburden Drilling Management Limited, Ottawa, Ontario. The zoned grain was mounted in epoxy and analyzed along a traverse with a step interval of 2 μm using a JEOL JXA–8900 electron microprobe at McGill University. Operating conditions employed wavelength-dispersion spectrometry mode (WDS) at 20 kV and 30 nA and a focused beam (<2 μm). The following standards were used: synthetic Au₆₀Ag₄₀ and HgS (AuMα, AgLα, and HgLα), and pure Cu, Fe, Ni, Pd and Pt (CuLα, FeKα, NiKα, PdLα, and PtMα). A CITZAF on-line data-reduction procedure was applied. No corrections were made for potential “loss” of Hg during analysis (Kucha 1986, pers. commun., 2008). However, any migration of Hg in response to heating by the electron beam is believed to be systematic, as analytical conditions and counting times on unknowns and well-characterized standards were kept identical.

TEXTURE, COMPOSITION AND ZONING

The Au–Ag–Hg amalgam occurs as a broad peripheral zone in an elongate grain (*ca.* 0.3 × 0.15 mm; Figs. 1A–D). This amalgam is notably porous, with abundant microcavities, and has “corroded” boundaries with relics of a primary, Hg-free Au–Ag alloy in the core. The Au:Ag ratio varies slightly in the core: 1.1–1.2 (Figs. 2A, B; Tables 1, 2). The principal components of the amalgam are Au, Ag and Hg. The abundances of the minor elements Cu, Fe, Ni, Pd, and Pt are close to or below the limit of detection in both the primary Au–Ag alloy and the secondary amalgam phase (Tables 1, 2).

In contrast to the core of Au–Ag alloy, the amalgam phase is strongly zoned and shows a systematic and gradual increase in Au (and corresponding decrease in Ag) toward the margin, where the Au:Ag ratio attains a maximum: 1.8 (Figs. 2A, B). The abundance of Au correlates negatively with Ag (*R* = –0.84, based on forty-three point-analyses of the amalgam). The content of Hg in the amalgam varies little (25–29 at.%), and the ratio ΣMe/Hg varies between *ca.* 2.5 and 3. Interestingly, narrow microzones seem to exist in the amalgam near its contact with the core of Au–Ag alloy. Values of ΣMe/Hg tend to be closer to the ideal stoichiometry of 3 in these microzones, which likely reflect diffusion of Au and Ag from the alloy into the amalgam (Table 2). The mean composition of the amalgam is Au 47.39 wt.%, Ag 19.28 wt.%, Hg 32.78 wt.%, for a total 99.45 wt.%.

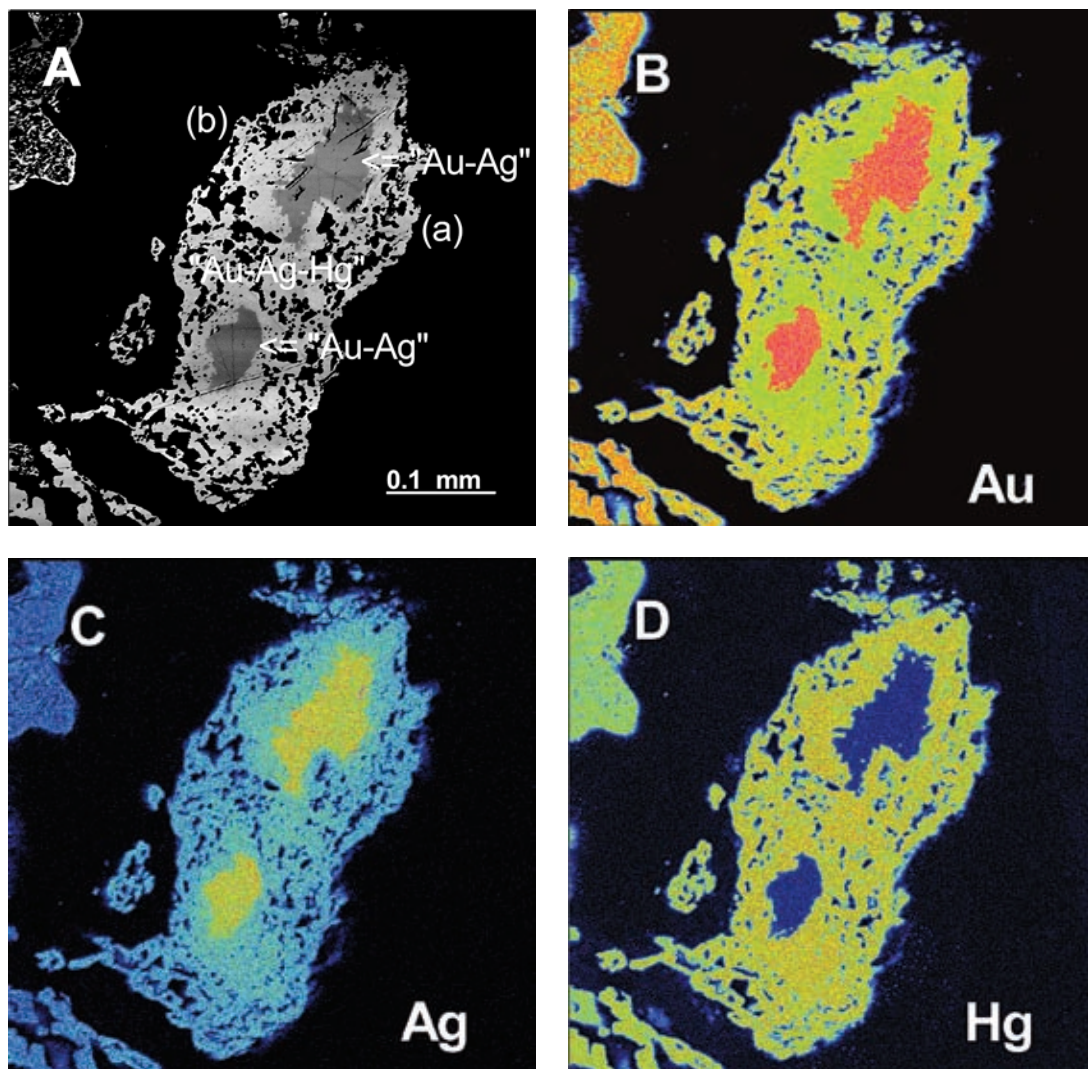


FIG. 1. Back-scattered electron image (A) and complementary color X-ray maps showing the distribution of Au (B), Ag (C), and Hg (D) in the composite grain of Au–Ag alloy (labeled “Au–Ag”: relics in the core) and zoned amalgam (labeled “Au–Ag–Hg”: peripheral zones). The concentration of an element decreases in the following order: red, orange, yellow, green, blue and violet.

which corresponds to $(\text{Au}_{1.65}\text{Ag}_{1.23})_{\Sigma 2.88}\text{Hg}_{1.12}$ ($n = 43$), *i.e.*, close to ideal $(\text{Au},\text{Ag})_3\text{Hg}$. The overall variations based on a total of four atoms per formula unit, *apfu*, are $(\text{Au}_{1.50-1.87}\text{Ag}_{1.06-1.40})_{\Sigma 2.81-3.00}\text{Hg}_{1.00-1.19}$.

COMPARISON WITH RELATED MINERALS AND PHASES

There are two mineral species approved by the IMA, weishanite and luanheite, ideally $(\text{Au},\text{Ag})_3\text{Hg}$ and Ag_3Hg , respectively, which are related to the compound $(\text{Au},\text{Ag})_3\text{Hg}$ in our placer. Weishanite was first discov-

ered *in situ* in a mineralized and silicified zone in biotite granulite from the Poshan district, Henan, China; it is hexagonal (a 2.93, c 4.82 Å; $Z = 2$), similar to synthetic Au_3Hg (Li *et al.* 1984). However, in contrast to our phase, the sample of type-locality weishanite is poor in Ag (3.2 wt.%). The type-locality specimen of luanheite was found in intergrowth with Hg-bearing silver and silicate minerals in a gold placer at Hebei, China. Its composition is close to stoichiometric Ag_3Hg , free of Au, and has a hexagonal symmetry (a 6.61, c 10.98 Å;

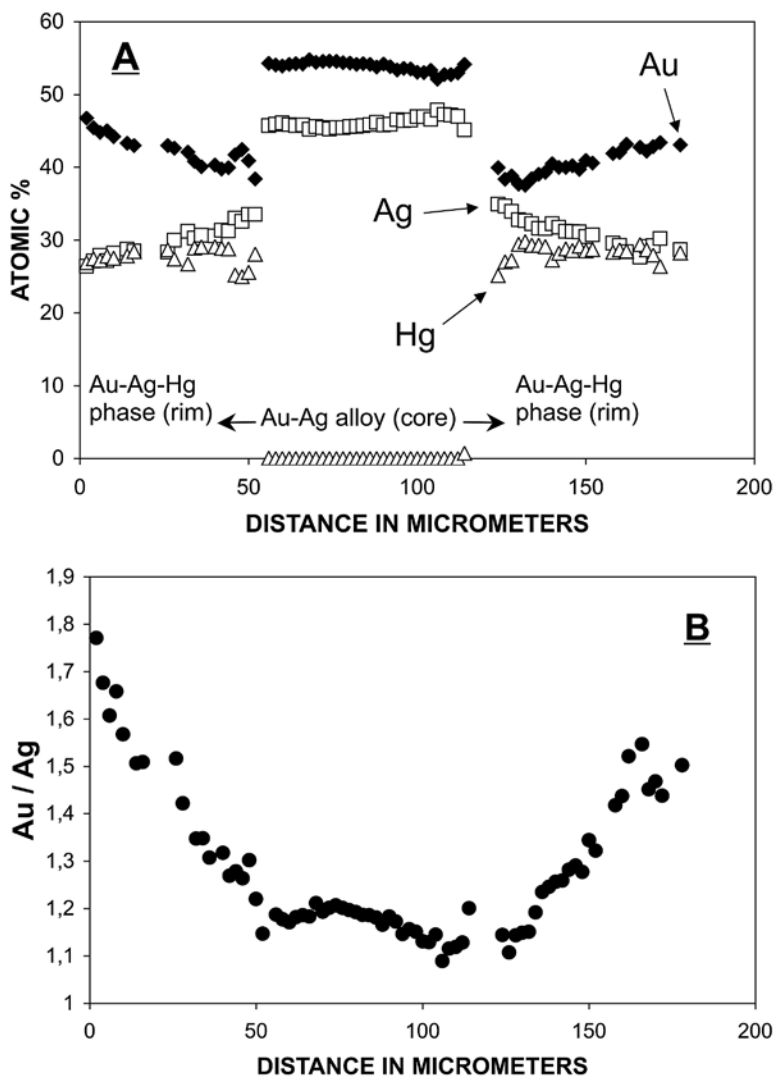


FIG. 2. Compositional variations observed in the composite grain of Au–Ag alloy (*i.e.*, relics in the core) and zoned amalgam (*i.e.*, peripheral zones). Results of point-analyses (WDS; atom %) done along an EMP traverse across the grain (point “a” to “b”: Fig. 1A) using a step interval of 2 μm are plotted *versus* distance (μm). Results with low analytical totals, caused by the porosity of the amalgam, are omitted. The symbols are: A) filled diamonds: Au, open squares: Ag, open triangles: Hg; in B) the filled circles indicate the Au:Ag ratio.

Z = 6; Shao *et al.* 1984). Thus, weishanite and luanheite are structurally related, although not isostructural.

Au–Ag–Hg compounds formed by natural processes

In the literature, there are numerous examples of compounds in the system Au–Ag–Hg that likely are of

natural origin, *e.g.*, phases of Au, Ag and Hg, in association with minerals of Pd and Pt in the Zechstein formations of the pre-Sudetic monocline, Poland (Kucha 1976). Basu *et al.* (1981) reported a ternary compound, $\text{Ag}_{74}\text{Au}_{16}\text{Hg}_9$, from the Rajpura–Dariba mine, Rajasthan, India. Baptista & Baptista (1987) described hexagonal prismatic crystals and microcrystalline

aggregates of unnamed Au₃Hg with *a* equal to 2.951 and *c* equal to 4.810 Å from Sumidouro de Mariana, Minas Gerais, Brazil. The latter locality also provides other examples of various phases rich in Hg (Fleet *et al.* 2002, and references therein). The phase Au₃Hg was also documented in association with Au–Ag alloy in zones of sulfide-rich mineralization in feldspathic metasomatic rocks in the Ukrainian Shield (Nechaev *et al.* 1986). A phase of composition Au₄₅Ag₄₅Hg₁₀ occurs in a volcanogenic sulfide deposit at Laangsele, Sweden (Nysten 1986). Elevated abundances of Hg (up to 5.9 at.%) have been documented in particles of gold from the Witwatersrand placer deposits, South Africa, and likely reflect mobilization of Hg from surrounding sediments and amalgamation as a result of metamorphism (Oberthür & Saager 1986, Erasmus *et al.* 1987). Mercury-bearing gold (up to 7.7 at.% Hg) was deposited owing to a low activity of sulfur in the Tsugu Au–Sb vein deposit, Japan (Shikazono & Shimizu 1988). Interestingly, about 93% of the Au is present in the form of micrograins in a Au–Ag–Hg phase from a volcanogenic massive sulfide ore at Trout Lake, Flin Flon, Manitoba (Healy & Petruk 1990). In addition, Desborough & Foord (1992) described micrograins of a mineral Au_{88–94}Hg_{6–12} from the Pleistocene Snake River alluvial deposits, southeastern Idaho. Also, Au–Ag–Hg

compounds are present in association with Cu–Zn–Pb–Bi–Sb–As-rich assemblages within fractures in pyrite ores in Cu-rich breccia in the Migollas deposit, Spain (Velasco *et al.* 1999) and in the Otago Schist quartz-vein deposits, New Zealand (Mackenzie & Craw 2005).

It is known that Au and Hg may well accompany each other in various late-stage hydrothermal environments *e.g.*, in listwanite, a mineralized carbonated serpentinite (Hansen *et al.* 2005). Also, Au, Ag and Hg may be intimately associated with Pd and Pt in low-temperature deposits of hydrothermal origin (*e.g.*, Tarbaev *et al.* 1996, Fleet *et al.* 2002, Nickel 2002). Interestingly, examples of Hg-bearing precious-metal-rich grains precipitated under supergene conditions from oxidizing saline fluids are found in south Devon, England (Leake *et al.* 1991).

Occurrences of man-made compounds of Au, Ag and Hg

In contrast to the Au–Ag–Hg compounds of natural origin, Au₃Hg and other phases of Au–Ag amalgam may have formed by the interaction of placer grains of Au–Ag alloys with liquid mercury introduced during mining operations. Examples of Au–Ag–Hg phases of presumably artificial origin were reported from Jamison Creek, California (Foster *et al.* 1978). Callahan *et al.* (1994) reported the presence of surficial spots rich in Hg (44.8%) on gold grains in the vicinity of old gold

TABLE 1. REPRESENTATIVE COMPOSITIONS ALONG A TRAVERSE ACROSS THE Au–Ag–(Hg) PLACER GRAIN

No.	Distance in µm	Cu	Ag	Au	Fe	Ni	Hg	Total
1	2	0	16.34	52.85	0.01	0	30.95	100.15
2	4	0	16.78	51.37	0	0	31.55	99.70
3	6	0.04	17.33	50.85	0	0	31.44	99.66
4	10	0	17.51	50.12	0.01	0	31.79	99.43
5	16	0.02	17.72	48.84	0	0.01	32.90	99.49
6	26	0.01	17.60	48.74	0.01	0	33.11	99.46
7	28	0	18.86	48.96	0	0	32.07	99.89
8	36	0.06	19.27	46.00	0.01	0	33.99	99.33
9	40	0	19.14	46.05	0	0	33.88	99.07
10	42	0	20.02	46.39	0	0	34.30	100.71
11	44	0	19.69	45.97	0.01	0.02	33.76	99.45
12	46	0	21.06	48.60	0	0	29.91	99.57
13	48	0.01	20.77	49.39	0	0	29.60	99.77
14	56	0	31.26	67.79	0	0.02	0.04	99.11
15	64	0.02	31.47	68.14	0	0.02	0	99.65
16	72	0	31.24	68.52	0	0.03	0	99.79
17	80	0.03	31.45	68.50	0	0	0	99.98
18	88	0.02	31.96	68.04	0.01	0.01	0	100.03
19	96	0	32.27	68.14	0.02	0.02	0	100.45
20	104	0.04	32.46	67.87	0	0	0	100.37
21	124	0	22.74	47.51	0	0	30.42	100.67
22	134	0	20.56	44.75	0.01	0	34.71	100.03
23	136	0.03	20.10	45.33	0	0.02	34.64	100.12
24	138	0.01	20.09	45.71	0.02	0.01	34.45	100.29
25	142	0.03	20.27	46.61	0.01	0	33.48	100.39
26	144	0.02	19.92	46.64	0	0	34.19	100.77
27	146	0.02	19.84	46.77	0.02	0.01	33.86	100.52
28	148	0	19.85	46.29	0	0	34.57	100.71
29	150	0.02	19.38	47.58	0.01	0	33.72	100.71
30	152	0	19.32	46.66	0	0.01	33.58	99.57
31	158	0.07	18.56	48.05	0	0	33.07	99.75
32	160	0	18.45	48.41	0	0	33.63	100.49
33	162	0	17.85	49.58	0.01	0	33.30	100.74
34	166	0.07	17.30	48.86	0	0	34.22	100.45

Analytical results (WDS electron-microprobe analyses) are expressed in weight % for a traverse across the composite placer grain (point "a" to "b" in Fig. 1A). Zero indicates a concentration below the detection limits.

TABLE 2. PROPORTIONS OF Au, Ag AND Hg IN THE COMPOSITE GRAIN

No.	Au	Ag	Cu	ΣMe	Hg	ΣMe/Hg	Au/Ag
1	46.74	26.39	0	73.12	26.88	2.72	1.77
2	45.46	27.12	0	72.58	27.42	2.65	1.68
3	44.81	27.89	0.10	72.79	27.21	2.68	1.61
4	44.23	28.22	0	72.45	27.55	2.63	1.57
5	43.01	28.49	0.05	71.55	28.45	2.52	1.51
6	42.98	28.34	0.01	71.33	28.67	2.49	1.52
7	42.62	29.98	0	72.59	27.41	2.65	1.42
8	40.09	30.67	0.16	70.91	29.09	2.44	1.31
9	40.30	30.59	0	70.89	29.11	2.43	1.32
10	39.78	31.34	0	71.12	28.88	2.46	1.27
11	39.95	31.24	0	71.19	28.81	2.47	1.28
12	41.74	33.03	0	74.77	25.23	2.96	1.26
13	42.43	32.58	0.02	75.03	24.97	3.00	1.30
14	54.27	45.70	0	99.97	0.03	-	1.19
15	54.22	45.72	0.06	100	0	-	1.19
16	54.57	45.43	0	100	0	-	1.20
17	54.35	45.57	0.08	100	0	-	1.19
18	53.81	46.15	0.04	100	0	-	1.17
19	53.63	46.37	0	100	0	-	1.16
20	53.34	46.58	0.09	100	0	-	1.15
21	39.96	34.92	0	74.88	25.12	2.98	1.14
22	38.45	32.26	0	70.71	29.29	2.41	1.19
23	39.03	31.60	0.08	70.71	29.29	2.41	1.24
24	39.32	31.55	0.03	70.90	29.10	2.44	1.25
25	39.98	31.75	0.07	71.80	28.20	2.55	1.28
26	39.99	31.18	0.05	71.22	28.78	2.47	1.26
27	40.21	31.15	0.05	71.41	28.59	2.50	1.29
28	39.74	31.12	0	70.86	29.14	2.43	1.28
29	40.96	30.47	0.06	71.49	28.51	2.51	1.34
30	40.61	30.70	0	71.31	28.69	2.48	1.32
31	41.92	29.57	0.19	71.67	28.33	2.53	1.42
32	42.05	29.26	0	71.32	28.68	2.49	1.44
33	43.16	28.37	0	71.53	28.47	2.51	1.52
34	42.76	27.65	0.18	70.59	29.41	2.40	1.55

Atomic proportions (atom %) for compositions given in Table 1.

operations in North Carolina. Indeed, mercury has been used in gold and silver mining since Roman times. Therefore, grains of artificial amalgam of Au and Ag were likely formed as a result of the ancient or medieval use of mercury in gold mining and metallurgy (*e.g.*, Zwahr & Ulrich 1999).

AU-RICH RIMS ON PLACER GRAINS OF AU-AG ALLOY

The observed enrichment in Au at the margin in the zoned amalgam, which is relatively poor in Ag (Fig. 2), is generally similar to patterns of zoning in grains of Au–Ag alloy from placers worldwide. For example, about 5% of grains of Au–Ag alloy in placers of Alberta are coated with “secondary” Au–Ag alloy rich in Au (Giusti 1986). There are different models to explain the development of such a rim rich in Au and poor in Ag. Desborough (1970) suggested that the greater solubility and ease of oxidation of Ag in grains of Au–Ag alloy in the placer environment lead to the observed depletion of Ag from the border of these grains. This type of mechanism is mentioned by many investigators. For example, Knight *et al.* (1999) inferred that the Au-rich rim is formed by removal of Ag, Hg, and Cu, rather than by precipitation of Au. No evidence was found for the removal of Hg in the Au–Ag amalgam analyzed in this study (Fig. 2A). The importance of the addition of Au also was noted (*e.g.*, McCready *et al.* 2003). Groen *et al.* (1990) inferred that self-electrorefining of placer grains is the likely process in the formation of a Au-rich rim as a result of the precipitation of Au from the surrounding solution, possibly involving different ligands (*e.g.*, CN^- , OH^- , NH_3 , Cl^- , I^- , Br^- , and HS^-) in transporting Au in stream environments. The formation of a rim depleted in the less noble metal may thus result from an electrochemical process leading to oxidative dissolution of the less noble metals (*e.g.*, Müller 1995). The precipitation of gold likely involves the reduction of ions of Au^+ or Au^{3+} , which is accompanied by the oxidation of Fe^{2+} to Fe^{3+} , as implied by the association of “secondary” gold with oxyhydroxides of Fe (Mann 1984). Thermodynamic data show that the silver component is relatively unstable in most weathering environments, leading to an enrichment in Au of a supergene Au–Ag alloy (*i.e.*, secondary) and detrital (or authigenic) Au–Ag alloy from modern placers (Krupp & Weiser 1992). Evidence for a supergene remobilization of both Au and Ag in Au–Ag alloy was reported from the Morning Star deposit, California (Sheets *et al.* 1995). Another hypothesis involves a bacteria-induced recrystallization of primary Au–Ag alloy (*e.g.*, Marakushev *et al.* 1989), which is corroborated by the presence of S- and P-rich compounds, possibly of organic origin, located on the outer surface (*i.e.*, the phase richer in Au) of Au–Ag nuggets from Yukon (Southam 1998).

Interestingly, a natural hydroxide of Au, $\text{AuO}(\text{OH}, \text{Cl})$ having a NaCl-type structure, occurs as a film on grains

of native gold from placers in the southern Urals (Novgorodova *et al.* 1995). Aggregates of Au–Ag-rich amalgam were reported from alluvial sands, Palakharya River, Bulgaria; they show the following core-to-rim zones: $(\text{Au}, \text{Ag}) \rightarrow (\text{Au}, \text{Ag}, \text{Hg}) \rightarrow (\text{Au}, \text{Ag})_3\text{Hg} \rightarrow (\text{Au}, \text{Ag})_2\text{Hg} \rightarrow (\text{Au}, \text{Ag})_3\text{Hg}_2 \rightarrow (\text{Au}, \text{Ag})\text{Hg}$, which exhibit a general increase in Hg outward (Atanasov & Jordanov 1983). In contrast, the level of Hg shows little variation in the zoned amalgam from British Columbia (Fig. 2A, Tables 1, 2).

DISCUSSION

Mechanism of formation of zoned $(\text{Au}, \text{Ag})_3\text{Hg}$: a natural origin?

Because of the existence of amalgams of Au and Ag in nature, a natural origin may be considered for the zoned phase of $(\text{Au}, \text{Ag})_3\text{Hg}$ from British Columbia. This phase is clearly secondary and formed at the expense of primary Au–Ag alloy, which is preserved as relics in the core of the placer grain (Figs. 1A, 2A, Tables 1, 2). This may have involved interaction with a late melt or an oxidizing fluid. The likely reaction is $3(\text{Au}_{1/2}\text{Ag}_{1/2}) + \text{Hg} \rightarrow (\text{Au}, \text{Ag})_3\text{Hg}$; it is possible that cinnabar oxidized to mercury *via* the reaction $\text{HgS} + \text{O}_2 \rightarrow \text{Hg} + \text{SO}_2$ to provide a source for the Hg. The observed zonation may reflect increasing activity of the Au species (and decreasing activity of Ag) during crystallization. A low temperature of crystallization is indicated by the fact that Au_3Hg melts incongruently at 420°C to $\alpha\text{-(Au-Hg)} + L$ in the system Au–Hg at 1 atm (Plaksin 1938).

As noted above, the rimward increase in Au and decrease in Ag (Figs. 2A, B) resembles the characteristic patterns described in grains of Au–Ag alloy from placers worldwide. These patterns of zoning in placer grains differ from those in Au–Ag–Hg-rich grains found *in situ* in volcanogenic sulfide ores at Flin Flon, Manitoba, which exhibit a sequence of increasingly Ag-rich compounds, implying an increase in the activity of bisulfide complexes of Ag (Healy & Petruk 1990). Grains of Au–Ag alloy from the Palai–Islica epithermal deposit, Spain, are also characterized by Ag enrichment in peripheral zones (Carrillo Rosua *et al.* 2002).

Zoned $(\text{Au}, \text{Ag})_3\text{Hg}$: a man-made origin is preferred

An artificial origin with an anthropogenic source for the Hg is a likely and preferred alternative hypothesis for the origin of the zoned amalgam, because historic gold mining employing amalgamation as a major technique for gold refining is known to have occurred in this region of British Columbia. Thus, the secondary phase $(\text{Au}, \text{Ag})_3\text{Hg}$ may have formed under supergene conditions as a result of introduction of Hg into the streams. This mode of formation is consistent with the synthesis of phases rich in Hg (AuHg_2 , Au_2Hg_3 , and Au_5Hg_8) by

a solid-state reaction with mercury at room temperature. The synthesis of phases richer in Au, such as Au₃Hg or Au₅Hg, may involve annealing of the Hg-rich amalgams (Aramyan *et al.* 1972).

By analogy with the rims of “secondary” gold in Au–Ag alloy, we hypothesize that the zonation in the analyzed amalgam was principally controlled by electrochemical factors related with the process of “self-electrorefining” of the phase produced by reaction of primary Au–Ag alloy with liquid Hg in the supergene environment. This zonation is probably not due to amalgamation of pre-existing peripheral zones in a placer grain of Au–Ag alloy because the relics of the Au–Ag alloy are not zoned; indeed, only the amalgam is zoned in this grain (Fig. 2). Furthermore, if dissolution of pre-existing zones accompanied amalgamation, we might expect some zonation; however, the observed pattern is notably regular, without signs of dissolution (Fig. 2). These observations suggest that this zoning formed during or immediately after amalgamation, rather than prior to amalgamation.

The crystallization history of the zoned grain presumably began in the placer gravels, where a grain of the Au_{54–55}Ag_{45–46} alloy came into contact with liquid mercury spilled during a mining operation. During reaction of the Au–Ag alloy with mercury in the supergene environment, ions of Au and Ag dissolved relatively homogeneously in a microvolume of solution saturated in Hg⁰, thereby transforming the original Au–Ag alloy into the amalgam. The porous nature of the amalgam may reflect the presence of inclusions of aqueous solution. The observed zoning may have formed by migration of ions of Au and Ag in opposite directions through the Hg-based solution, which acted as an electrolyte. Gold is more “noble” than silver, and Au is lower than Ag in the electrochemical series, so that Au migrated and was preferentially deposited closer to the rim, analogous to the process of forming an Au-rich rim in placer grains of Au–Ag alloy (*e.g.*, Groen *et al.* 1990).

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