

**GOLD-ENRICHED RIMS ON PLACER GOLD GRAINS:  
AN EVALUATION OF FORMATIONAL PROCESSES**

by  
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Blacksburg, Virginia

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(ABSTRACT)

Placer gold is frequently reported to assay at overall higher values of fineness than the gold in the rock from which it was liberated. A related phenomenon is the historical discovery of many extremely large gold nuggets (up to 28 lbs) in the southeastern United States that have no apparent source rock. Placer gold grains from the southeastern United States have been examined and found to frequently exhibit the development of nearly pure to pure gold rims around their borders. These gold rims are suggested as a possible cause of the high fineness placer deposits. Formation of very thick rims may also be the cause of the large nuggets. Formation of these gold-enriched rims by the often attributed mechanism of simple silver leaching is disputed on the basis of ineffective mechanisms for the removal of silver from the alloy. Diffusion of silver through the gold at low temperatures proceeds far too slowly to produce the chemical gradients observed in the placer gold grains. Comparison of the complexation capacities of 41 ligands with subsequent modelling of expected complex concentrations in natural stream and stream sediment waters indicates  $\text{CN}^-$  and  $\text{S}^{2-}$  as the most likely functional ligands for the transport and redeposition of supergene gold. Electrolytic refining of placer Au-Ag grains is also a process for forming gold-enriched rims that can operate together with secondary enrichment to produce the observed phenomena.

## ACKNOWLEDGMENTS

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## INTRODUCTION

Since before recorded history gold has been the most prized of mineral possessions. It has long represented power and wealth and has thus served as the impetus for many of man's great explorations and adventures. Because of its great value, economic concentrations of gold which are commonly 1-3 ppm can be physically small in size and can contain gold so dispersed that they are difficult to locate and recognize. Consequently, most of the great gold rushes of history, and indeed many of the discoveries made today, result not from initial location of the primary gold-bearing deposits, but rather from the detection and recovery of placer gold grains that have eroded from their original source rocks and been transported by rivers and streams. In many areas, it has been only the placer deposits that have proven economical to exploit. Commonly stated, but rarely written (Wilson 1984), are observations that the gold grains in placer deposits are frequently much larger than those in the lodes from which the placers were derived. The following is an example of such an account.

In 1799, twelve year old Conrad Reed was bow fishing with his younger sister and brother when he spotted and retrieved a shiny, metallic object from the stream. This curious 7.6 kg (16.7 lb) stone served his family as a doorstep for nearly three years until the day Conrad's father, John, took it to a jeweler at the market in nearby Fayetteville, NC. The jeweler told Mr. Reed that his doorstep was a large gold nugget. Not being familiar with the value of gold, Mr. Reed thought he made a profitable sale as he walked away from the jeweler with three dollars and fifty cents (true 1802 value being \$4000 to \$4722, depending on the purity). Returning to his property, John started looking for more of the "valuable stones" along a one-mile stretch of the stream and soon found numerous nuggets totalling up to at least 69.5 kg (153 lb), the largest recorded nugget

weighing an awesome 12.7 kg (28 lb) (Crayon 1857) .

The onset of surface mining on the Reed property thus represented the first commercial gold production of the fledgling United States of America. This story actually contains some very important scientific information, in addition to its historical interest. When lode mining commenced on the Reed property, the primary gold was found to occur not as large grains, but rather as a myriad of fine, disseminated grains. This discovery suggests that some process converted the small lode gold grains to large placer nuggets.

Both lode and placer gold grains, or nuggets, are rarely pure gold. They invariably contain significant amounts of silver, and more rarely noteworthy amounts of copper (Stumpfl & Clark 1965), palladium (Harrison & Fuller 1987), selenium (DiLabio et al. 1985), mercury (Nysten 1986), and 45 or more other elements including: Fe, Pb, Pt, Bi, Cd, Ni, Te, As, Sb, Rh, and Al (Erasmus et al. 1987). Gold which contains more than approximately 20% silver is often referred to as electrum, but there is considerable variation in this arbitrarily set composition, so for this study "electrum" will be used more as a qualitative term, simply emphasizing the fact that silver is present in the alloy. Craig & Rimstidt (1985), compiled analyses of nearly 6500 (now over 7000) natural gold samples and found virtually all the samples ranged from 500 to 1000 fine with the mode at approximately 920 fine (fineness is the weight percent of gold in an alloy divided by the weight percent of gold plus silver). Several researchers (Mackay 1944, Fisher 1945, Koshman & Yugay 1972, Mann 1984) have made the observation that placer gold often assays at a higher fineness than the gold from the source lode. This phenomena has been properly attributed by Fisher (1945) and Koshman & Yugay (1972) to the occurrence of gold-enriched rims on the surface of placer grains of which there are numerous published examples (Stumpfl and Clark 1965, Desborough 1970, Mann 1984).

The present study examines the nature of placer gold grains from some southeastern United States localities and attempts to evaluate the processes that may contribute to the formation of large nuggets and gold-enriched rims. Specific topics discussed include: (1) the results of a light microscopic and scanning electron microscopic study of the surface morphologies of gold grains from the southeastern United States, (2) data on the chemical heterogeneity/homogeneity of the same gold grains as determined by standard reflected light microscopy and electron microprobe analysis of polished sections through the gold grains, (3) an evaluation of previously proposed mechanisms of the genesis of large nuggets and the formation of gold-enriched rims in light of the newly obtained data.

In as much as the processes active in the study area are representative of those operating in other localities, the conclusions of this study are believed to have general applicability.

## SAMPLE LOCALITIES

The samples examined in this study were obtained from numerous localities in the southeastern United States (Fig. 1), an area with a moist, temperate climate and an eastern deciduous hardwood forest vegetation type. Extensive weathering has occurred due to longstanding subaerial exposure and a current annual precipitation of 100-200 cm (40-80 in). These environmental conditions subject the gold grains to substantial chemical attack with local variations manifested in differing water and gold chemistries, and human influences. Specific investigative emphasis was placed upon the gold from the Brush Creek area of southwestern Virginia.

Brush Creek flows through Floyd and Montgomery Counties along the south flank of Pilot Mountain before emptying into the Little River. Two potential sources of the gold are the Precambrian granitic gneisses of the Little River Formation, and numerous sulfide-bearing quartz veins which cut the gneisses (Fontaine 1882, Craig et al. 1980). The Little River Formation has been extensively sheared by the Fries Fault which runs through the gold bearing area. The quartz veins range in size from minute stringers to massive veins a meter in thickness and up to a kilometer in length. At least two other small streams in the area are known to contain gold - Laurel Creek and Black Creek - indicating outcrops of auriferous rocks to the south of Pilot Mountain and on Laurel Ridge. The best known and richest gold occurrences are in the headwater region of Brush Creek. Brush Creek extends approximately 27 km (17 mi) and the current investigation has demonstrated the existence of gold over the lower 19 km (12 mi) of the creek. The samples recovered during this study were thus examined in part to determine the effects of transport distance on gold grain morphology and chemistry.

Gold was first discovered in the area by J. M. Thomas in the summer of 1879

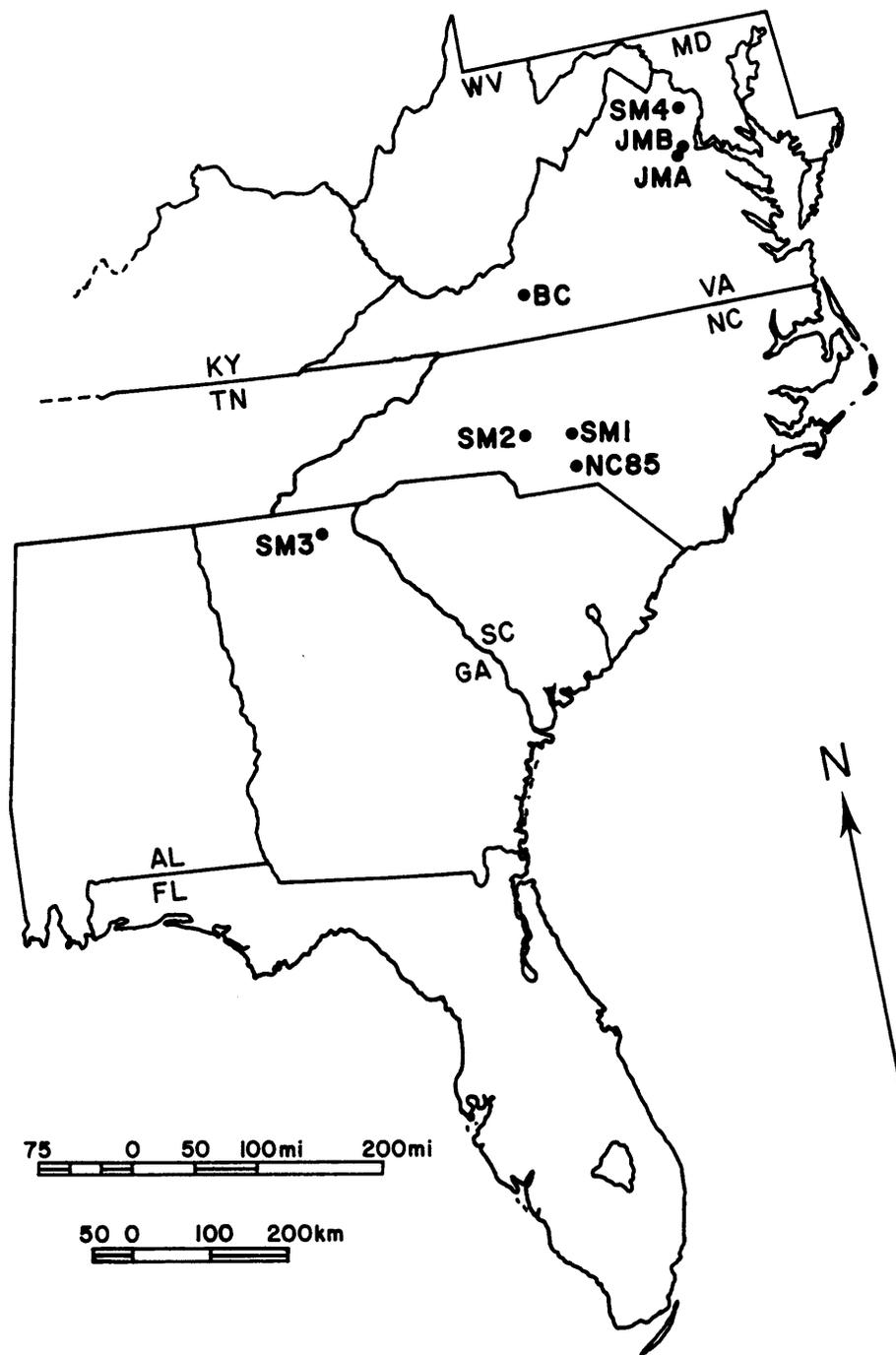


FIG. 1. Sample localities of examined gold grains: BC = Brush Creek, VA; NC85 = Lilesville quadrangle, NC; JMA = Chancellorsville quadrangle, VA; JMB = Storck quadrangle, VA; SM1 = Montgomery County, NC; SM2 = Cabarrus County, NC; SM3 = White County, GA; SM4 = Manassas quadrangle, VA.

(Hotchkiss 1880). A small gold rush commenced but it was soon discovered that there were no fortunes to be made, so interest quickly diminished. A few individuals, however, worked the area intermittently by both placer and stamp mill methods until the 1940's. It has been estimated that about 1500 ounces of gold have been recovered from the area since its discovery (Dietrich 1959, Luttrell 1966).

## METHODS

The majority of gold grains investigated in this study were recovered from stream sediments by standard panning procedures (Theobald 1957), and cleaned if necessary under a microscope in the laboratory. The samples were photographed, weighed, and examined using a scanning electron microscope. The density of the larger grains was measured using a Berman balance or a pycnometer. The grains were then mounted in epoxy and polished (some were also etched), inspected and photographed in reflected light, and analyzed with an electron microprobe.

### *Recovery Methods*

A riffled "Garrett Gravity Trap" gold pan was used to recover most of the gold samples for this study. Gold-bearing gravels, sands, and clays were dug from stream channels and sieved using a 6 mm mesh steel screen to facilitate faster separation of the coarse debris. Individual gold grains were retrieved either directly on site or from microscopically examined heavy mineral concentrates which had been returned to the laboratory. Many grains display silver to gray colored areas, resulting from mercury contamination. This contamination effect will be discussed below. The samples examined are detailed in Tables 1 and 2.

### *Analytical Methods*

Many of the placer gold grains were weighed with a Mettler H20 analytical balance with an accuracy of  $\pm 0.02$  milligrams. Density determinations were performed on all gold grains that appeared to be free of foreign inclusions and that weighed at least 15 mg. A Berman balance was used to measure the density of the grains weighing less than 100

mg and a pycnometer was used for all grains weighing over 100 mg. The overall accuracy of the Berman balance and pycnometer density determinations was approximately  $\pm 0.25 \text{ g/cm}^3$  for the average grain weight handled by each method. The fluid used for both the Berman balance and pycnometer density determinations was distilled, deionized water, treated with a surfactant to reduce surface tension and to increase its wetting properties.

Scanning electron microscopic work was done using a JEOL JSM 35C instrument at an operating voltage of 15 kV. All reflected light observations and photographs were made on a Leitz Orthoplan Polarizing Microscope at magnifications of 60x to 1000x.

Chemical analyses were performed using an ARL-SEM-Q electron microprobe, operated at 15 kV and 20 nA with counting times of 40 seconds on peak and 20 seconds on either side of the peak for background corrections. The following characteristic X-ray lines were used:  $\text{AuM}\alpha$ ,  $\text{AgL}\alpha$ ,  $\text{HgM}\beta$ , and  $\text{CuK}\alpha$ .

## RESULTS

### *Morphological and Textural Characteristics*

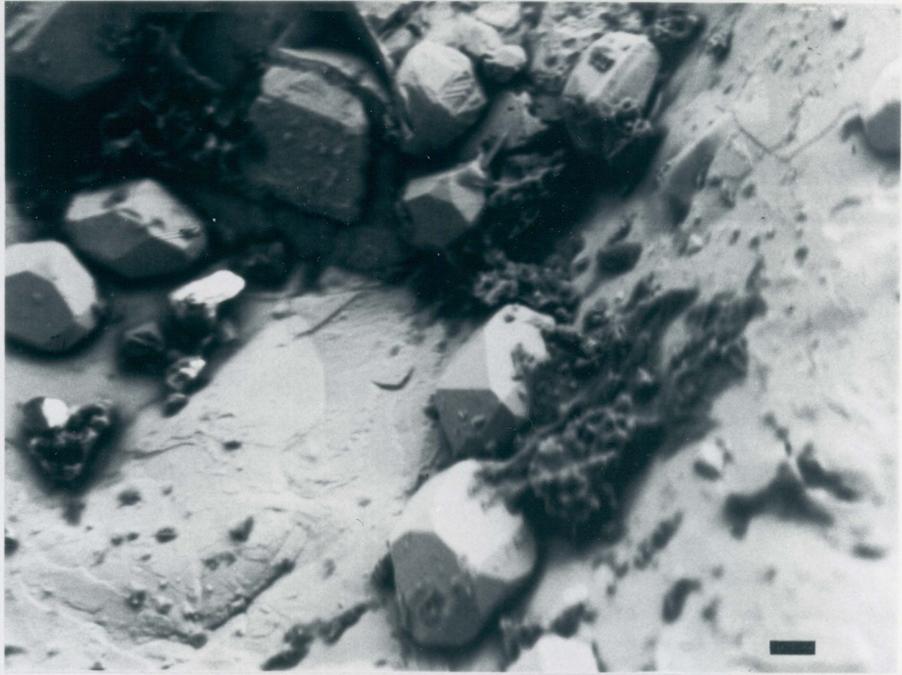
The morphology of placer gold grains is influenced by numerous factors including character of the original lode particles, degree of stream agitation, nature of accompanying channel material, time spent in the stream, distance of transport, and chemistry of the stream water. Numerous possible permutations of the above influences will undoubtedly result in slightly different characteristic morphologies for each locality. The morphologies of gold grains from Brush Creek were examined to identify relationships between morphology and other parameters. The grain morphologies were divided into the following groups: irregular (~41%), spherical to semi-spherical (~33%), wafer-shaped (width to thickness ratio  $\sim \leq 5$ ) (~14%), flake-shaped (~11%), and rod-like (~1%). The grains recovered from Brush Creek during this study range from less than 0.01 mm to 2 mm in maximum dimension with corresponding weights of less than 0.01 mg up to about 10 mg.

The surficial features of many of the gold grains were observed both by standard reflected light and by scanning electron microscopy. The surficial textures were classified into the six types shown and described in Figure 2. All six of these features have not yet been found on the grains from any single locality, but instead represent the major types observed on placer grains from throughout the study area. Correlations between surface textures and grain morphologies are tentative, yet a few broad generalizations have been noted. The most obvious correlation (predominating in about 90% of the cases) is that of irregular grain morphology with smooth, unpitted surfaces. The branching coral texture occurs primarily on rounded irregular and semi-spherical to spherical grains, however, not all grains with these morphologies necessarily show such a texture. The

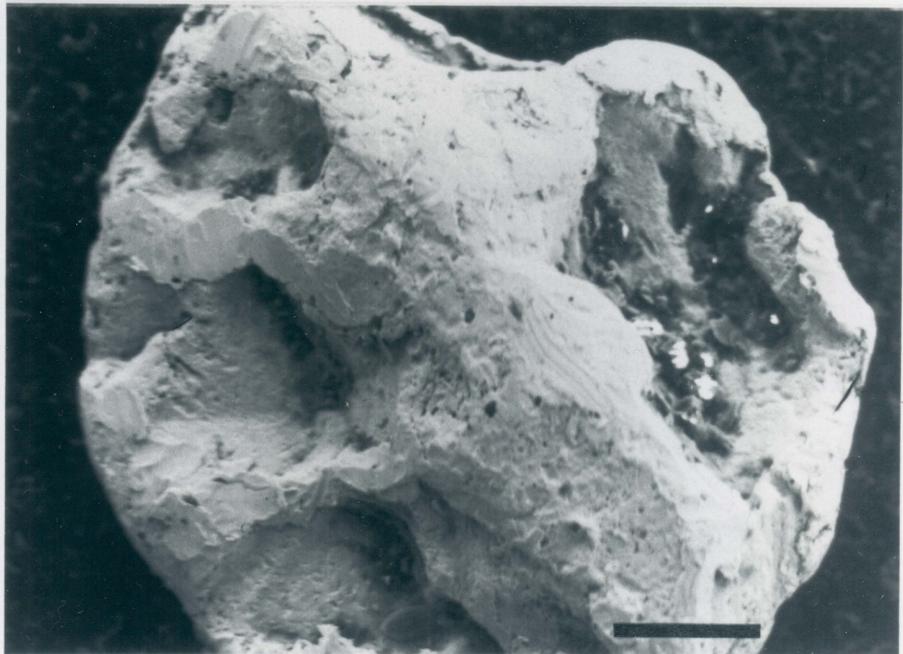
FIG. 2. Scanning electron photomicrographs of the six major surface texture types observed in this study (following three pages): (a) euhedral isometric gold crystals on solid, fairly flat gold substrates (scale bar = 10  $\mu\text{m}$ )\*; (b) well rounded, smooth surfaces with little if any evidence of chemical attack (scale bar = 50  $\mu\text{m}$ ); (c) smoothly rounded yet pitted surfaces (scale bar = 50  $\mu\text{m}$ ); (d) smoothly rounded surfaces with large pits containing branching-coral type features (scale bar = 10  $\mu\text{m}$ ); (e) hackly, very irregular surfaces with a texture similar to that of foundry slag or weathered, grainy sandstone (scale bar = 100  $\mu\text{m}$ ); (f) irregular, lobate, "stromatolitic-like" texture with occasionally stepped but usually smooth individual lobe surfaces (scale bar = 10  $\mu\text{m}$ ).

\* - The exact origin of the crystals on this placer grain is not yet known. The grain's history is also unknown other than its reported location of discovery (Manassas quad., VA). The crystals contain about 20% silver, which suggests that they may have formed in the lode deposit. Webster & Mann (1984), however, suggest the possibility of secondary precipitation of gold-silver alloys in near neutral solutions.

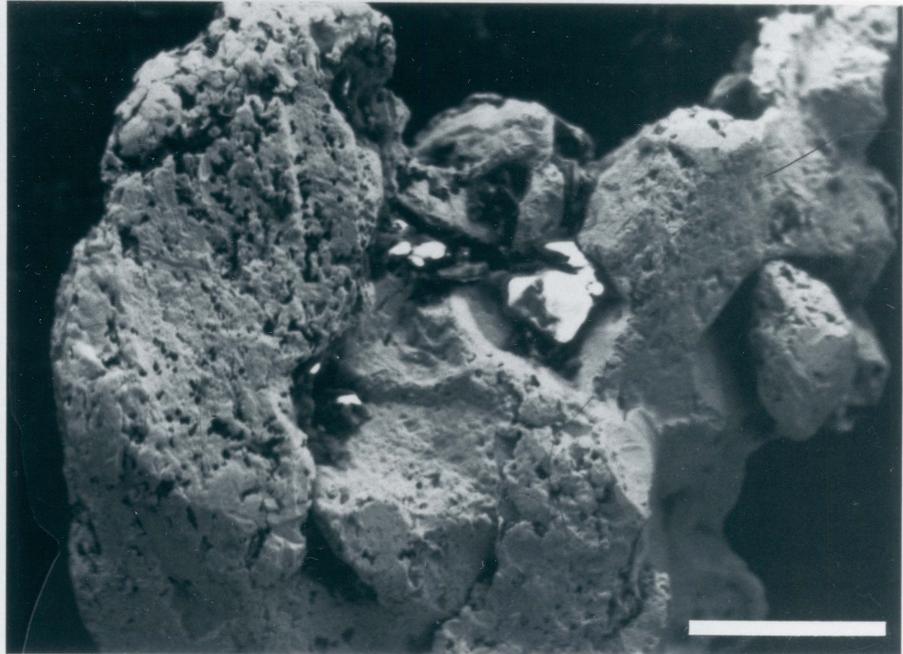
**a**



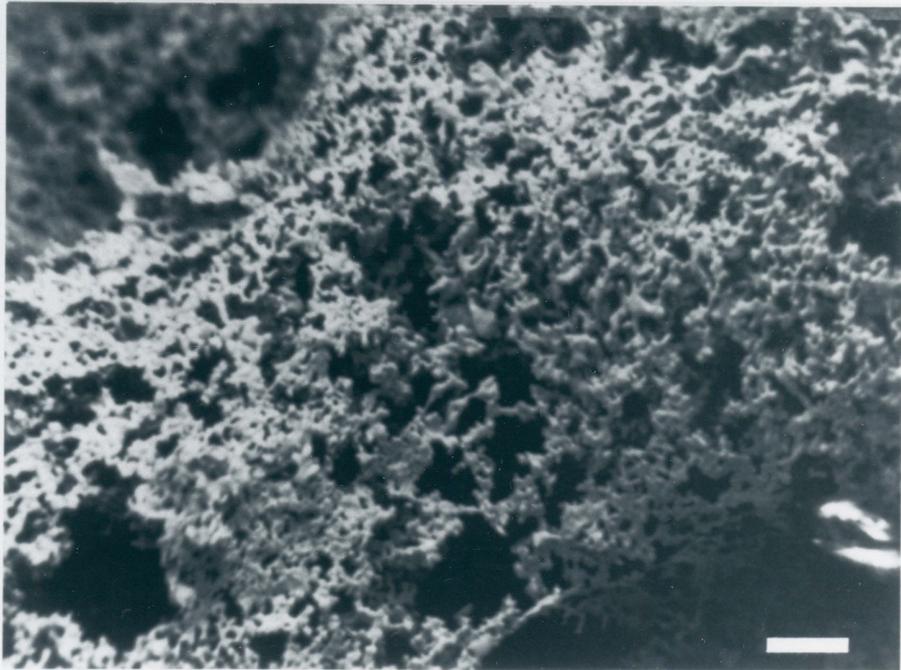
**b**



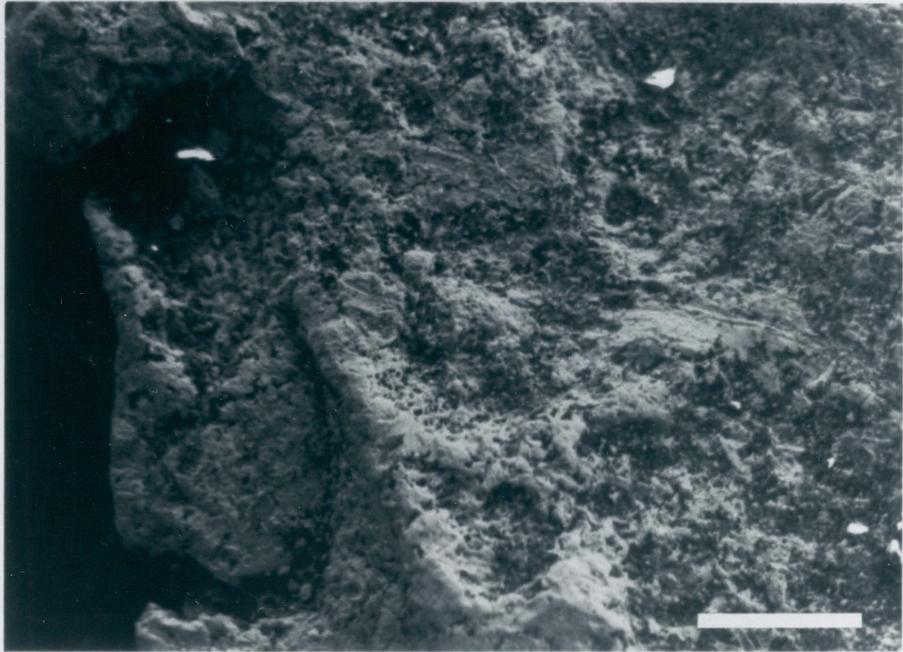
**c**



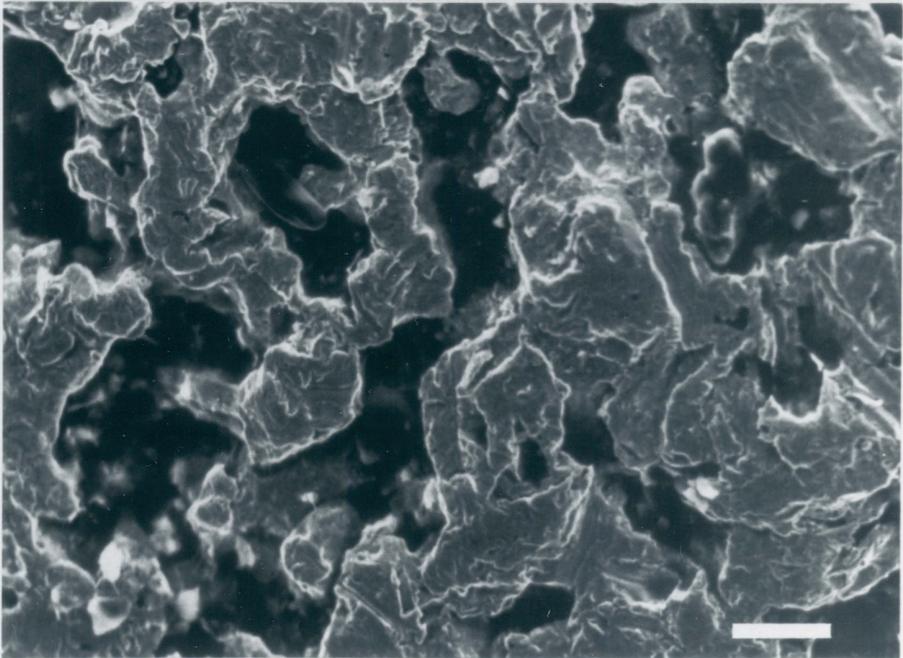
**d**



**e**



**f**



smooth-pitted texture also correlates with rounded irregular, and semi-spherical to spherical grains, but this relationship holds for only about 60 to 70 percent of such grains. The hackly texture presented in Figure 2 occurs predominantly on flake-shaped grains and the lobate surfaces appear on numerous morphologies including wafer-shaped, flake-shaped, and semi-spherical to spherical grains.

An apparent relationship between grain size and distance of transport was noticed for the gold grains from Brush Creek. Near the headwaters of the creek, gold grains up to 1 mm are not uncommon and the grains average about 0.2 mm in maximum dimension. The average size of the gold grains further downstream though, is generally less than 0.1 mm.

### *Analytical Results*

Electron microprobe analyses of 44 gold grains from Brush Creek (Tables 1 and 2), show that the composition of the grain cores ranges from 549 to 849 fine. This compositional range is quite large relative to that of other localities in this study (i.e. Storck quad., Chancellorsville quad., Lilesville quad.) and other southeastern U.S. localities in the literature (Craig et al. 1981). Polished sections of Brush Creek gold grains reveal their high silver (i.e. low fineness) core compositions by their generally quite pale yellow color. The grains have very chemically homogeneous cores (as borne out by the microprobe traverse data in Figure 3), even though considerable variation exists between the compositions of individual grains. Mineral inclusions are quite uncommon in these grains except for the abundant inclusions in thin gold-enriched rims which are discussed below.

Density measurements were carried out on nine natural grains that were large enough to yield reliable values, to examine the extent to which such measurements could be used

TABLE 1. CHEMICAL AND PHYSICAL DATA  
OF PLACER GOLD GRAINS

Grain Number <sup>1</sup>	Size (mm) <sup>2</sup>	Mass (mg)	Shape	Fineness	
				Core <sup>3</sup>	Rim <sup>3</sup>
BC 1-1 <sup>4</sup>	0.18	0.04	sphere	727-729 (2)	985-995 (3)
BC 1-2	0.25	0.06	wafer	580-596 (4)	~983-990 (4)
BC 1-3	0.30	0.02	irreg.	655 (1)	987 (1)
BC 2-1	1.10	4.09	sphere	~604-614 (4)	988-989 (2)
BC 2-2	1.20	3.87	wafer	577~579 (2)	~992-993 (2)
BC 2-3	1.30	4.73	irreg.	570~578 (3)	~977 (1)
BC 2-4	1.40	1.21	flake	664~667 (3)	987~988 (2)
BC 2-5	0.65	n.m. <sup>5</sup>	wafer	693-716 (2)	980-987 (2)
BC 2-6	0.50	n.m.	sphere	553 (1)	996 (1)
BC 2-7	0.95	n.m.	flake	677-684 (2)	992 (1)
BC 2-8	0.60	n.m.	irreg.	558-562 (2)	990 (1)
BC 2-9	0.55	n.m.	wafer	650 (1)	992~997 (3)
BC 2-10	0.50	n.m.	sphere	633-644 (2)	985 (1)
BC 2-11	0.55	n.m.	flake	593 (1)	976-982 (2)
BC 2-12	0.60	n.m.	irreg.	668 (1)	967-969 (2)
BC 2-13	0.55	n.m.	wafer	591 (1)	987 (1)
BC 2-14	0.55	n.m.	sphere	549 (1)	988 (1)
BC 2-15	0.80	n.m.	flake	625-639 (2)	~985-994 (3)
BC 2-16	0.60	n.m.	irreg.	685 (1)	988 (1)
BC 2-17	0.50	n.m.	wafer	554 (1)	991 (1)
BC 2-18	0.70	n.m.	sphere	555 (1)	991 (1)
BC 2-19	0.60	n.m.	flake	562 (1)	987 (1)
BC 2-20	0.65	n.m.	irreg.	781 (1)	995 (1)
BC 2-26	0.60	n.m.	irreg.	554 (1)	993 (1)
BC 2-27	0.47	n.m.	wafer	685 (1)	997 (1)
BC 3-1	0.70	0.84	sphere	608 (1)	997 (1)
BC 4-1	0.50	0.26	wafer	713 (1)	~994-997 (2)
BC 5-1	0.90	0.65	flake	849 (1)	991 (1)
BC 7-1	0.20	0.02	irreg.	776 (1)	989 (1)
NC85L86-1 <sup>6</sup>	1.15	n.m.	flake	874 (1)	992 (1)
NC85L86-2	1.45	n.m.	flake	948 (2)	993 (1)
NC85L86-3	1.10	n.m.	irreg.	~953-955 (2)	n.d. <sup>7</sup>
NC85L86-4	0.50	n.m.	sphere	957~958 (2)	n.d.
NC85L86-5	1.25	n.m.	flake	866 (1)	995 (1)

<sup>1</sup> Grains beginning with "JM" were generously donated by Mr. James McCloud of Fredericksburg, VA.

Grains beginning with "SM" are on loan from the United States National Museum of Natural History and are identified with their sample numbers following the "SM".

<sup>2</sup> Values determined by means of optical estimation.

<sup>3</sup> Values in parentheses indicate the number of analyses made to determine the value or range shown, and "~" indicates values which have analytical sums deviating from 100% by more than 4%.

<sup>4</sup> Grains beginning with "BC" were panned from recent sediments in Brush Creek, VA.

<sup>5</sup> "n.m." = not measured

<sup>6</sup> Grains beginning with "NC" are paleo-placer grains recovered from a sand and gravel operation in the Lilesville quad., NC.

<sup>7</sup> "n.d." = not detected

TABLE 1. CHEMICAL AND PHYSICAL DATA  
OF PLACER GOLD GRAINS (cont'd)

Grain Number <sup>1</sup>	Size (mm) <sup>2</sup>	Mass (mg)	Shape	Fineness	
				Core <sup>3</sup>	Rim <sup>3</sup>
NC85L86-6 <sup>6</sup>	0.70	n.m. <sup>5</sup>	sphere	862 (1)	992 (1)
NC85L86-7	1.20	n.m.	wafer	994 (1)	n.d. <sup>7</sup>
NC85L86-8	0.90	n.m.	irreg.	945 (1)	999 (1)
NC85L86-9	1.00	n.m.	sphere	869 (1)	991-998(2)
NC85L86-10	1.15	n.m.	flake	966 (1)	n.d.
NC85L86-11	0.65	n.m.	sphere	881 (1)	~996-997 (3)
NC85L86-12	0.75	n.m.	irreg.	805~839 (2)	n.d.
NC85L86-13	0.85	n.m.	irreg.	961 (1)	998 (1)
NC85L86-14	0.65	n.m.	sphere	941-943 (2)	999 (1)
NC85L86-15	0.70	n.m.	sphere	972 (2)	998 (1)
NC85L86-16	0.55	n.m.	sphere	977 (2)	n.d.
NC85L86-17	0.65	n.m.	wafer	947 (1)	996 (1)
NC85L86-18	0.60	n.m.	irreg.	947 (1)	n.d.
NC85L86-19	0.45	n.m.	irreg.	836-850 (2)	n.d.
JMA 1 <sup>8</sup>	3.35	8.58	rod	957-959 (3)	n.d.
JMA 2	4.35	19.90	rod	947-949 (3)	n.d.
JMA 3	3.10	27.53	irreg.	944-946 (3)	985 (1)
JMA 4	5.05	81.39	irreg.	970-971 (3)	999 (1)
JMB 1 <sup>9</sup>	3.15	21.21	irreg.	820-822 (4)	~996-998 (3)
JMB 5	1.95	14.92	wafer	939 (1)	997~999 (2)
SM C-126 <sup>10</sup>	3.95	88.45	sphere	1000 (2)	1000 (1)
SM 67994 <sup>11</sup>	5.45	231.68	wafer	863-864 (3)	987-996 (3)
SM 96982 <sup>12</sup>	8.20	464.25	irreg.	961 (2)	992-1000 (3)
SM 97398-1 <sup>13</sup>	0.80	0.95	x-talline	809-812 (3)	n.d.
SM 97398-2	2.55	1.96	x-talline	816-818 (3)	n.d.
SM 97398-3	3.00	3.46	x-talline	818 (1)	~992-993 (2)
SM 105364 <sup>14</sup>	0.75	3.52	thin plate	807-820 (6)	n.d.

<sup>1</sup> Grains beginning with "JM" were generously donated by Mr. James McCloud of Fredericksburg, VA. Grains beginning with "SM" are on loan from the United States National Museum of Natural History and are identified with their sample numbers following the "SM".

<sup>2</sup> Values determined by means of optical estimation.

<sup>3</sup> Values in parentheses indicate the number of analyses made to determine the value or range shown, and "~" indicates values which have analytical sums deviating from 100% by more than 4%.

<sup>5</sup> "n.m." = not measured

<sup>6</sup> Grains beginning with "NC" are paleo-placer grains recovered from a sand and gravel operation in the Lilesville quad., NC.

<sup>7</sup> "n.d." = not detected

<sup>8</sup> Grains beginning with "JMA" were panned from recent sediments in the Chancellorsville quad., VA.

<sup>9</sup> Grains beginning with "JMB" were panned from recent sediments in the Storck quad., VA.

<sup>10</sup> Grain SM C-126 is from an unknown locality in North Carolina and appears to be of placer origin.

<sup>11</sup> Grain SM 67994 is from the Eldorado Mine, Montgomery Co., NC, yet is well worn and well rounded indicating previous stream transport.

<sup>12</sup> Grain SM 96982 is from Silver Creek, Cabarrus Co., NC.

<sup>13</sup> Grains SM 97398 (1-3) are worn crystals from the Dugas Gold Mine, White Co., GA.

<sup>14</sup> Grain SM 105364 is from Bull Run, Fairfax Co., VA.

TABLE 2. CHEMICAL AND PHYSICAL DATA OF NATURAL AND PREPARED MERCURY-BEARING GOLD GRAINS

Grain Number <sup>1</sup>	Size (mm) <sup>2</sup>	Shape	Fineness		At % Hg <sup>3,4</sup>
			Core <sup>3</sup>	Rim <sup>3</sup>	
BC 2-21 <sup>5</sup>	0.33	wafer	753 (1)	~823~848 (2)	~22.3~22.4 (2)
BC 2-21'	0.33	irreg.	627 (1)	720~745 (2)	~30.0-31.6 (2)
BC 2-22	0.41	irreg.	~741 (1)	993 (1)	17.2 (1)
BC 2-22'	0.29	irreg.	692~701 (2)	~701 (1)	~29.3 (1)
BC 2-23	0.42	flake	605 (2)	~654~671 (2)	~29.7~30.2 (2)
				~975 (1)	~15.4 (1)
BC 2-24	0.37	irreg.	635 (1)	~659 (1)	~12.1
				981 (1)	0.2 (1)
BC 2-25	0.94	irreg.	838 (1)	~975 (1)	~34.0 (1)
BC 2-28	0.42	irreg.	586 (1)	~960 (1)	~28.8 (1)
BC 2-29	0.28	sphere	582 (1)	723 (1)	28.0 (1)
BC 2-30	0.37	wafer	627 (1)	~851~859 (2)	~23.5~23.7 (2)
BC 2-31	0.39	flake	~705 (1)	699 (1)	29.7 (1)
BC 2-32	0.14	sphere	769 (1)	~866 (1)	~22.6 (1)
BC 2-33	0.33	wafer	617 (1)	980 (1)	21.7 (1)
BC 2-34	0.37	flake	707 (1)	~723 (1)	~27.7 (1)
BC 2-35	0.33	irreg.	730 (1)	~833 (1)	~23.9 (1)
BC 2-37	0.16	wafer	n.d. <sup>6</sup>	677-680 (2)	29.5-31.4 (2)
JMA 5 <sup>7</sup>	5.65	flake	891-892 (2)	995-998 (2)	24.8-26.1 (2)
JMB 2 <sup>8</sup>	2.10	sphere	906 (2)	~990-994 (2)	~2.3~5.0 (3)
JMB 3	3.35	flake	836 (1)	996 (2)	10.0~10.8 (2)
JMB 4	3.20	flake	861 (1)	997 (1)	~9.0 (1)
JMB 6	2.60	rod	952 (1)	~994-997 (2)	~6.1-10.1 (2)
AuHg-1 <sup>9</sup>	n.d.s. <sup>10</sup>	n.d.s.	566-569 (2)	569-587 (4)	22.5-33.6 (5)
AuHg-2	n.d.s.	n.d.s.	645-655 (2)	653 (1)	~27.5-30.5 (2)
AuHg-3	n.d.s.	n.d.s.	731-734 (2)	728-743 (2)	29.5-30.9 (2)
AuHg-4	n.d.s.	n.d.s.	828-832 (2)	~831-852 (2)	~29.8-31.3 (2)
AuHg-5	n.d.s.	n.d.s.	885-895 (2)	893 (2)	~26.7-39.0 (4)
AuHg-6	n.d.s.	n.d.s.	945-946 (2)	961~977 (2)	44.1~47.2 (2)
AuHg-7	n.d.s.	n.d.s.	1000 (2)	999 (2)	~43.2-45.3 (2)
AuHg-8	n.d.s.	n.d.s.	551-553 (2)	~537~555 (3)	~34.0~35.6 (3)
AuHg-9	n.d.s.	n.d.s.	555 (2)	~552-561 (3)	29.4~31.3 (3)
AuHg-10	n.d.s.	n.d.s.	652-658 (2)	~643-649 (2)	27.6~31.1 (2)
AuHg-11	n.d.s.	n.d.s.	644-648 (2)	~650 (1)	~31.0 (1)
AuHg-12	n.d.s.	n.d.s.	768-774 (2)	764 (1)	28.8 (1)
AuHg-13	n.d.s.	n.d.s.	699-701 (2)	~713 (1)	~30.5 (1)
AuHg-14	n.d.s.	n.d.s.	814-815 (2)	~815 (1)	~29.1 (1)

<sup>1</sup> Grains beginning with "JM" were generously donated by Mr. James McCloud of Fredericksburg, VA.

<sup>2</sup> Values determined by means of optical estimation.

<sup>3</sup> Values in parentheses indicate the number of analyses made to determine the value or range shown, and "~" 's indicate values which have analytical sums deviating from 100% by more than 4%.

<sup>4</sup> Values are for the amalgamated rims, as the grain cores are generally deficient of mercury.

<sup>5</sup> Grains beginning with "BC" were panned from recent sediments in Brush Creek, Pilot quad., VA.

<sup>6</sup> "n.d." = not detected

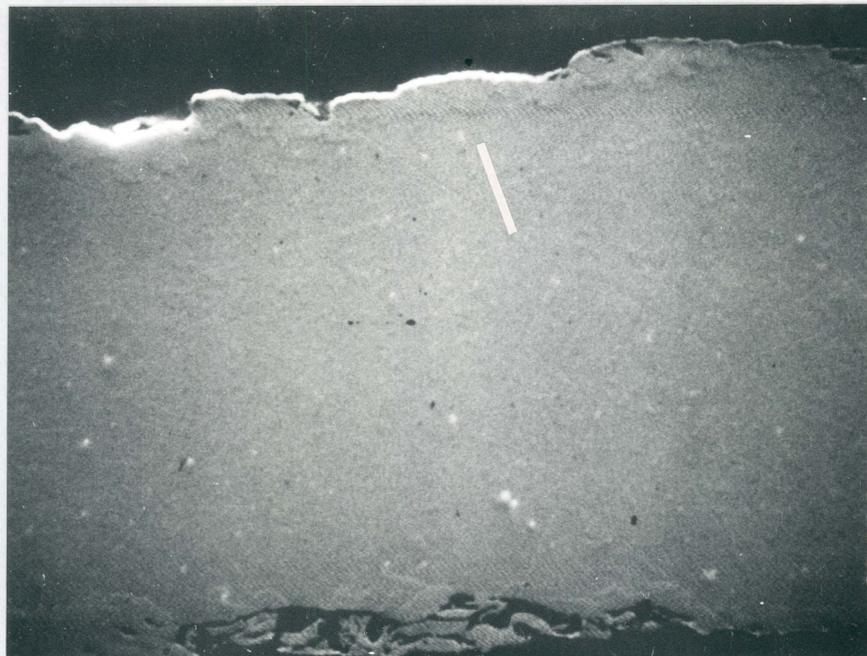
<sup>7</sup> Grains beginning with "JMA" were panned from recent sediments in the Chancellorsville quad., VA.

<sup>8</sup> Grains beginning with "JMB" were panned from recent sediments in the Storck quad., VA.

<sup>9</sup> Grains beginning with "AuHg" are prepared alloys which have been exposed to mercury vapor, #'s 1-7 were kept at room temperature, whereas #'s 8-14 were kept at 100°C.

<sup>10</sup> "n.d.s." = not deemed significant

a



b

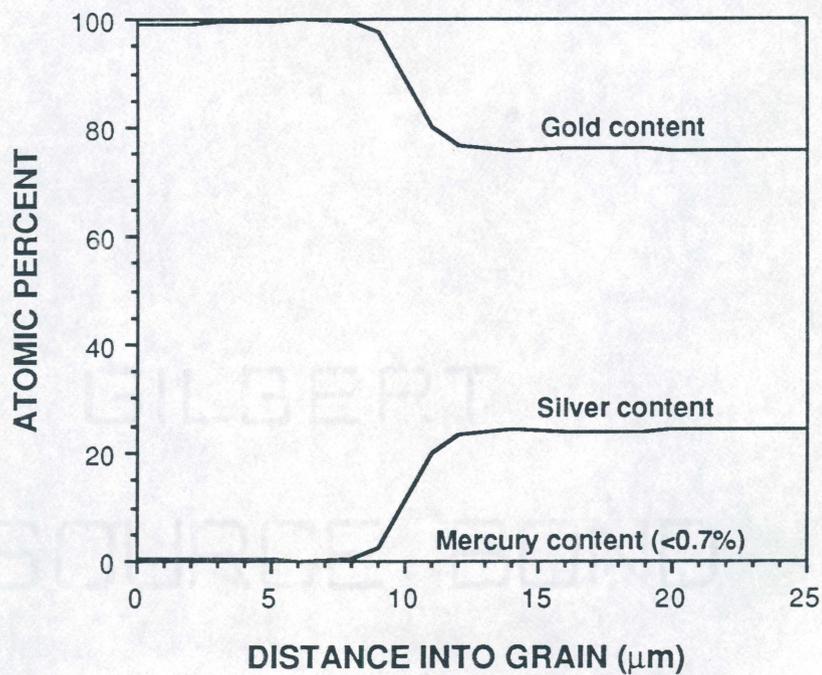
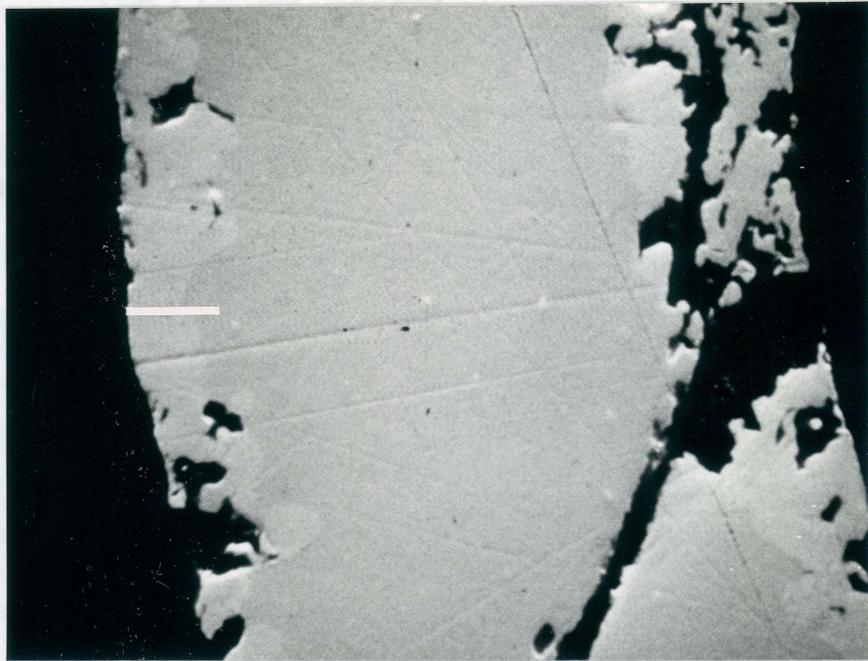


FIG. 3-1. Illustration of placer gold grain compositions: (a) back scattered electron image (500x) of a portion of the polished section of grain number BC 5-1 (white line across grain indicates microprobe traverse path), (b) plot of the change in major element chemistry along the white line shown in 3-1a, average microprobe traverse stepping increment = 1.5  $\mu\text{m}$ .

a



b

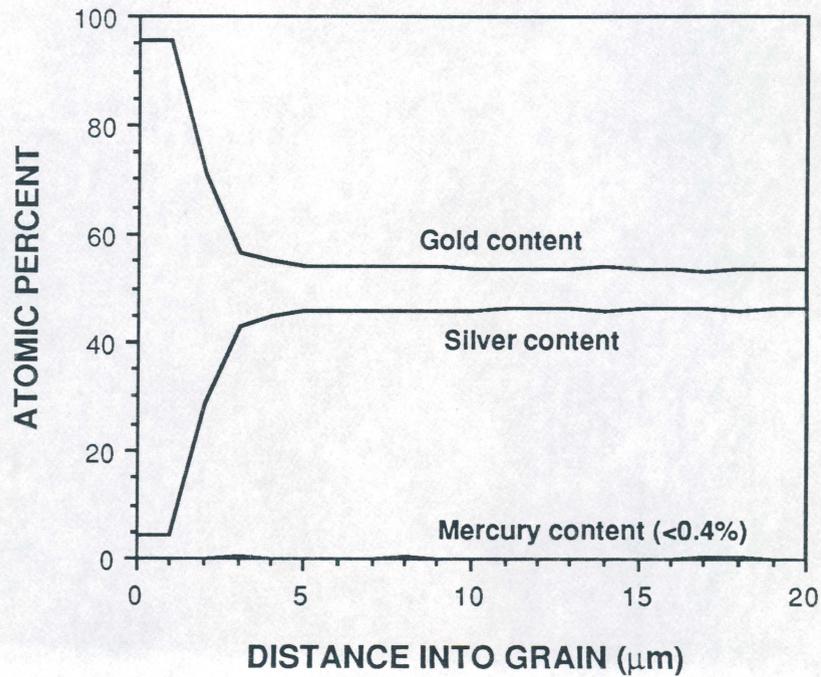
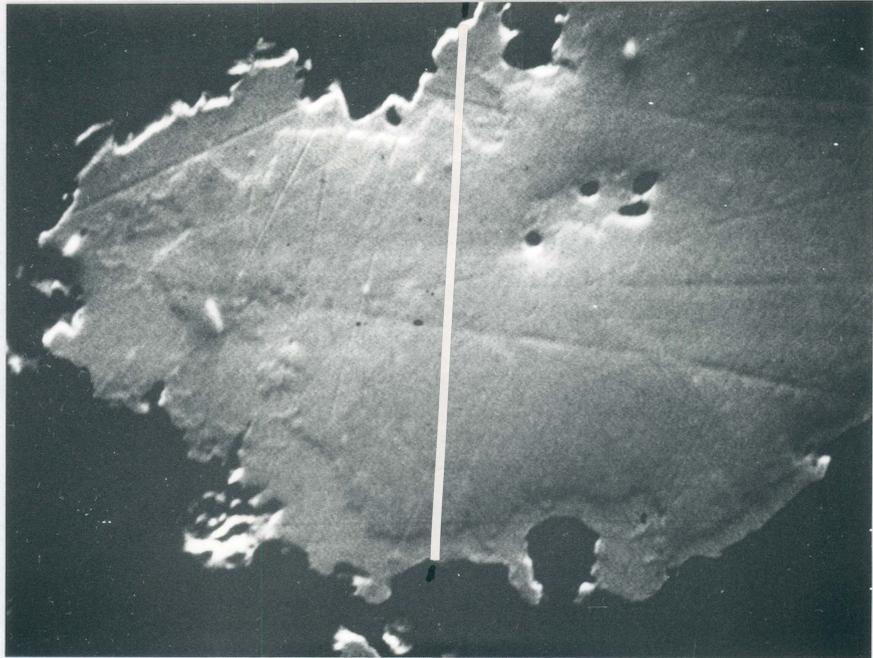


FIG. 3-2. Illustration of placer gold grain compositions: (a) back scattered electron image (600x) of a portion of the polished section of grain number BC 2-7 (white line across grain indicates microprobe traverse path), (b) plot of the change in major element chemistry along the white line shown in 3-2a, microprobe traverse stepping increment = 1 μm.

a



b

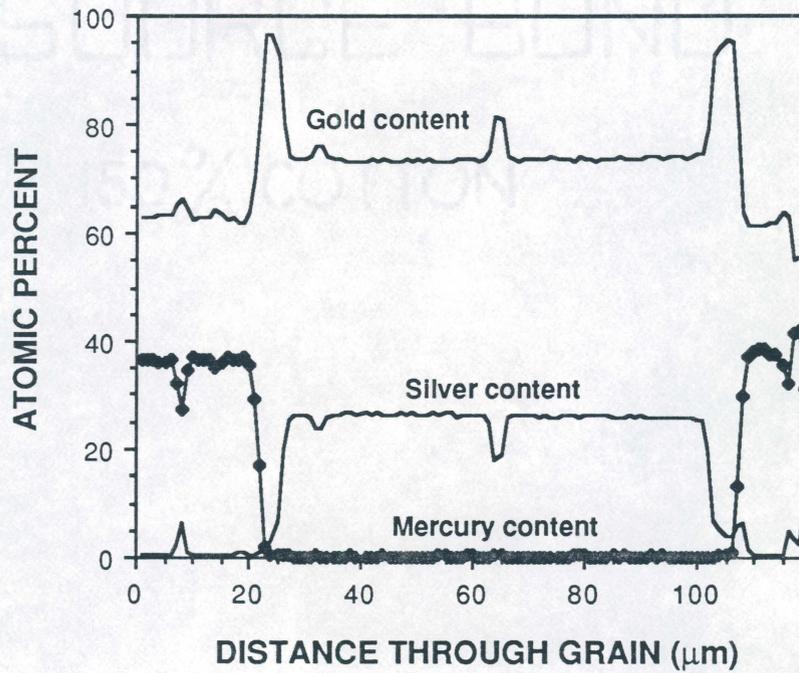


FIG. 3-3. Illustration of placer gold grain compositions: (a) back scattered electron image (600x) of a portion of the polished section of grain number BC 2-25 (white line across grain indicates microprobe traverse path), (b) plot of the change in major element chemistry along the white line shown in 3-3a, microprobe traverse stepping increment = 1 $\mu$ m.

to determine the fineness of the gold when more time consuming and expensive techniques such as electron probe microanalysis are not available. These values are plotted on the density vs. fineness diagram of Figure 4 and for comparison, a line representing the density of an ideal Au-Ag mixture is also shown. Figure 4 shows that the measured densities were always lower than the ideal density, one by as much as 2.25 g/cc (equivalent to ~270 fineness units). This systematic deviation is probably the result of several factors including lower density mineral inclusions in the gold and incomplete removal of small surficial air bubbles from the grain during the weight determinations in water. The average deviation of the measured densities from the calculated density line was -1.1 g/cc (~130 fineness units low) and the standard deviation was 0.6 g/cc (~75 fineness units). There is thus a crudely defined systematic deviation of measured densities as compared to ideal densities that might be used to roughly approximate placer gold fineness on the basis of density determinations.

#### *Gold-Enriched Rims*

The existence of gold-enriched rims on placer grains has been noted by several authors; the earliest known account is that by Fontaine (1882) on grains from the Brush Creek locality:

"The gold contains about 32 per ct. of silver. Most of it has a rich gold color, and, judged by the color of the surface, would seem to contain over 90 per ct. of gold. This color, however, is confined to a thin, external film. When this is removed by the file or knife the color is quite white. It would seem that the silver had been removed from the surface by solution in some naturally formed solvent, and the gold thus was concentrated in the external film. When particles are obtained from the interior of quartz in the veins, they often show the white color."

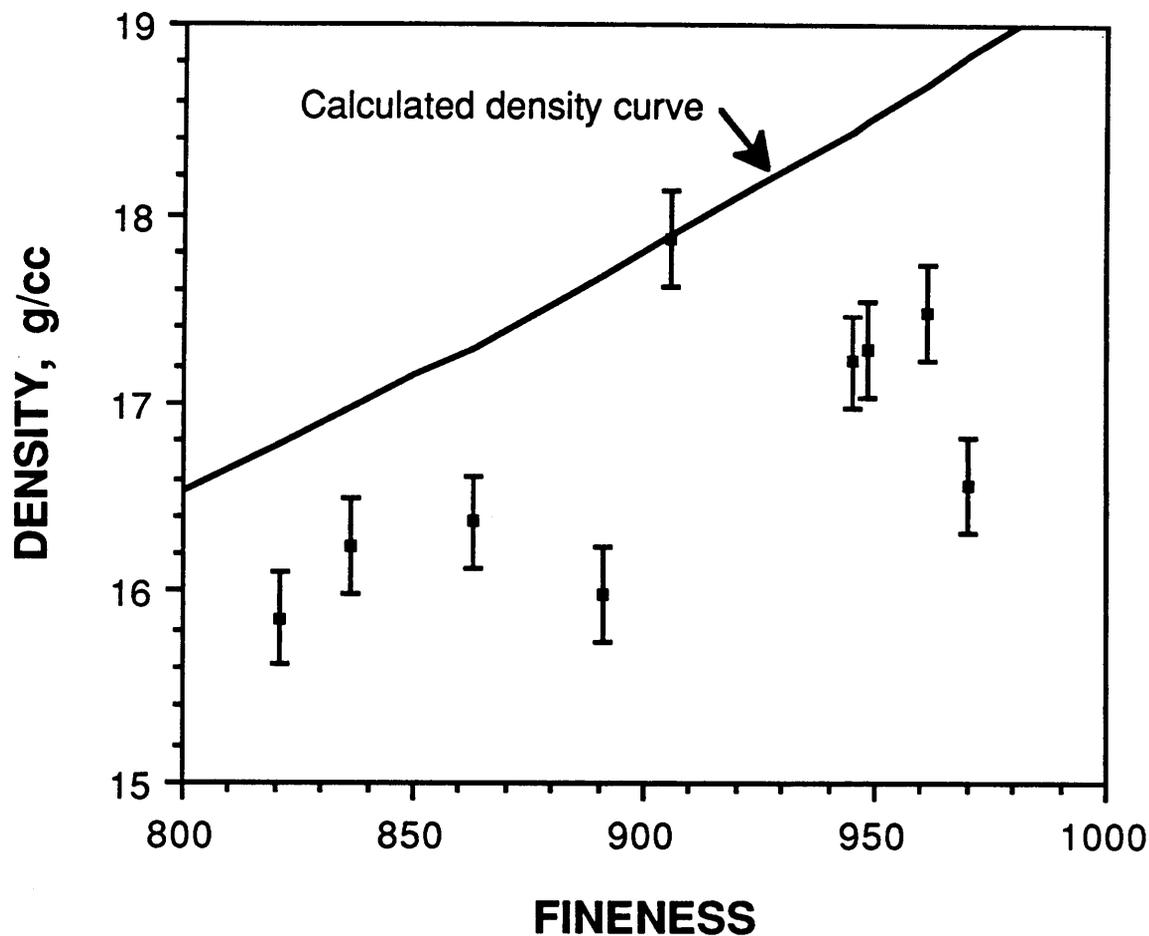


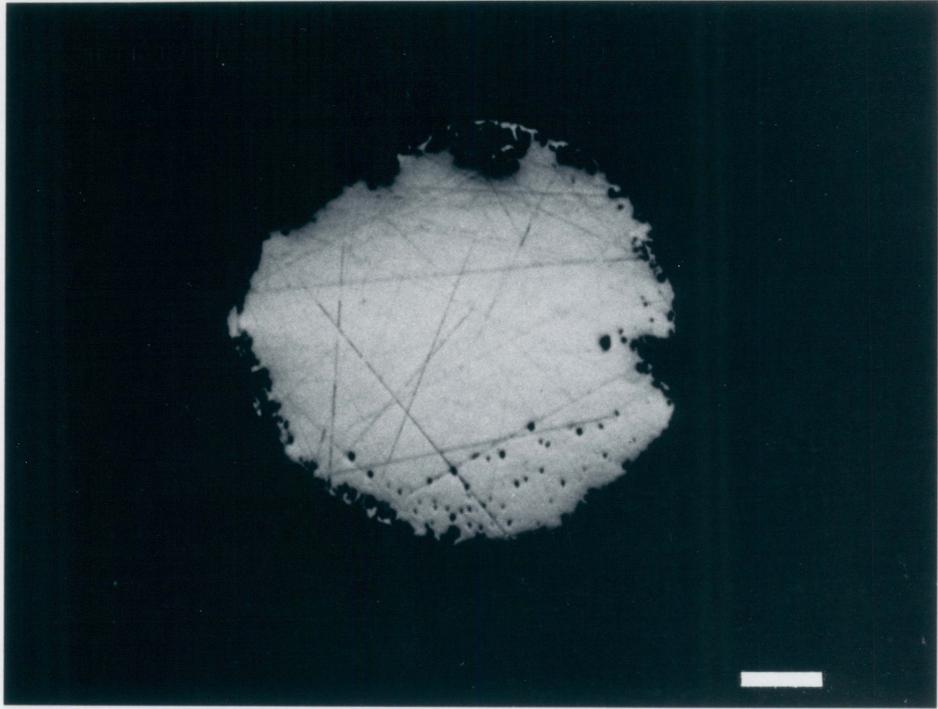
FIG. 4. Density vs. fineness plot showing the nine analytical data points and a curve calculated for the density of an ideal Au-Ag solid solution. The error in the density measurements is indicated by the vertical error bars and the error of the microprobe analyses to determine the finenesses are approximately  $\pm 2$  fineness units (about the width of the black squares).

Subsequent note of the rims on some grains at Brush Creek was made by (Solberg and Craig 1981). One hundred percent of the placer gold grains examined from the Brush Creek locality exhibit minor and spotty to very intense development of gold-enriched rims such as those shown in Figures 3 and 5. Microprobe analysis of gold-enriched rims on grains from all the various sample localities shows that 95% of the rims have compositions of  $\geq 985$  fine, and that some of the rims have mercury contents of up to 28.4 wt %. The remaining 5% of the rims ranged in composition down to 967 fine (Table 1). It should be noted that some of the optically distinct rims which analyze at finenesses lower than about 995 may be purer, because the portions of the analyzing raster may overlap onto non-enriched areas. Furthermore, the depth of excitation, small though it may be in gold, could be sufficient to detect underlying, more silver-rich core composition. When viewed in cross section, these rims are not uniform in thickness, but vary from  $<1\mu\text{m}$  to  $60\mu\text{m}$ . The boundaries between the cores and the rims are generally sharp, and are especially visible when the surface is lightly etched. Grains with incomplete enriched rims tend to have enriched "pockets" wherein the enrichment areas occur in small depressions and pits on the surface. Other rims are so highly developed that they completely enclose the core (Fig. 5). The enriched rims on such grains commonly exhibit a "swiss cheese" texture in which numerous small rounded voids occur within the rim.

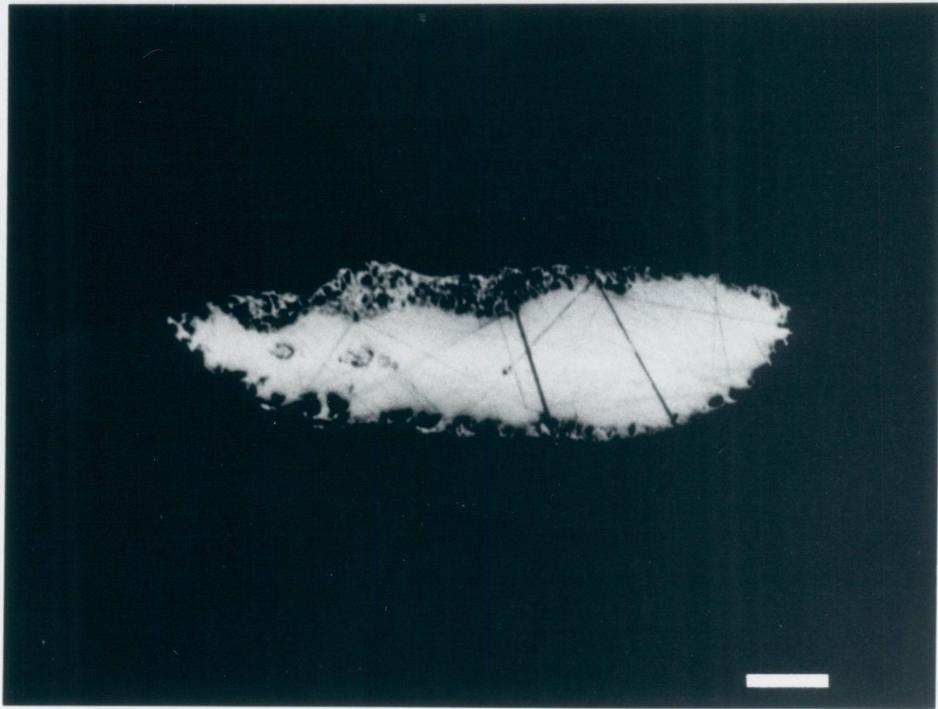
A few definite relationships were observed between the character and prevalence of gold-enriched rims and the morphologies of the gold grains. Firstly, polished sections of irregularly shaped, presumably recently liberated gold grains show virtually no signs of enriched rimming, indicating that the rims develop after liberation from the country rock. On the other hand, flat, well worn, flake-shaped grains have the greatest abundance of, and most highly developed gold rims. The other grain geometries, spherical,

FIG. 5. Photographs of polished sections viewed in reflected light of two placer gold grains from Brush Creek, VA; (a) grain number BC 2-6 shows partially complete formation of a gold-enriched rim with preferential rim development in and around embayments and pits on the surface, (b) grain number BC 2-15 shows a thick, very well developed gold-enriched rim with many voids and mineral inclusions (swiss cheese texture). Scale bars on both photographs equal 100  $\mu\text{m}$ .

**a**



**b**



semi-spherical, and wafer shaped, show varying degrees of rim development, not strongly dependent on the shape.

The surface features observed by scanning electron microscopy also show a general relationship to rim enrichment. Smooth, smooth-pitted, pitted with branching features, irregular hackly, and lobate surfaces (as shown above) generally display respective increases in rim development as defined by increased thickness and surficial coverage. The "euhedral crystals on gold substrate" texture was observed on one grain only, #SM105364, which has a fineness of approximately 818, but no signs of rim enrichment.

Incorporating the above observations, a roughly progressive trend (Fig. 6) was recognized with respect to gold-enriched rimming, morphology, surface texture, and presumably time since liberation. Most of the observed morphologies and surface textures can be roughly placed into this trend of greater rim development with time spent in the stream. This relationship suggests that surficial characteristics of placer grains can give clues to the potential existence and nature of gold-enriched rims without going through the sample preparation necessary to verify such phenomena.

The gold rims on the grains from Brush Creek exhibit very well defined, sharp contacts with the lower fineness cores, facilitating immediate identification, even when they are very thin and irregular (Fig. 5). The enriched rims on grains from most other localities are often less distinct due to the higher fineness cores. The chemical characteristics of these two types of rims were determined by electron microprobe traverses (Fig. 3). These traverses were especially useful for revealing compositional gradients in such types of rimmed grains.

The chemistry of coexisting rims and cores from gold grains in this study as well as from other published data are presented in Figure 7. These data, based on analyses of 246 grains from 30 localities, have a skewed distribution similar to that illustrated in Craig

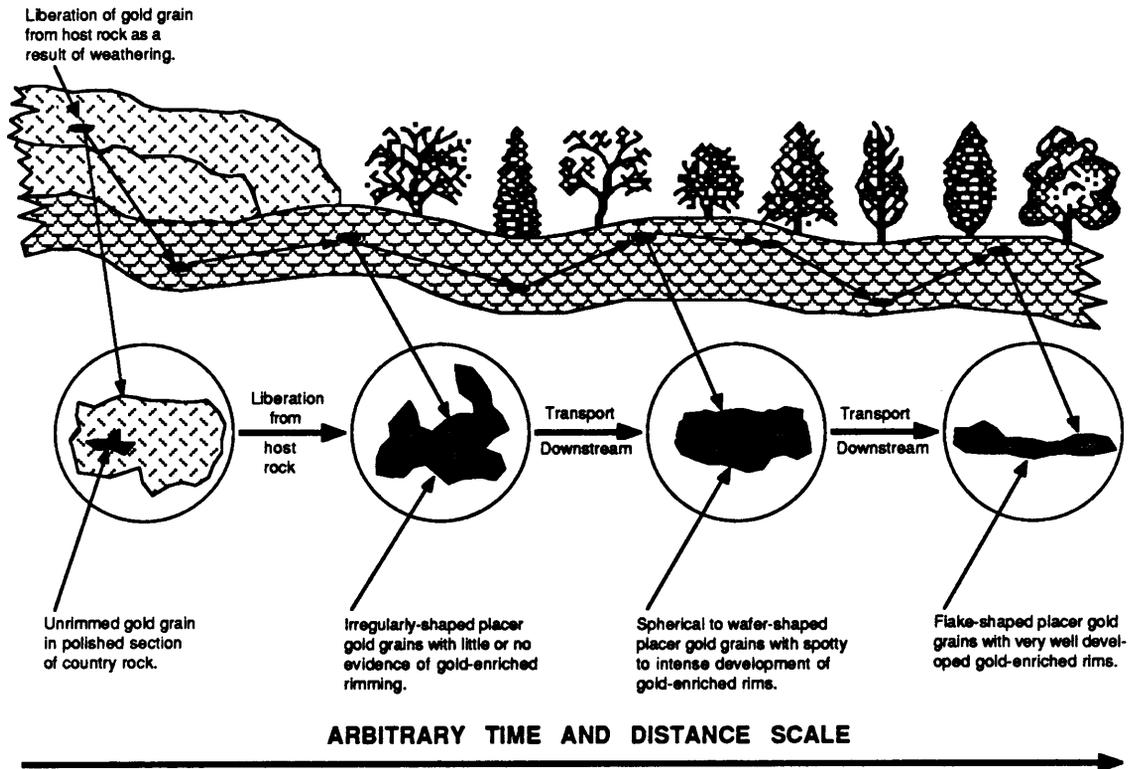


FIG. 6. Schematic illustration depicting the chemical and mechanical alterations experienced by placer gold grains as they are carried downstream.

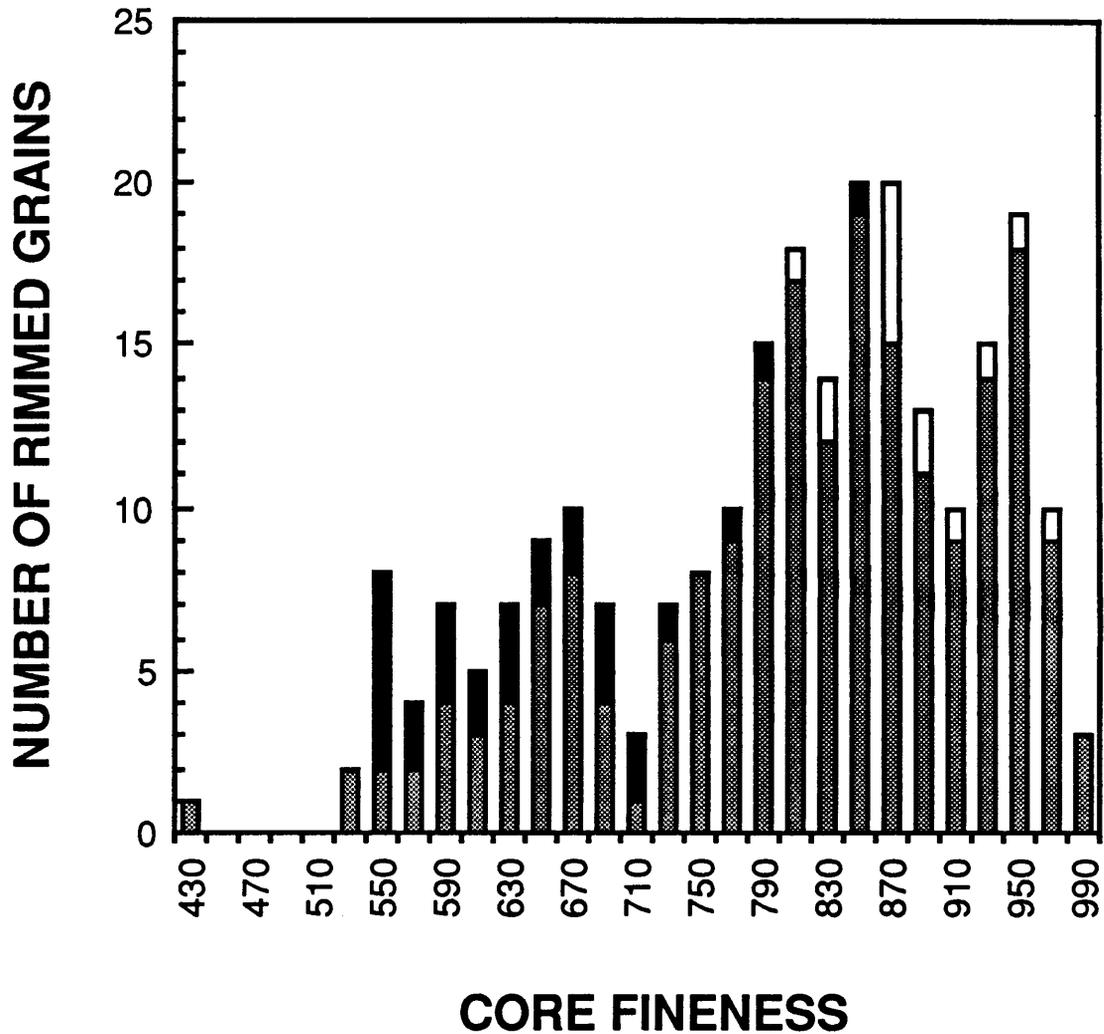


FIG. 7. Histogram showing the frequency of gold-enriched rim occurrence with respect to the fineness of the coexisting grain core for placer grains from Brush Creek, VA (solid black), other localities in this study (white with outline) and from Desborough (1970) (shaded). Core fineness values shown are the median value of the 20 fineness unit increment between tick marks (e.g. "930" represents all values between 920 and 940).

& Rimstidt (1985) for gold grains from world-wide localities. This similarity suggests that there is no systematic relationship between grain core composition and the potential for rim development. The rim and core analyses from Brush Creek alone (Fig. 7), illustrate the unusual composition of Brush Creek gold. The 246 compositions presented as a scatter plot (Fig. 8), show no correlation between rim fineness and core fineness as a first order computer generated polynomial fit yielded an R-value of only 0.23.

The mineral inclusions observed in the gold grains from Brush Creek are primarily present in the rims (Fig. 5). The occasional mineral inclusions that are present in the cores tend to be considerably larger than those in the rims. The majority of inclusions, both in the rims and in the cores, appear to be one of the amphiboles as they usually contain substantial amounts of Si, Al, Fe, and Ti  $\pm$  subordinate K and Ca (determined by energy dispersive X-ray (EDX) analysis). Some (~20%) of the inclusions in the rims are believed to be iron oxides and hydroxides, as iron is the only major element indicated by EDX. Gold samples from the other localities tend to have more mineral inclusions than the Brush Creek gold, but often show a similar relative distribution with respect to the cores and rims. Inclusions in the cores of all the grains from this study appear to be primary, whereas those in the enriched rims have either been injected into the ductile, high purity gold by mechanical working, or have been incorporated during a chemical growth process (see discussion below).

#### *Mercury Amalgamation*

Many placer gold grains examined were found to be distinctly silver-colored rather than golden yellow. Electron microprobe analysis of these grains showed that they contain significant amounts of mercury around their borders. This phenomenon, also noted by Foster et al. (1978) and Solberg & Craig (1981), apparently results from the

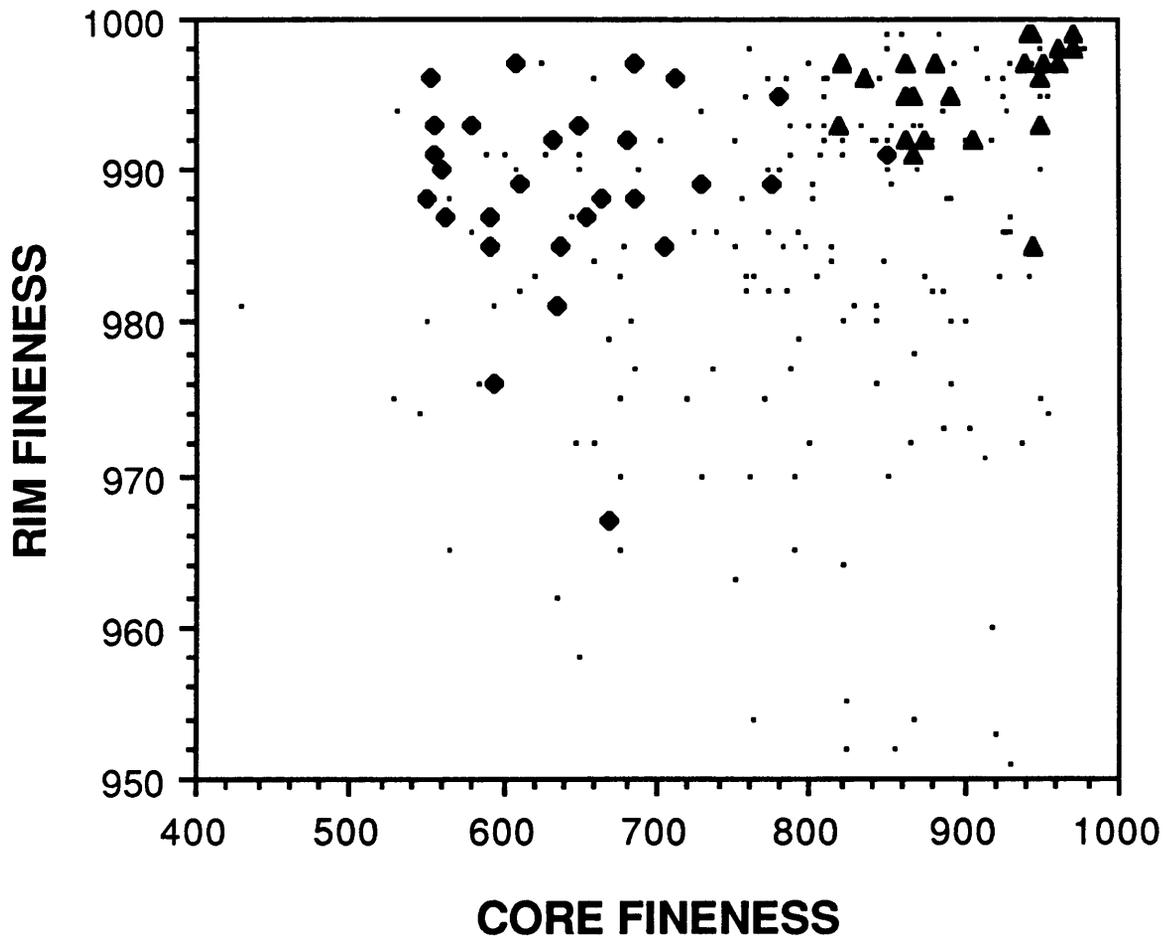


FIG. 8. Scatter plot of rim vs. core composition for placer grains with gold-enriched rims from Brush Creek (solid diamonds), other localities in this study (solid triangles), and from Desborough (1970) (small solid squares).

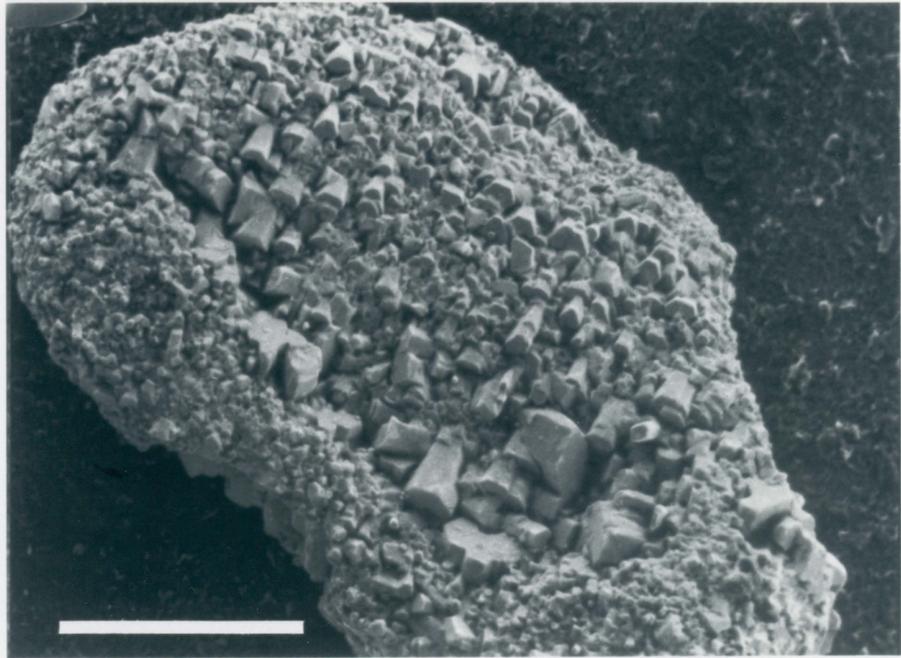
reaction of placer gold grains with free mercury which was lost into the stream during previous panning and stamp mill recovery efforts. In fact, small droplets of free mercury were recovered during gold panning in Virginia and South Carolina. Furthermore, some of the gold grains found while panning were completely engulfed by mercury beads or had a bubbly, mercury-wetted appearance. Many of the silver colored, but non-bubbly surfaced grains are very friable and easily crushed.

SEM examination of the mercury-contaminated placer gold grain surfaces reveals several textures: (1) very smooth rounded-to-lumpy, (2) "dried mudcrack"-like, (3) highly crystalline with myriads of subhedral to euhedral crystals up to 35  $\mu\text{m}$  in maximum dimension (Fig. 9). These crystals are whitish to silver colored in reflected light and have the compositions listed in Table 2. Many of the crystals appear to be hexagonal, however, others appear to be isometric. Arguments propounding secondary enrichment of gold in the placer environment as evidenced by "isometric" crystals on placer grain surfaces should therefore be viewed with caution as they may actually be amalgam crystals. Polished section studies show that grains of differing fineness as well as gold-enriched rims have all reacted with mercury to form Au-Ag-amalgam rims. The mercury-contaminated rims on the examined grains are up to about 16  $\mu\text{m}$  thick and are fairly distinct, especially on the grains with higher fineness cores. These mercury-contaminated rims frequently have the same fineness (i.e. the same Au/Ag ratio) that was present prior to the mercury attack indicating that they are simply "diluted" by the mercury. The mercury content of the amalgams is variable, but controlled by the fineness of the gold grain (Fig. 10).

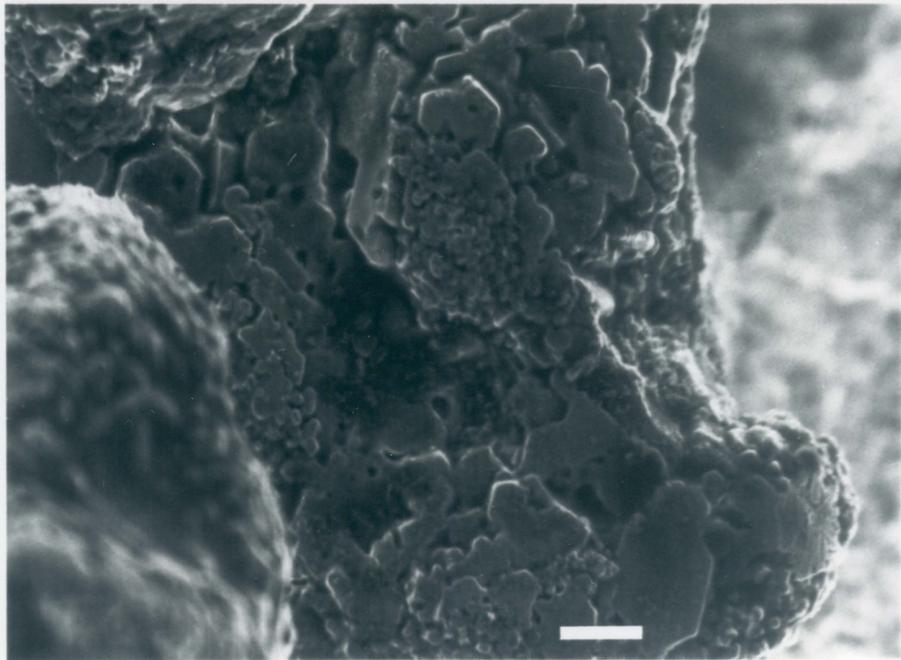
In order to investigate the rates and nature of formation of Au- and Au-Ag- amalgams at low temperatures, a series of experiments were conducted at both room temperature and at 100°C. Prepared Au-Ag alloys of varied proportions were sealed in quartz glass

FIG. 9. Scanning electron photomicrographs of typical Au-Ag-Hg amalgam crystal forms on natural placer gold grains from Brush Creek, VA, (a) grain number BC 2-31 (scale bar = 100  $\mu\text{m}$ ), (b) grain number BC 2-22 (scale bar = 10  $\mu\text{m}$ ).

**a**



**b**



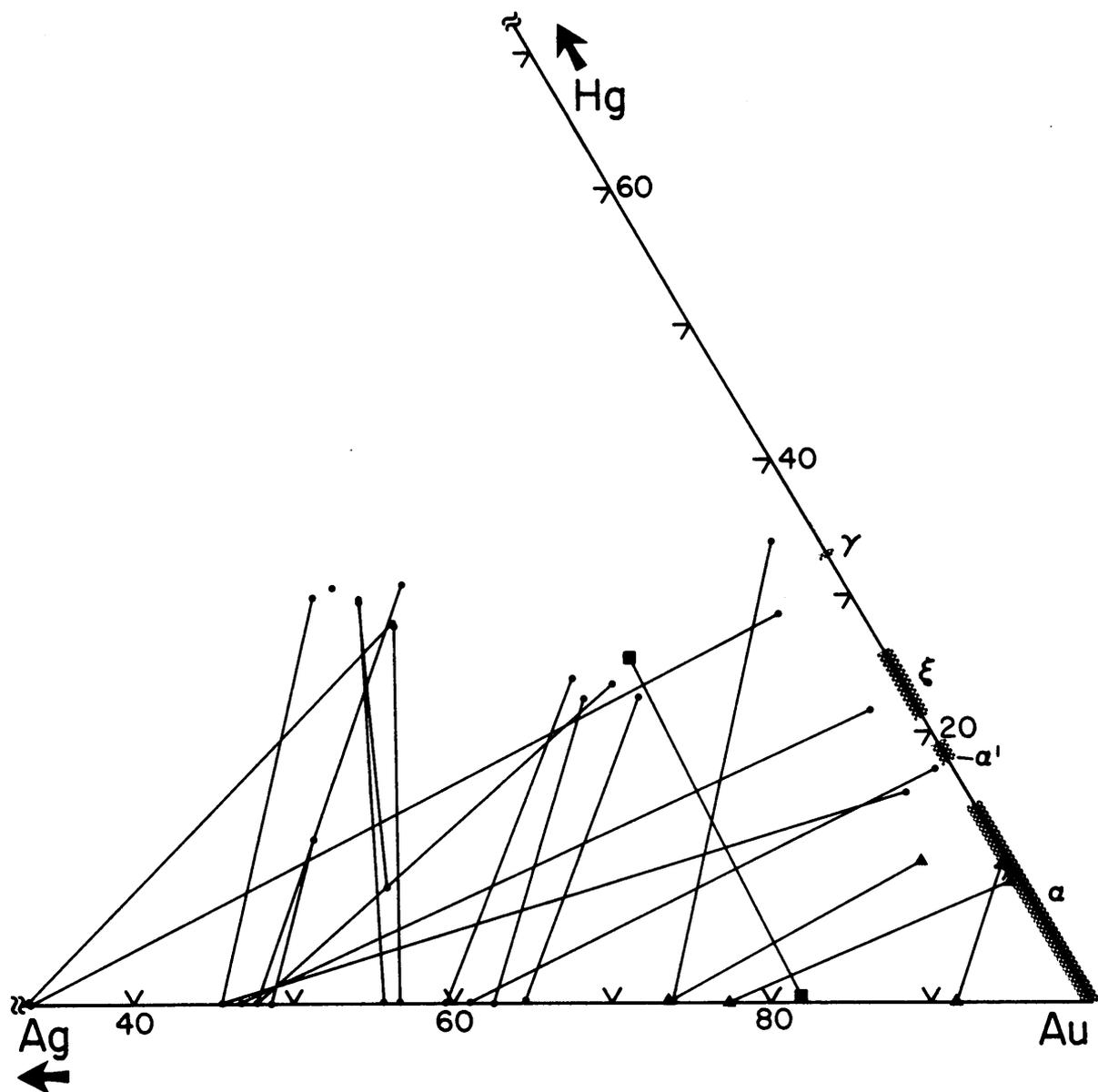


FIG. 10. Gold-rich corner of a ternary Au-Ag-Hg diagram showing the compositions of Au-Ag grain cores and Au-Ag amalgam rims (both crystalline and massive) developed on placer gold grains. Tie lines connect coexisting compositions from individual grains. Low angle tie lines terminating near the Au-Hg join represent the vector sum of a two step process: gold-enriched rim formation followed by mercury-contamination of the gold-enriched rim. Circles represent grains from Brush Creek, VA, triangles represent grains from the Storck quad., VA, and squares represent grains from the Chancellorsville quad., VA. The shaded areas along the Au-Hg join represent the stable intermetallic compounds at 25°C reported in Rolfe & Hume-Rothery (1967).

capsules (Fig. 11) along with a small droplet of mercury so that no direct physical contact could occur between the two phases. A set of these capsules was placed in an oven at 100°C, another was allowed to react at room temperature. Within one day of preparation, the gold grains in both sets of experiments exhibited smooth silvery surfaces. Subsequent periodic examinations showed the grain surfaces to grow progressively rougher but to retain the same silvery color. After approximately 276 days, the capsules were opened and the mercury-contaminated grains removed for study.

SEM examination of these synthetic amalgams shows development of surficial coatings of euhedral crystals on all grains which were kept at room temperature, whereas the seven grains which reacted at 100°C formed bubbly looking surfaces, similar to that of botryoidal kidney ore. The synthetic crystals display even more diverse morphologies than do the natural amalgam crystals (Fig. 12). Upon sectioning, homogeneous off-white rims of uniform thickness (8-40  $\mu\text{m}$ , depending on core composition) were found to have developed on both the high and low temperature experimental grains. These synthetic amalgam rims are similar in color and form, but generally thicker than those observed on contaminated placer grains. The compositions of the cores and coexisting amalgam rims plotted on a ternary Au-Ag-Hg diagram (Fig. 13), display trends which are consistent with those of the amalgams formed on the placer grains. The fineness vs. mercury content relationship holds for the grains reacted at both room temperature and 100°C, even though the surface features are different.

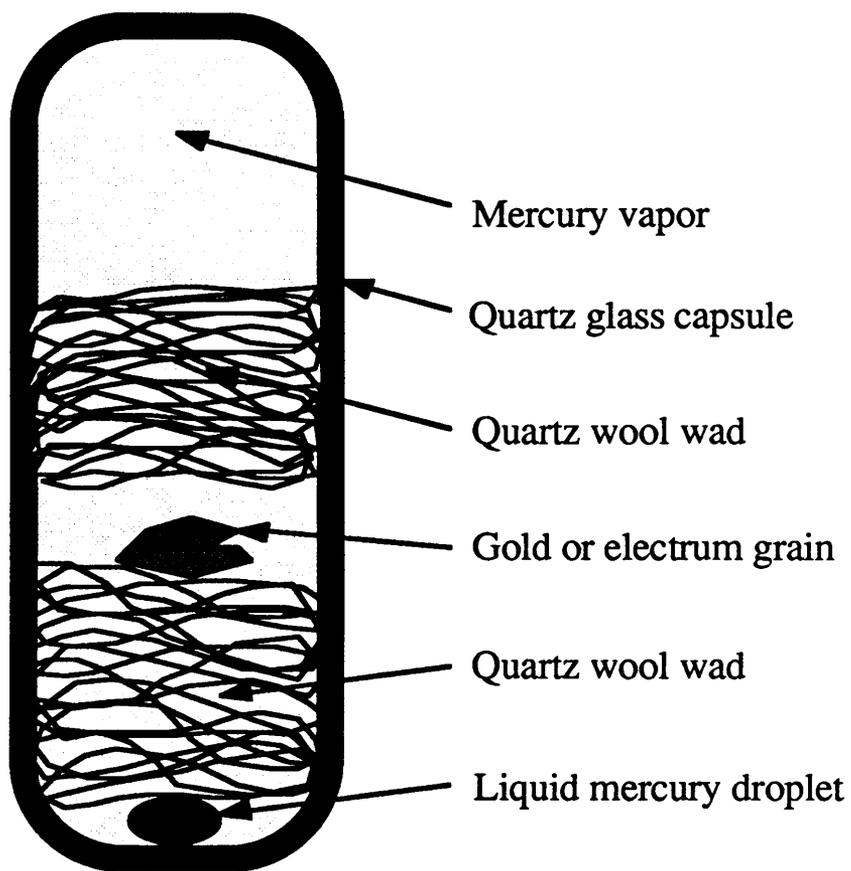
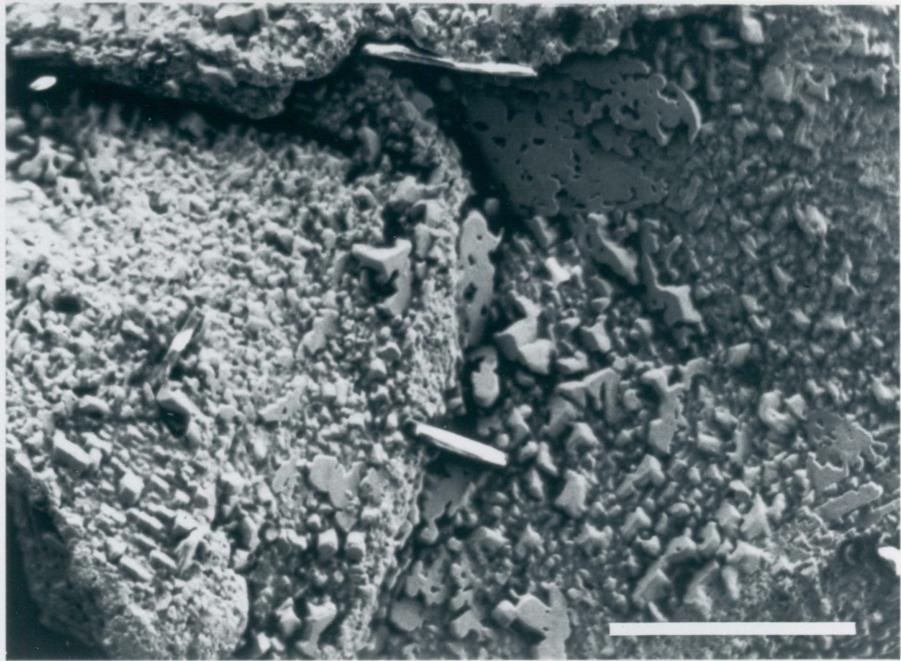


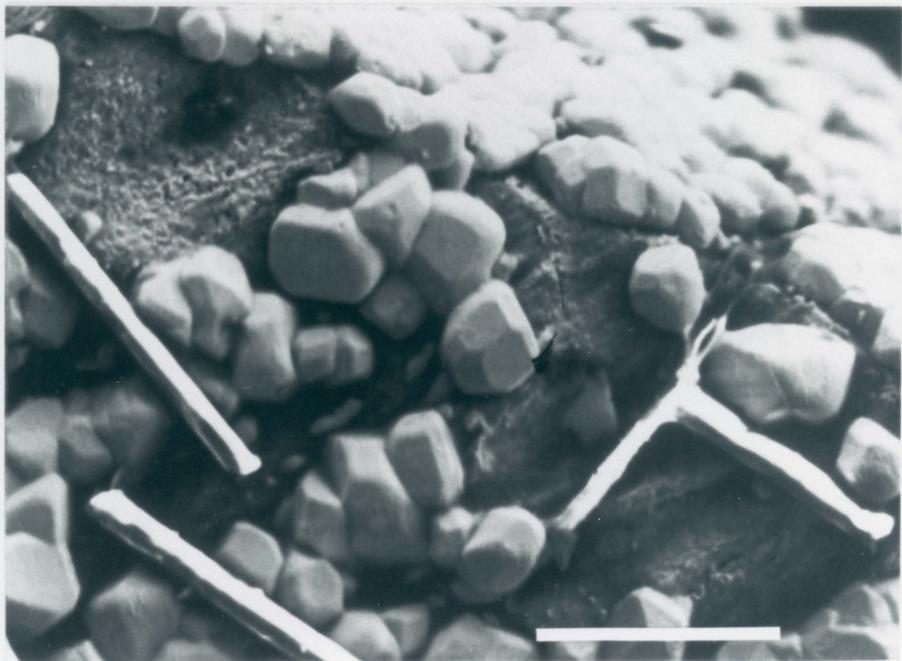
FIG. 11. Electrum / mercury-vapor sealed quartz capsule experimental design, with the quartz wool being sufficiently well packed to prevent liquid mercury from flowing through it upon inversion. Actual size of capsules is about one inch long.

FIG. 12. Scanning electron photomicrographs of some representative Au-Ag-Hg amalgam crystal forms on the experimental grains prepared in the fused quartz capsules illustrated in Figure 11, (a) grain number AuHg-3 (core composition =  $\text{Au}_{60}\text{Ag}_{40}$ , scale bar =  $100\ \mu\text{m}$ ), (b) grain number AuHg-4 (core composition =  $\text{Au}_{70}\text{Ag}_{30}$ , scale bar =  $50\ \mu\text{m}$ ), (c) grain number AuHg-7 (pure gold core, scale bar =  $10\ \mu\text{m}$ ). The white rod-shaped features are fragments of quartz wool.

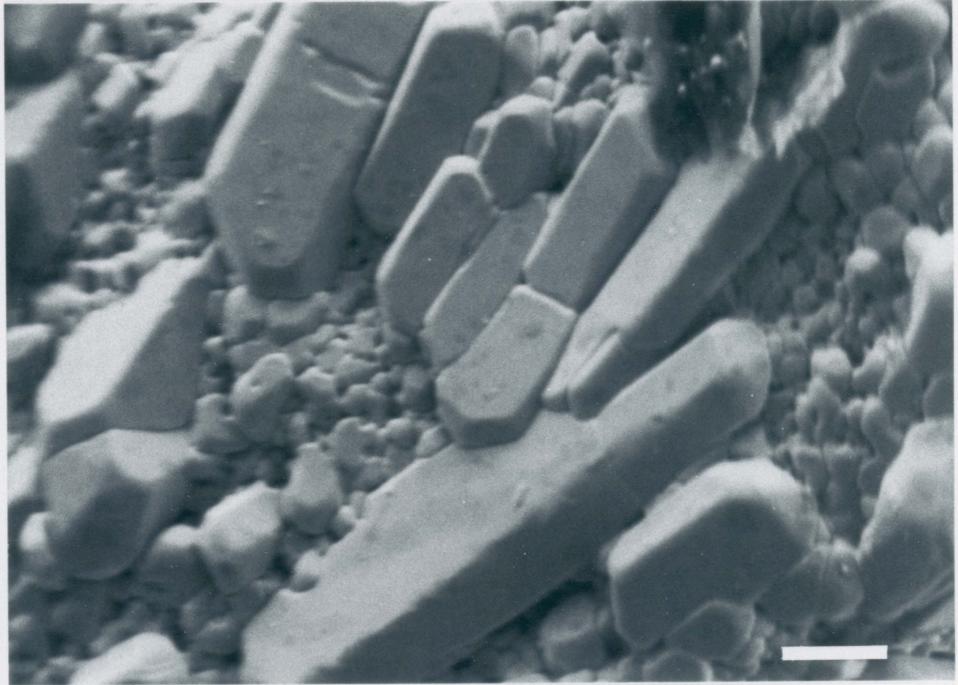
**a**



**b**



**C**



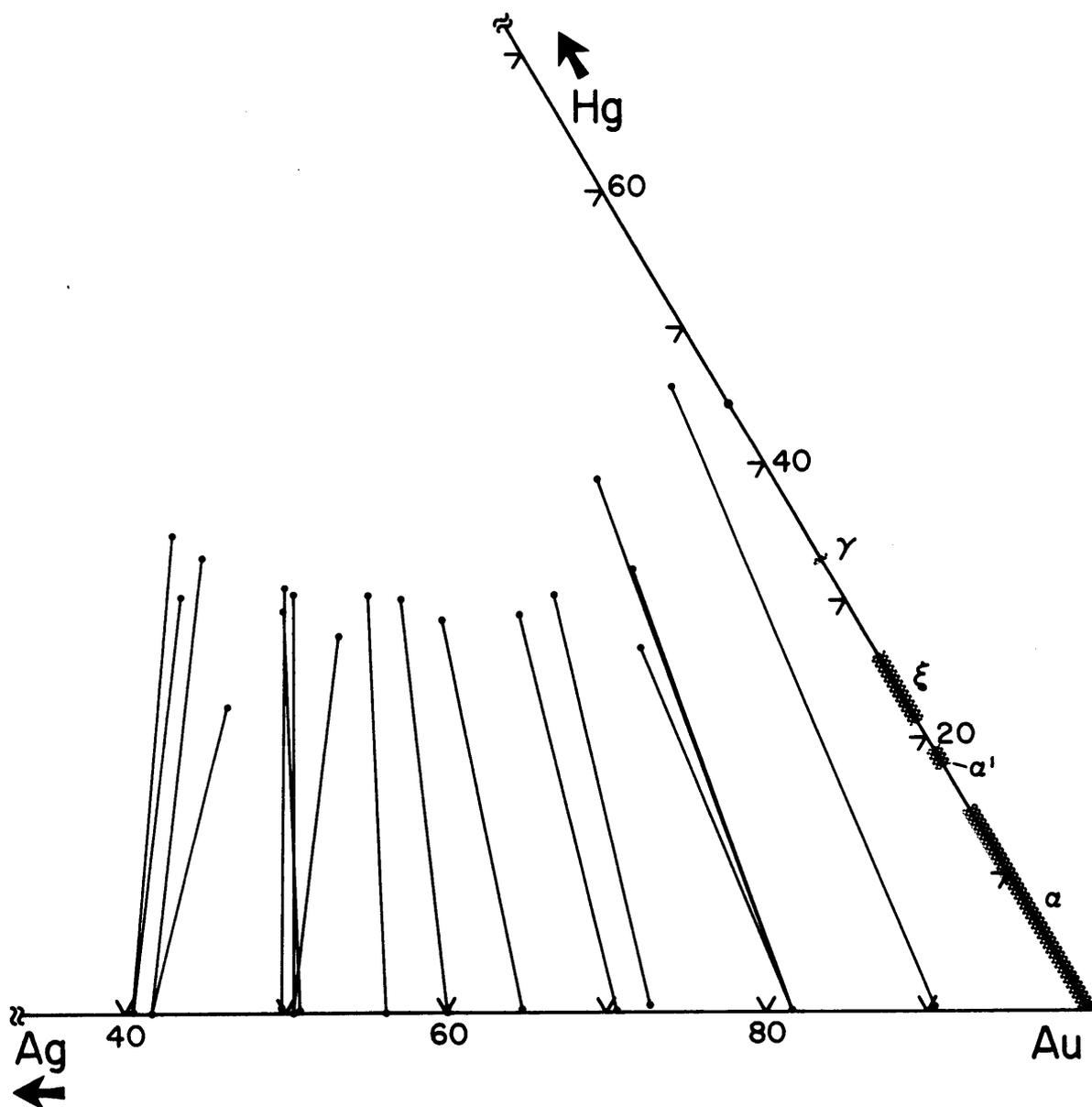


FIG. 13. Gold-rich corner of a ternary Au-Ag-Hg diagram showing the compositions of Au-Ag grain cores and Au-Ag-amalgam rims (both crystalline and massive), experimentally developed on synthetic electrum grains. Tie lines connect coexisting compositions from individual grains. Grains which have more than one tie line indicate differing compositions at different locations on the rim of the particular grain. The shaded areas along the Au-Hg join represent the stable intermetallic compounds at 25° C from Rolfe & Hume-Rothery (1967).

## DISCUSSION

Several explanations have been proposed to account for the higher finenesses and relatively larger sizes of gold grains in placer deposits as compared to those in the lode deposit. Three models of gold-enriched rim formation (leading to high fineness placer deposits) are most plausible: (1) preferential dissolution of silver from placer grains during weathering and transport, (2) precipitation of pure, or nearly pure gold onto placer grains from stream water or stream sediment solutions, or (3) an electrorefining process at the placer grain/solution interface. The occurrence of large gold nuggets is generally ascribed to one of the following processes: (1) preservation of large primary nuggets, (2) accretionary growth by the physical agglomeration of smaller primary nuggets, or (3) chemical growth by supergene enrichment processes active in the soil horizons or the stream waters. Each of these processes is considered; however, the aqueous transport/secondary enrichment process will be the most rigorously examined hypothesis, as it is the only one capable of producing both large nuggets and high fineness placer deposits.

### *Gold-Enriched Rim Formation*

#### (1) Silver Removal from Electrum Grain Margins

The explanations given for the development of gold-enriched rims in the literature most generally invoke a process involving the preferential dissolution of silver from the Au-Ag alloy. The relative solubilities of Au and Ag in low temperature solutions are discussed by Mann (1983 & 1984), and Xue & Osseo-Asare (1985). Although these studies indicate that the preferential silver dissolution model is chemically reasonable, it is not physically reasonable because there is no effective means of bringing the silver atoms

from deeper than a few Ångstroms in the grain into contact with the solution so they can dissolve. One of the few researchers to address this problem was Desborough (1970), who suggested:

"Oxidation of silver from the metal to the ion reduces its size and affords the needed mobility for removal from its site in the alloy, and it is thus placed in solution. The porosity resulting from continued silver removal provides a new interface in the gold-silver alloy for a repetition of the process."

This explanation is rather unlikely because the volume change resulting from the ionization of the silver is insufficient to allow water molecules to access deeper layers in the grain. Also, there are no reports of a similar process acting on other alloys. Finally, gold grains with core finenesses of up to 972 have been observed to develop distinct rims of 998 fineness which would seem improbable according to the above stated mechanism, as the general paucity of silver in the original grain would afford almost no increased porosity along which a leaching solution could encroach. This leaves no physically viable mechanism for removing the silver from a Au-Ag alloy by a leaching type of process.

Another conceivable way to remove the silver from the rims of the electrum grains is by diffusing the silver to the surface where it can dissolve into solution. This possibility was tested by modelling diffusion profiles formed at 25°C in grains initially composed of Au<sub>50</sub>Ag<sub>50</sub> and Au<sub>75</sub>Ag<sub>25</sub>, (equivalent to 646 fine and 846 fine, respectively). These calculations are based on the non-steady-state diffusion in a semi-infinite medium model presented in Darken & Gurry (1953, pp. 441-445). In accordance with this model's requisite boundary conditions, the instantaneous and constant surface concentration of silver in the electrum grain is taken as zero and the initial concentration at the semi-infinite distance remains fixed at the values stated above. The diffusion coefficient of silver in gold at 25°C was estimated from Askill (1984).

Diffusion profiles (Fig. 14a) calculated for reasonable geologic time periods show that silver diffuses much too slowly in such alloys to deplete silver from more than about the outer 2-3Å of the gold grain. In fact, the number of years necessary to produce gold rims approximately equal in thickness to those seen on natural grains (~5 µm) (Fig. 14b), is somewhere between  $10^{17}$  and  $10^{18}$  years (about one million times the age of the universe). Also, this mechanism is incapable of producing the very sharp contacts between the nearly pure gold rims and the electrum cores (Fig. 14b).

## (2) Precipitation of High Fineness Gold from Aqueous Solutions

Despite gold's chemical inertness, it is transported in significant quantities as aqueous complexes at high temperatures to form hydrothermal deposits. At low temperatures, gold is obviously much less soluble, yet it can be complexed by a host of ligands (Tables 3a and 3b). Depending on the concentrations of such ligands, and ambient conditions of Eh, and pH, several of them appear to be capable of causing significant gold transport in the supergene environment. The following pieces of evidence support the hypothesis of low temperature aqueous gold transport: (1) transported gold grains with smooth, well formed crystal faces (Warren 1982), (2) high purity gold crystals on iron oxides in laterites (Mann 1984), (3) gold impregnations of originally carbonaceous matter (Wilson 1984), and (4) secondarily enriched concentrations of gold associated with the recent deposition of iron hydroxides (Lesure 1971).

There are at least two detailed accounts that suggest that there has been secondary enrichment of gold in deposits in the southeastern USA. Lesure (1971) reports on secondary enrichment at the Calhoun mine in Lumpkin Co. GA, where significant concentrations of gold (2.9 ppm) occur in fresh limonite coatings on the walls of an adit. He furthermore suggests that "if a concentration of limonite were found near the water

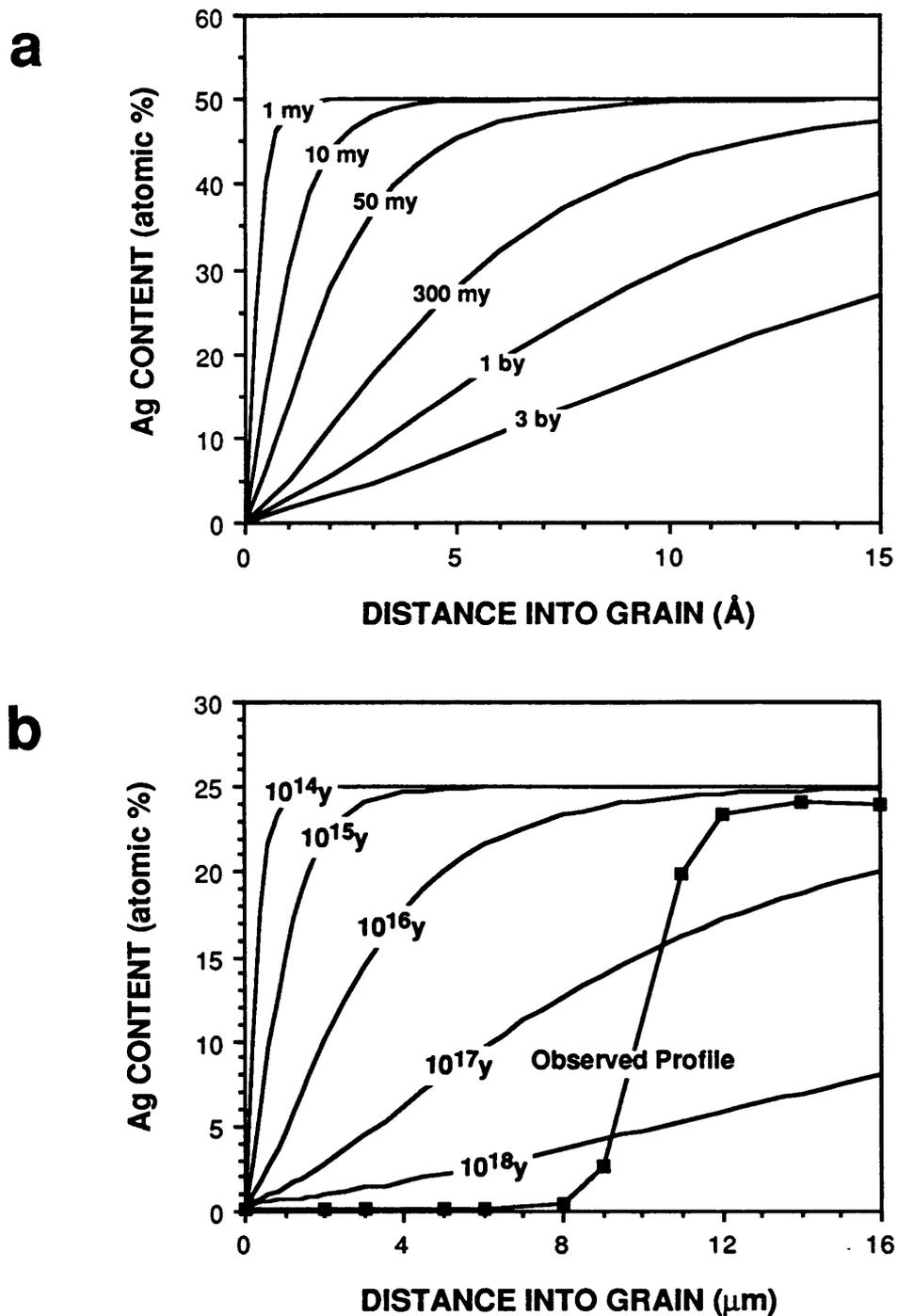


FIG. 14. Calculated diffusion profiles of silver in gold, (a) diffusion profiles of a 50 atomic percent silver, Au-Ag alloy, for all geologically reasonable time periods; (b) diffusion profiles generated for a 25 atomic percent silver, Au-Ag alloy, in an attempt to reproduce the microprobe traverse profile of grain #BC 5-1 (Fig. 3).

TABLE 3a. DISSOLUTION REACTIONS FOR Au<sup>1+</sup> SPECIES

LIGAND	$\Delta G_f^1$	REACTION	log K	$S_C^2$	Ref <sup>3</sup>
<u>No Ligands</u>					
n.a. <sup>4</sup>	176	$\text{Au(s)} + 0.25\text{O}_2 + \text{H}^+ = \text{Au}^+ + 0.5\text{H}_2\text{O}$	-9.34	n.a.	c,d
<u>One Ligand</u>					
S <sup>2-</sup>	21.2	$\text{Au(s)} + 0.25\text{O}_2 + \text{H}^+ + \text{S}^{2-} = \text{AuS}^- + 0.5\text{H}_2\text{O}$	32.80	-31.20	e,d
OH <sup>-</sup>	-38.6	$\text{Au(s)} + 0.25\text{O}_2 + 0.5\text{H}_2\text{O} = \text{Au(OH)(aq)}$	-13.34	n.a.	b,d
HS <sup>-</sup>	61.1	$\text{Au(s)} + 0.25\text{O}_2 + \text{H}^+ + \text{HS}^- = \text{AuHS(aq)} + 0.5\text{H}_2\text{O}$	12.90	-11.30	e,d
SO <sub>3</sub> <sup>2-</sup>	-393.5	$\text{Au(s)} + 0.25\text{O}_2 + \text{H}^+ + \text{SO}_3^{2-} = \text{AuSO}_3^- + 0.5\text{H}_2\text{O}$	5.20	-3.60	e,d
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	-418.7	$\text{Au(s)} + 0.25\text{O}_2 + \text{H}^+ + \text{S}_2\text{O}_3^{2-} = \text{AuS}_2\text{O}_3^- + 0.5\text{H}_2\text{O}$	3.30	-1.71	e,d
<u>Two Ligands</u>					
Cl <sup>-</sup>	-151.12	$\text{Au(s)} + 0.25\text{O}_2 + \text{H}^+ + 2\text{Cl}^- = \text{AuCl}_2^- + 0.5\text{H}_2\text{O}$	1.98	-0.19	d
Br <sup>-</sup>	-115	$\text{Au(s)} + 0.25\text{O}_2 + \text{H}^+ + 2\text{Br}^- = \text{AuBr}_2^- + 0.5\text{H}_2\text{O}$	5.21	-1.81	d
I <sup>-</sup>	-47.6	$\text{Au(s)} + 0.25\text{O}_2 + \text{H}^+ + 2\text{I}^- = \text{AuI}_2^- + 0.5\text{H}_2\text{O}$	11.76	-5.08	c,d
OH <sup>-</sup>	-275.5	$\text{Au(s)} + 0.25\text{O}_2 + 1.5\text{H}_2\text{O} = \text{Au(OH)}_2^- + \text{H}^+$	-13.33	n.a.	a,d
CN <sup>-</sup>	285.8	$\text{Au(s)} + 0.25\text{O}_2 + \text{H}^+ + 2\text{CN}^- = \text{Au(CN)}_2^- + 0.5\text{H}_2\text{O}$	31.82	-15.11	d
HS <sup>-</sup>	0.11	$\text{Au(s)} + 0.25\text{O}_2 + \text{H}^+ + 2\text{HS}^- = \text{Au(HS)}_2^- + 0.5\text{H}_2\text{O}$	25.70	-12.05	e,d
SCN <sup>-</sup>	251.9	$\text{Au(s)} + 0.25\text{O}_2 + \text{H}^+ + 2\text{SCN}^- = \text{Au(SCN)}_2^- + 0.5\text{H}_2\text{O}$	9.84	-4.12	d
SO <sub>3</sub> <sup>2-</sup>	-962.8	$\text{Au(s)} + 0.25\text{O}_2 + \text{H}^+ + 2\text{SO}_3^{2-} = \text{Au(SO}_3)_2^{3-} + 0.5\text{H}_2\text{O}$	19.70	-9.05	e,d
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	-1030.8	$\text{Au(s)} + 0.25\text{O}_2 + \text{H}^+ + 2\text{S}_2\text{O}_3^{2-} = \text{Au(S}_2\text{O}_3)_2^{3-} + 0.5\text{H}_2\text{O}$	19.00	-8.70	e,d
OH <sup>-</sup> , Cl <sup>-</sup>	-215.2	$\text{Au(s)} + 0.25\text{O}_2 + 0.5\text{H}_2\text{O} + \text{Cl}^- = \text{AuOHCl}^-$	-5.34	0.94	a,d
OH <sup>-</sup> , Br <sup>-</sup>	-199.9	$\text{Au(s)} + 0.25\text{O}_2 + 0.5\text{H}_2\text{O} + \text{Br}^- = \text{AuOHBr}^-$	-3.25	-1.16	a,d
<u>Three Ligands</u>					
HS <sup>-</sup> , S <sup>2-</sup>	20.2	$2\text{Au(s)} + 0.5\text{O}_2 + 2\text{H}^+ + 2\text{HS}^- + \text{S}^{2-} = \text{Au}_2(\text{HS})_2\text{S}^{2-} + \text{H}_2\text{O}$	58.70	-14.43 <sup>5</sup>	e,d

<sup>1</sup> Free energy of formation of the gold complex or free gold ion, given in kJ/mol for 25°C and 1 bar.

<sup>2</sup>  $S_C$  = Complexing strength = the logarithm of the activity of the ligand in equilibrium with the corresponding aqueous gold complex solution yielding 1-ppm of gold.

<sup>3</sup> References: a - Hogfeldt 1982, b - Phillips and Williams 1966, c - Schmid 1985, d - Wagman et. al. 1982, e - Webster 1986.

<sup>4</sup> n.a. = Not applicable.

<sup>5</sup> This value is for the logarithm of the HS<sup>-</sup> activity, using a second dissociation constant of hydrogen sulfide equal to 10<sup>-12.9</sup>.

TABLE 3b. DISSOLUTION REACTIONS FOR Au<sup>3+</sup> SPECIES

LIGAND	$\Delta G_f^1$	REACTION	log K	$S_C^2$	Ref <sup>3</sup>
<u>No Ligands</u>					
n.a. <sup>4</sup>	440	$\text{Au(s)} + 0.75\text{O}_2 + 3\text{H}^+ = \text{Au}^{3+} + 1.5\text{H}_2\text{O}$	-12.61	n.a.	d,f
<u>One Ligand</u>					
OH <sup>-</sup>	182.3	$\text{Au(s)} + 0.75\text{O}_2 + 2\text{H}^+ = \text{AuOH}^{2+} + 0.5\text{H}_2\text{O}$	-9.00	n.a.	a,f
<u>Two Ligands</u>					
OH <sup>-</sup>	-52.0	$\text{Au(s)} + 0.75\text{O}_2 + \text{H}^+ + 0.5\text{H}_2\text{O} = \text{Au(OH)}_2^+$	-9.51	n.a.	a,f
SO <sub>4</sub> <sup>2-</sup>	-1090.4	$\text{Au(s)} + 0.75\text{O}_2 + 3\text{H}^+ + 2\text{SO}_4^{2-} = \text{Au(SO}_4)_2^- + 1.5\text{H}_2\text{O}$	-5.37	10.38	g,f
<u>Three Ligands</u>					
Cl <sup>-</sup>	220.1	$\text{Au(s)} + 0.75\text{O}_2 + 3\text{H}^+ + 3\text{Cl}^- = \text{AuCl}_3(\text{aq}) + 1.5\text{H}_2\text{O}$	-43.06	19.48	a,f
OH <sup>-</sup>	-283.37	$\text{Au(s)} + 0.75\text{O}_2 + 1.5\text{H}_2\text{O} = \text{Au(OH)}_3(\text{aq})$	-10.51	n.a.	f
OH <sup>-</sup> , Cl <sup>-</sup>	-217.3	$\text{Au(s)} + 0.75\text{O}_2 + \text{H}^+ + 0.5\text{H}_2\text{O} + \text{Cl}^- = \text{Au(OH)}_2\text{Cl}(\text{aq})$	-3.54	6.93	a,f
OH <sup>-</sup> , Cl <sup>-</sup>	148.4	$\text{Au(s)} + 0.75\text{O}_2 + 2\text{H}^+ + 2\text{Cl}^- = \text{AuOHCl}_2(\text{aq}) + 0.5\text{H}_2\text{O}$	-49.05	29.22	a,f
OH <sup>-</sup> , FA <sup>2-</sup>	----- <sup>5</sup>	$\text{Au(s)} + 0.75\text{O}_2 + \text{H}^+ + 0.5\text{H}_2\text{O} + \text{FA}^{2-} = \text{Au(OH)}_2\text{FA}^-$	-9.04	12.42	e,a,f
<u>Four Ligands</u>					
Cl <sup>-</sup>	-235.14	$\text{Au(s)} + 0.75\text{O}_2 + 3\text{H}^+ + 4\text{Cl}^- = \text{AuCl}_4^- + 1.5\text{H}_2\text{O}$	13.70	0.42	f
Br <sup>-</sup>	-167.3	$\text{Au(s)} + 0.75\text{O}_2 + 3\text{H}^+ + 4\text{Br}^- = \text{AuBr}_4^- + 1.5\text{H}_2\text{O}$	20.92	-1.38	f
I <sup>-</sup>	-45	$\text{Au(s)} + 0.75\text{O}_2 + 3\text{H}^+ + 4\text{I}^- = \text{AuI}_4^- + 1.5\text{H}_2\text{O}$	13.70	0.42	d,f
OH <sup>-</sup>	-453.3	$\text{Au(s)} + 0.75\text{O}_2 + 2.5\text{H}_2\text{O} = \text{Au(OH)}_4^- + \text{H}^+$	-22.28	n.a.	a,f
SCN <sup>-</sup>	561.6	$\text{Au(s)} + 0.75\text{O}_2 + 3\text{H}^+ + 4\text{SCN}^- = \text{Au(SCN)}_4^- + 1.5\text{H}_2\text{O}$	31.05	-3.92	f
OH <sup>-</sup> , Cl <sup>-</sup>	-431.4	$\text{Au(s)} + 0.75\text{O}_2 + 1.5\text{H}_2\text{O} + \text{Cl}^- = \text{Au(OH)}_3\text{Cl}^-$	-7.58	4.96	b
OH <sup>-</sup> , Cl <sup>-</sup>	-371	$\text{Au(s)} + 0.75\text{O}_2 + \text{H}^+ + 0.5\text{H}_2\text{O} + 2\text{Cl}^- = \text{Au(OH)}_2\text{Cl}_2^-$	0.39	1.50	b
OH <sup>-</sup> , Cl <sup>-</sup>	-306	$\text{Au(s)} + 0.75\text{O}_2 + 2\text{H}^+ + 3\text{Cl}^- = \text{AuOHCl}_3^- + 0.5\text{H}_2\text{O}$	7.55	0.61	b
OH <sup>-</sup> , Br <sup>-</sup>	-252	$\text{Au(s)} + 0.75\text{O}_2 + 1.5\text{H}_2\text{O} + \text{Br}^- = \text{Au(OH)}_3\text{Br}^-$	-34.22	31.60	c,f
OH <sup>-</sup> , Br <sup>-</sup>	-334	$\text{Au(s)} + 0.75\text{O}_2 + \text{H}^+ + 0.5\text{H}_2\text{O} + 2\text{Br}^- = \text{Au(OH)}_2\text{Br}_2^-$	3.47	-0.04	c,f

<sup>1</sup> Free energy of formation of the gold complex or free gold ion, given in kJ/mol for 25°C and 1 bar.

<sup>2</sup>  $S_C$  = Complexing strength = the logarithm of the activity of the ligand in equilibrium with the corresponding aqueous gold complex solution yielding 1-ppm of gold.

<sup>3</sup> References: a - Baes and Mesmer 1976, b - Naumov et al. 1974, c - Sillen 1971, d - Schmid 1985, e - Varshal et al. 1984, f - Wagman et al. 1982, g - Webster 1986.

<sup>4</sup> n.a. = Not applicable

<sup>5</sup> FA = Fulvic acid - stoichiometry unknown, therefore  $\Delta G_f$  undeterminable.

TABLE 3b. DISSOLUTION REACTIONS FOR Au<sup>3+</sup> SPECIES (cont'd)

LIGAND	$\Delta G_f^1$	REACTION	log K	$S_C^2$	Ref <sup>3</sup>
----- Five Ligands -----					
OH <sup>-</sup>	-614.2	$\text{Au(s)} + 0.75\text{O}_2 + 3.5\text{H}_2\text{O} = \text{Au(OH)}_5^{2-} + 2\text{H}^+$	-35.64	n.a. <sup>4</sup>	a,f
SCN <sup>-</sup>	654.5	$\text{Au(s)} + 0.75\text{O}_2 + 3\text{H}^+ + 5\text{SCN}^- = \text{Au(SCN)}_5^{2-} + 1.5\text{H}_2\text{O}$	31.01	-3.13	f
----- Six Ligands -----					
OH <sup>-</sup>	-766.4	$\text{Au(s)} + 0.75\text{O}_2 + 4.5\text{H}_2\text{O} = \text{Au(OH)}_6^{3-} + 3\text{H}^+$	-50.51	n.a.	a,f
SCN <sup>-</sup>	747	$\text{Au(s)} + 0.75\text{O}_2 + 3\text{H}^+ + 6\text{SCN}^- = \text{Au(SCN)}_6^{3-} + 1.5\text{H}_2\text{O}$	31.05	-2.61	f

<sup>1</sup> Free energy of formation of the gold complex or free gold ion, given in kJ/mol for 25°C and 1 bar.

<sup>2</sup>  $S_C$  = Complexing strength = the logarithm of the activity of the ligand in equilibrium with the corresponding aqueous gold complex solution yielding 1-ppm of gold.

<sup>3</sup> References: a - Baes and Mesmer 1976, b - Naumov et al. 1974, c - Sillen 1971, d - Schmid 1985, e - Varshal et al. 1984, f - Wagman et al. 1982, g - Webster 1986.

<sup>4</sup> n.a. = Not applicable

table, it might be expected to show supergene enrichment in gold". Cook (1987) has compiled a series of historical accounts of gold mines of Georgia and Alabama, which document large accumulations of coarse gold in quartz veins above the water table but upon intersection with the water table, the veins frequently drop in ore grade. This suggests that gold was oxidized and dissolved near the surface, transported downward by infiltrating meteoric water, and precipitated by the more reducing conditions at depth.

The equilibrium solubility of gold in water as a function of pH is shown in Figure 15 constructed for  $P(O_2) = 0.2$  atm. At the near neutral pH's found in most stream waters, the expected dissolved gold concentrations might range from 200 ppt at pH 4.5 to 50,000 ppt at pH 7.0. These values are only slightly higher than those reported in the literature for some natural solutions (Fig. 15). Nevertheless, these concentrations are probably too low to allow significant gold transport and enrichment, suggesting that gold complexes other than the hydroxy complexes are required for this process.

Tables 3a and 3b were constructed to examine the transporting efficacy of a wide variety of naturally occurring gold complexing ligands. The complexing strength ( $S_C$ ) of the various gold complexes is defined as the logarithm of the concentration of the ligand necessary to yield a solution with 1 ppm of dissolved gold (not gold complex) in equilibrium with metallic gold at pH = 6.0 and  $P(O_2) = 0.2$  atm. The choices of pH and oxidation state are consistent with values commonly found in fresh surface waters (Baas-Becking et. al. 1960). This value of  $S_C$  is used as a "yardstick" to eliminate from consideration all complexing agents which would in no way be capable of producing significant supergene gold transport. Ligands with values of  $S_C$  greater than 0 (equal to a ligand concentration of one molal) are eliminated from further consideration because it is unusual for ligands in average surface and shallow groundwaters to occur at concentrations higher than one molal. Because the solutions in these environments are

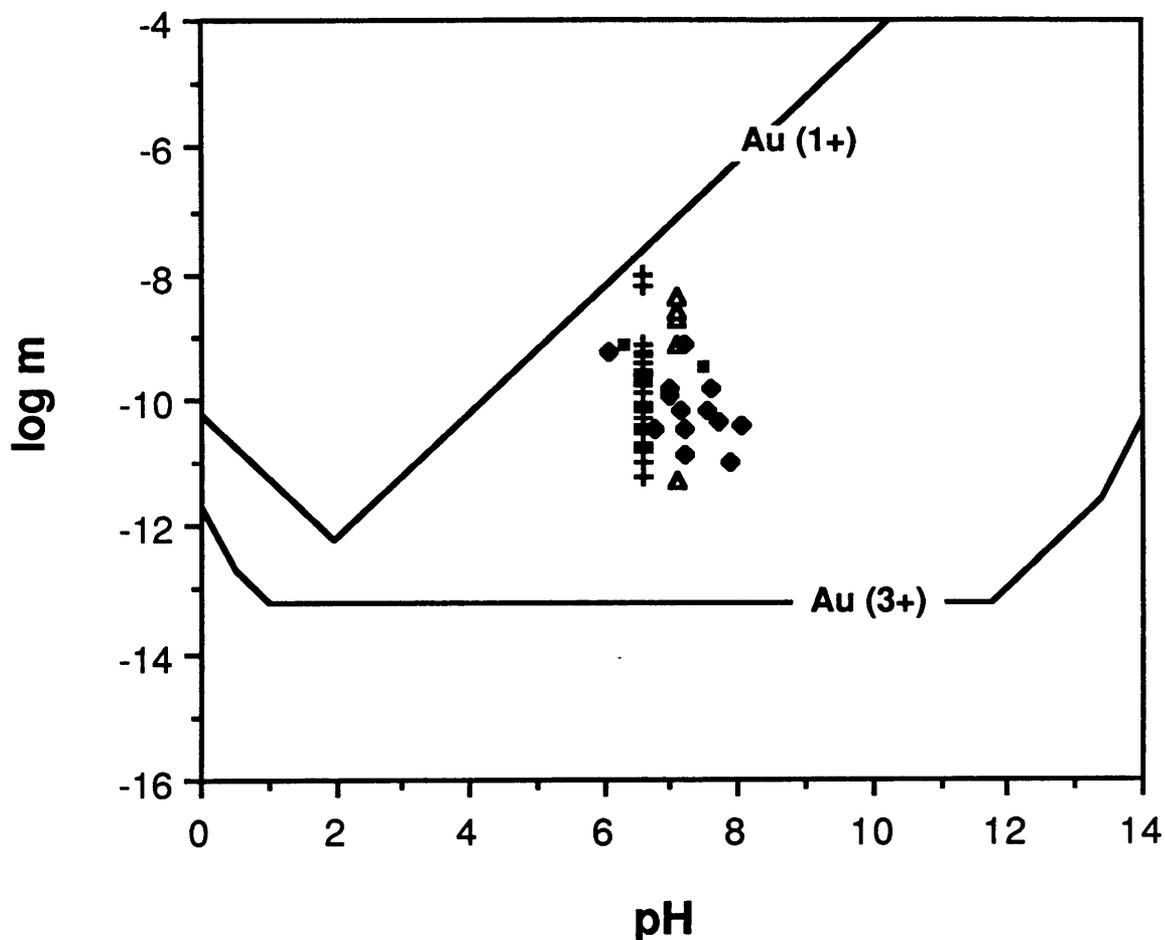


FIG.15. Log concentration (molality) vs. pH diagram for gold-hydroxide complexes and free gold ions in the absence of other ligands. The predominant univalent gold species (indicated by the upper 2 connecting straight line segments) from low to high pH's are:  $\text{Au}^{1+}$  and  $\text{Au}(\text{OH})_2^-$ ; with the concentration of the neutral  $\text{AuOH}$  complex constant at  $10^{-14.23}$  m. The predominant trivalent gold species (indicated by the lower five connecting straight line segments) from low to high pH include:  $\text{AuOH}^{2+}$ ,  $\text{Au}(\text{OH})_2^+$ ,  $\text{Au}(\text{OH})_3(\text{aq})$ ,  $\text{Au}(\text{OH})_4^-$ , and  $\text{Au}(\text{OH})_5^{2-}$ . The  $\text{Au}^{3+}$  concentration line lies approximately parallel to, but about 3.5 log m units below the  $\text{AuOH}^{2+}$  line at low pH's, and the  $\text{Au}(\text{OH})_6^{3-}$  line lies approximately parallel to, but about one log unit below the  $\text{Au}(\text{OH})_5^{2-}$  at high pH's. The solid diamonds represent measured natural gold concentrations of stream waters where the pH was specified (Gosling et al. 1971), and the solid squares represent measured natural gold concentrations for ground waters where the pH was specified (Crocket 1978). The crosses at pH 6.6 represent natural measured gold concentrations of stream waters where the pH was not specified (Jones 1971, Brooks et al. 1981, Lomonosov et al. 1985). The pH value of 6.6 was estimated from Baas Becking et al. (1960). Similarly, a pH of 7.1 was estimated from Baas Becking et al. (1960) to plot natural measured gold concentrations (open triangles) of groundwaters that did not have specified values of pH (Jones 1971, Crocket 1978).

normally quite dilute all activity coefficients were assumed to equal one. According to Table 3, the realistic candidates for supergene gold transport are  $S^{2-}$ ,  $HS^-$ ,  $S_2O_3^{2-}$ ,  $SO_3^{2-}$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $CN^-$ ,  $SCN^-$ , mixed ( $OH^- Br^-$ ), and mixed ( $(HS)^- S^{2-}$ ).

Although all of the candidate ligands selected from Table 3 form strong Au complexes, only a few occur at sufficient concentrations in natural waters to potentially cause significant gold transport. The average concentrations of each ligand in streams and stream sediment solutions were estimated as shown in Table 4 and used in combination with the equilibrium constants given in Table 3 to calculate expected concentrations of the gold complexes. The pH value of 6.0 used for both stream waters and stream sediment waters in Table 4 was estimated from the large compilation of field measurements by Baas Becking et al. (1960). The activity of dissolved oxygen used for the stream water calculations in Table 4 is for an air/water equilibrium wherein the partial pressure of oxygen equals 0.2 atm. The value of  $a(O_2)$  in stream sediment solutions was estimated to be  $10^{-68.6}$ , assuming the solution persists at the  $H_2S/SO_4^{2-}$  boundary (see the log  $a(O_2)$  vs. pH diagram for  $25^\circ C$  and  $\Sigma S = 0.001$  in Barnes 1979). The equilibrium assumption between  $H_2S$  and  $SO_4^{2-}$  is probably valid as the stream sediments build up a sharp redox boundary where  $H_2S$  exists just below the stream bed/stream water interface and  $SO_4^{2-}$  is stable in the stream water. The concentrations of the gold complexes are generally much higher for stream waters than for stream sediment solutions, because the more oxidizing conditions in the stream waters result in much higher activities of gold ions. The most likely complex for significant gold transport in oxidizing stream waters indicated by Table 4 is  $Au(CN)_2^-$ , and in reducing stream sediment solutions both  $Au(CN)_2^-$  and  $AuS^-$  are potentially important, however  $Au(CN)_2^-$  once again dominates. These two complexes were singled out as they are the only ones capable of yielding dissolved gold in quantities close to or greater than 1 ppm. The value given in Table 4 for the "concentration" of

**TABLE 4a. PREDICTED AQUEOUS CONCENTRATIONS OF Au<sup>1+</sup> - COMPLEXES**

Au-complex	log [lig] <sub>sw</sub> <sup>1</sup>	log [cmx] <sub>sw</sub> <sup>2</sup>	log [lig] <sub>sss</sub> <sup>3</sup>	log [cmx] <sub>sss</sub> <sup>4</sup>	Ref. <sup>5</sup>
----- <u>One Ligand</u> -----					
AuS <sup>-</sup>	----- <sup>6</sup>	-----	-16.25	-6.60	d,e,a
AuHS(aq)	-----	-----	-7.99	-18.24	d,e,a
AuS <sub>2</sub> O <sub>3</sub> <sup>-</sup>	-----	-----	-13.47	-33.32	d,e,a
AuSO <sub>3</sub> <sup>-</sup>	-----	-----	-13.25	-31.20	d,e,a
----- <u>Two Ligands</u> -----					
AuCl <sub>2</sub> <sup>-</sup>	-3.65	-12.21	-3.65	-28.47	b,a
AuBr <sub>2</sub> <sup>-</sup>	-6.35	-14.38	-6.35	-30.64	b,a
AuI <sub>2</sub> <sup>-</sup>	-7.42	-9.97	-7.42	-26.23	b,a
Au(OH) <sub>2</sub> <sup>-</sup>	-8.00	-8.22	-8.00	-8.22	a
Au(CN) <sub>2</sub> <sup>-</sup>	-7.42	10.10	-5.81	-2.95	c,e,a
Au(HS) <sub>2</sub> <sup>-</sup>	-----	-----	-7.99	-13.43	d,e,a
Au(SCN) <sub>2</sub> <sup>-</sup>	-7.42	-11.88	-5.81	-28.14	c,a
Au(SO <sub>3</sub> ) <sub>2</sub> <sup>3-</sup>	-----	-----	-13.25	-29.95	d,e,a
Au(S <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> <sup>3-</sup>	-----	-----	-13.47	-31.09	d,e,a
AuOHBr <sup>-</sup>	-8.00, -6.35	-10.49	-8.00, -6.35	-26.74	b,a
----- <u>Three Ligands</u> -----					
Au <sub>2</sub> (HS) <sub>2</sub> S <sup>2-</sup>	-----	-----	-7.99, -16.25	-19.83	d,e,a

<sup>1</sup> log [lig]<sub>sw</sub> = the logarithm of the activity (~ concentration) of the ligand in average stream waters.

<sup>2</sup> log [cmx]<sub>sw</sub> = the logarithm of the activity (~ concentration) of the Au-complex in average stream waters.

<sup>3</sup> log [lig]<sub>sss</sub> = the logarithm of the activity (~ concentration) of the ligand in average stream sediment solutions.

<sup>4</sup> log [cmx]<sub>sss</sub> = the logarithm of the activity (~ concentration) of the Au-complex in average stream sediment solutions.

<sup>5</sup> References: a - Barnes 1979; b - Fuge 1978a,b,c; c - Krutz 1981; d - Shu-zhen 1981; e - Wagman et al. 1982.

<sup>6</sup> Reduced sulfur species are not stable in aerated stream waters. Although they may be released from stream sediments and persist metastably in the stream waters, there are no reports of measurable concentrations of S<sup>2-</sup>, HS<sup>-</sup>, SO<sub>3</sub><sup>2-</sup>, or S<sub>2</sub>O<sub>3</sub><sup>2-</sup> in unpolluted stream waters.

**TABLE 4b. PREDICTED AQUEOUS CONCENTRATIONS OF Au<sup>3+</sup> - COMPLEXES**

Au-complex	log [lig] <sub>sw</sub> <sup>1</sup>	log [cmx] <sub>sw</sub> <sup>2</sup>	log [lig] <sub>sss</sub> <sup>3</sup>	log [cmx] <sub>sss</sub> <sup>4</sup>	Ref. <sup>5</sup>
----- <u>Two Ligands</u> -----					
Au(OH) <sub>2</sub> <sup>+</sup>	-8.0	-18.19	-8.0	-66.96	a
----- <u>Three Ligands</u> -----					
Au(OH) <sub>3</sub> (aq)	-8.0	-13.19	-8.0	-61.96	a
----- <u>Four Ligands</u> -----					
AuBr <sub>4</sub> <sup>-</sup>	-6.35	-25.15	-6.35	-73.93	b,a
AuI <sub>4</sub> <sup>-</sup>	-7.42	-14.14	-7.42	-62.91	b,a
Au(OH) <sub>4</sub> <sup>-</sup>	-8.0	-18.96	-8.0	-67.73	a
Au(SCN) <sub>4</sub> <sup>-</sup>	-7.42	-19.29	-5.81	-61.64	c,a
Au(OH) <sub>2</sub> Br <sub>2</sub> <sup>-</sup>	-8.0, -6.35	-17.91	-8.0, -6.35	-66.70	b,a
----- <u>Five Ligands</u> -----					
Au(SCN) <sub>5</sub> <sup>2-</sup>	-7.42	-26.74	-5.81	-67.49	c,a
----- <u>Six Ligands</u> -----					
Au(SCN) <sub>6</sub> <sup>3-</sup>	-7.42	-34.12	-5.81	-73.26	c,a

<sup>1</sup> log [lig]<sub>sw</sub> = the logarithm of the activity (~ concentration) of the ligand in average stream waters.

<sup>2</sup> log [cmx]<sub>sw</sub> = the logarithm of the activity (~ concentration) of the Au-complex in average stream waters.

<sup>3</sup> log [lig]<sub>sss</sub> = the logarithm of the activity (~ concentration) of the ligand in average stream sediment solutions.

<sup>4</sup> log [cmx]<sub>sss</sub> = the logarithm of the activity (~ concentration) of the Au-complex in average stream sediment solutions.

<sup>5</sup> References: a - Barnes 1979; b - Fuge 1978a,c; c - Krutz 1981; d - Shu-zhen 1981; e - Wagman et al. 1982.

$\text{Au}(\text{CN})_2^-$  is obviously misleading as 2.5 billion metric tons of gold per liter of solution is unrealistic. What the value can be interpreted to mean, however, is that every hydrocyanic acid molecule which is available in solution will complex any available atom of gold to form an  $\text{Au}(\text{CN})_2^-$  complex and hence the limiting factor in terms of attainable concentrations of gold is the amount of hydrocyanic acid molecules that can be produced and supplied to the stream.

The  $\text{CN}^-$  concentration used for stream waters in Table 4 was  $1 \mu\text{g/l}$  ( $10^{-7.42} \text{ m}$ ) which was estimated from the values given by Krutz (1981) who measured the yearly variation in cyanide content of the Wehebach Brook, which drains a wooded and pastured area in Germany. Krutz (1981) also states "The sediment fraction with a particle diameter less than 1 mm contains about 0.2 mg/kg of total cyanide, only a small amount of it being easily set free (0.04 mg/kg)." Accordingly, the  $\text{CN}^-$  concentration used in Table 4 for stream sediments was  $40 \mu\text{g/l}$  ( $10^{-5.81} \text{ m}$ ). The same respective estimates were used for the concentrations of  $\text{SCN}^-$  in Table 4, as it was assumed that cyanide would probably be present in similar concentrations whether or not the solutions were sulfur-rich enough to convert the  $\text{CN}^-$  to  $\text{SCN}^-$ . The values of  $\text{H}_2\text{S}$  and  $\text{S}^{2-}$  concentration used for soil solutions in Table 4 were taken from the work of Shu-zhen (1981) who measured the concentrations of these species in a neutral paddy soil which was regulated to different pH values. The reported concentrations are likely to be reasonably close to those expected in waterlogged stream sediments containing some organic matter. The stream sediment solution concentrations of the other sulfur-bearing ligands ( $\text{HS}^-$ ,  $\text{S}_2\text{O}_3^{2-}$ , and  $\text{SO}_3^{2-}$ ) were calculated assuming that they are in equilibrium with the estimated  $\text{H}_2\text{S}$  concentration under the redox and pH conditions specified for the stream sediments. This approach is likely to underestimate the concentrations as these species are formed by partial oxidation of  $\text{H}_2\text{S}$  and may persist at higher metastable concentrations (Giggenbach 1974, Hoffman

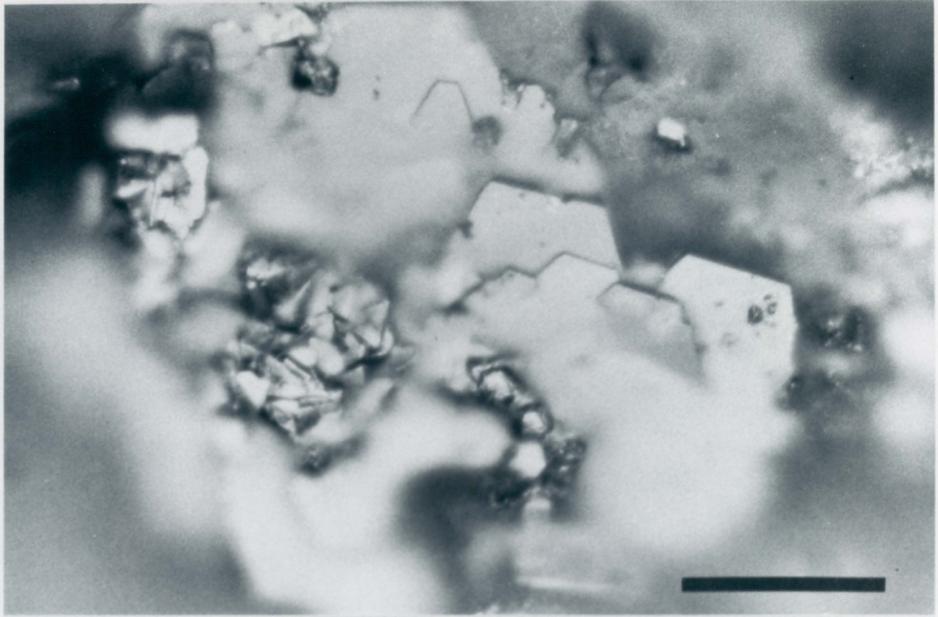
1977). The discovery of numerous small copper sulfide crystals growing on the surfaces of recent U.S. coins found while panning in Brush Creek substantiates the presence of significant amounts of sulfide in these stream sediments (Groen et al. 1986). The crystals basically have two different types of morphology: roughly orthogonal prisms and trigonal to hexagonal plates, the latter being more common (Fig. 16). The hexagonal plates are presumed to be covellite and the orthogonal crystals to be chalcocite. Based on the  $\log a(\text{S}_2)$  vs.  $\log a(\text{O}_2)$  diagram for copper of Garrels and Christ (1965, p. 160), the covellite is only stable for  $\log a(\text{S}_2)$  greater than about -21.0 ( $\log a(\text{S}^{2-}) = -33.2$ ) with corresponding  $\log a(\text{O}_2)$  values of less than about -2 to -3. These estimates are consistent with those given by Shu-zhen (1981), but indicate that the  $\text{S}^{2-}$  concentration used in Table 4 might be high for some environments, but not for all (i.e. paddy soils).

Various studies indicate a wide variety of natural sources of cyanide, including certain plants (Krutz 1981, Warren 1982), and algae (Vennesland et al. 1981). Seigler (1981) describes some of the natural sources of cyanogenic glycosides and cyanolipids, which upon hydrolysis liberate hydrogen cyanide; they include apricot, peach, and almond trees as well as other important food plants, ferns, gymnosperms, both monocotyledonous and dicotyledonous angiosperms, fungi, bacteria, and several insects. Altogether, cyanide is produced by more than 2050 plant species. Human sources of cyanide such as steel and galvanic industries, fertilizers, and domestic sewage can elevate the cyanide level of streams to 200  $\mu\text{g/l}$  Krutz (1981).

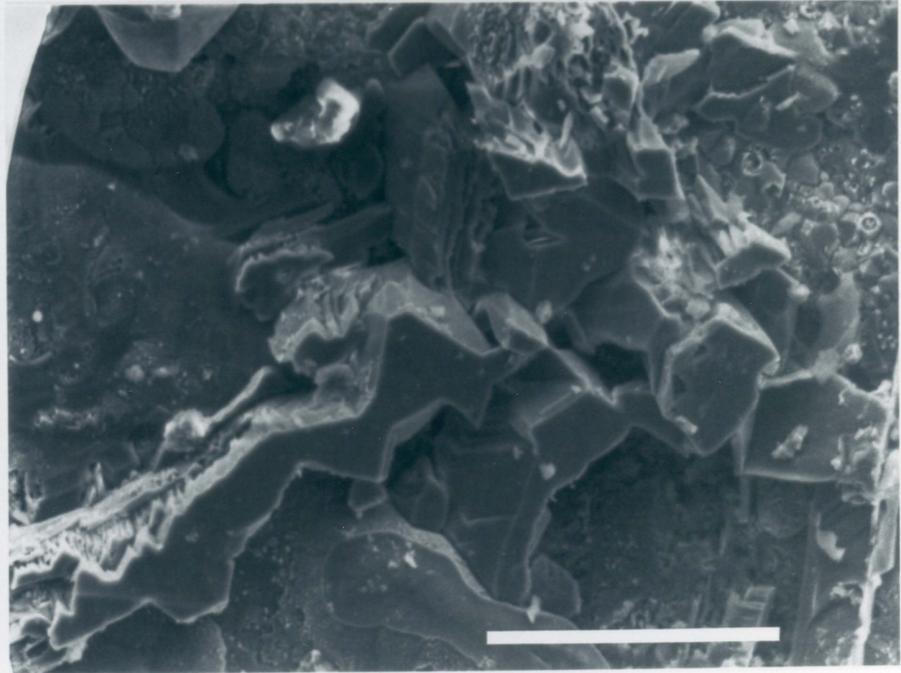
Table 4 indicates that cyanide is by far the most effective complexing agent of gold in both oxidizing and reducing conditions but there are currently very few actual measurements of  $\text{CN}^-$  concentrations in natural waters, so the values estimated here might be significantly too low. The sulfur-bearing ligands are the most effective complexers of gold in reducing environments after cyanide, with the bisulfide and sulfide species as

FIG. 16. Photomicrographs of copper sulfide crystals. (a) Reflected light photomicrograph of crystals on the surface of a 1984 quarter (scale bar = 50  $\mu\text{m}$ ), (b) scanning electron photomicrograph of crystals on the surface of a 1969 dime (scale bar = 50  $\mu\text{m}$ ), (c) scanning electron photomicrograph of crystals on the surface of a 1969 dime (scale bar = 50  $\mu\text{m}$ ). All samples were panned from Brush Creek, Virginia.

**a**



**b**



**C**

most important under the model conditions used in this study. In oxidizing waters the  $\text{Au}(\text{OH})_2^-$  species appears to be the most important complexing agent after cyanide, even though at a pH of 6.0, it can produce aqueous gold concentrations of only a few parts per billion. Table 4 also indicates the  $\text{AuI}_2^-$  and  $\text{AuOHBr}^-$  complexes as being worthy of notice, but iodine and bromine rarely attain significant concentrations in natural systems.

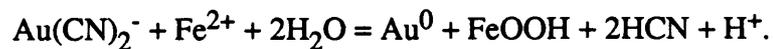
Thiosulfate has been attributed as a likely transporter of gold in low temperature aqueous systems (Goleva et al. 1970, Stoffregen 1986). Table 4 indicates that this ligand is not especially important, but as stated above, metastable concentrations of thiosulfate are quite possible which would increase the transporting capacity of the species. The maximum metastable concentrations that thiosulfate can attain, however, are unknown. Furthermore, Stoffregen's study area is one of low pH and presumably high sulfur species concentrations (weathering sulfide ore deposit), which both favor the formation of the gold thiosulfate complexes of Table 3. As this study is modelling gold transport for a pH of 6.0, and metastable thiosulfate concentrations are unknown, the conclusion reached above is retained.

### (3) Mechanisms of Precipitation.

Gold precipitation from solution takes place by the reduction of the  $\text{Au}^{1+}$  or  $\text{Au}^{3+}$  ion. A commonly cited method is by contact of the aqueous gold complex with reducing ground waters. Other distinct redox boundaries exist in nature other than at the top of the groundwater table though, such as at the interface between stream waters and organic rich sediments in stream channels. In Brush Creek such sharp redox boundaries obviously exist as copper sulfides are able to grow only an inch or two below the stream water/sediment interface.

Precipitation of aqueous gold complexes appears, however, to have only recently been examined on a realistically detailed chemical basis (e.g. Mann 1984, Stoffregen

1986). The precipitation mechanism put forth by Mann (1984) utilizes the reducing agent  $\text{Fe}^{2+}$  which is released from weathering rocks. The  $\text{Fe}^{2+}$  ion, upon liberation, can migrate in solution until it encounters oxidizing conditions, such as at the ground water table or at the stream water/sediment interface. At this point, oxidation of the ferrous iron can take place in a variety of ways, one of which is by releasing its available electron to a gold complex which results in the simultaneous precipitation of native gold and a ferric hydroxide, as in the following reaction:



Strong supportive evidence for this sort of process is provided by observations made in this study, such as the occurrence of iron-hydroxide coatings on many of the recovered placer grains and the presence of such inclusions in the gold-enriched rims described above. Finally, there is an abundance of published works which mention the frequent association of the two phases (Desborough 1970, Lesure 1971, Mann 1984, Wilson 1984, DiLabio et al. 1985).

### (3) Electrorefining at the Placer Grain/Solution Interface

Another process which could produce gold-enriched rims on placer electrum grains is electrorefining (Wadsworth & Miller 1979). Strickland and Lawson (1973) describe "cementation" (a hydrometallurgical term for electrorefining) as: "...the electrochemical precipitation of a metal, usually from an aqueous solution of its salts, by a more electropositive metal." This process results in surfaces bearing lobate protrusions of the deposited metal (crystalline growths have also been reported) because random sites on the surface of the more electropositive metal must remain exposed to the solution so dissolution and electron liberation can occur and hence there are also sites on the surface where the metal tends to deposit out (i.e. the lobate texture). The branching coral-texture

of Figure 5 is very similar to the lobate, branching diagrammatic representations of cementation in Strickland and Lawson (1973) and suggests a precipitative origin for the observed texture. Mann (1984) performed some electrochemical experiments which show that in certain solutions (i.e. 0.03 M HCl - 1 M NaCl) there is a distinct increase in Au-Ag alloy stability with increasing electrum fineness as measured against a pure gold electrode, suggesting lower reduction potentials for lower fineness alloys. Microprobe analysis of portions of electrum grains exhibiting this texture showed them to be essentially pure gold (grain no. SM96982, 992 to 1000 fine, Table 1). The more highly developed (i.e. thicker and more widespread surficial coverage) cases of this texture grade into the less skeletal, but still porous, gold-enriched rims described as swiss-cheese-like (Fig. 5). This chemical and textural similarity of the gold-enriched rims to the branching coral-texture suggest the latter to simply be an incipient case of the former.

The results of Mann (1984), provide the background for looking into the possibility of the same process occurring to placer gold wherein electrum grains would oxidize releasing Au-ions, Ag-ions, and electrons into solution. Once in solution, however, the less electropositive Au-ions would immediately plate back out of solution, yielding the textures described above. The resulting electrolytic reaction would be self perpetuating, provided the ambient solution was of adequate composition to allow the initial oxidation of the Au-Ag alloy and also retain the silver in solution but not the gold. Rudimentary forms of this idea were suggested more than 50 years ago (Fisher 1935).

### *Formation of Large Nuggets*

#### (1) Preservation of Large Primary Nuggets

The simplest explanation for large nuggets is that they are merely large lode grains that have survived weathering and erosional processes. If this origin were valid, it would

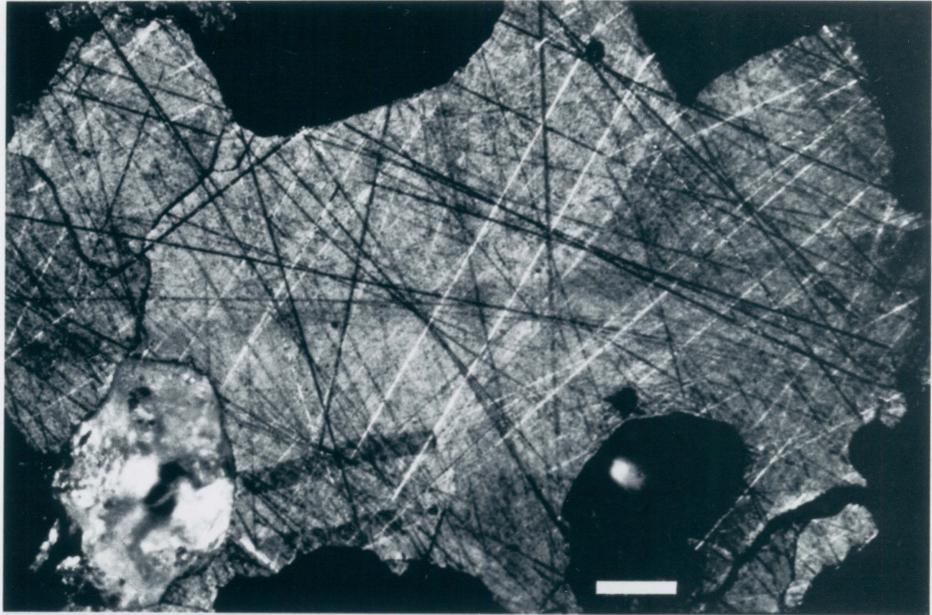
seem likely that at least some large nuggets would have been discovered in lode deposits in all the years of active mining, especially considering the wide geographical distribution of large placer nugget finds in the southeastern U.S. Furthermore, the only large non-placer gold grains yet found in the southeastern U.S. have come from shallow horizons above the water table (Cook 1987), an observation consistent with a secondary enrichment origin.

## (2) Accretionary Mechanical Growth

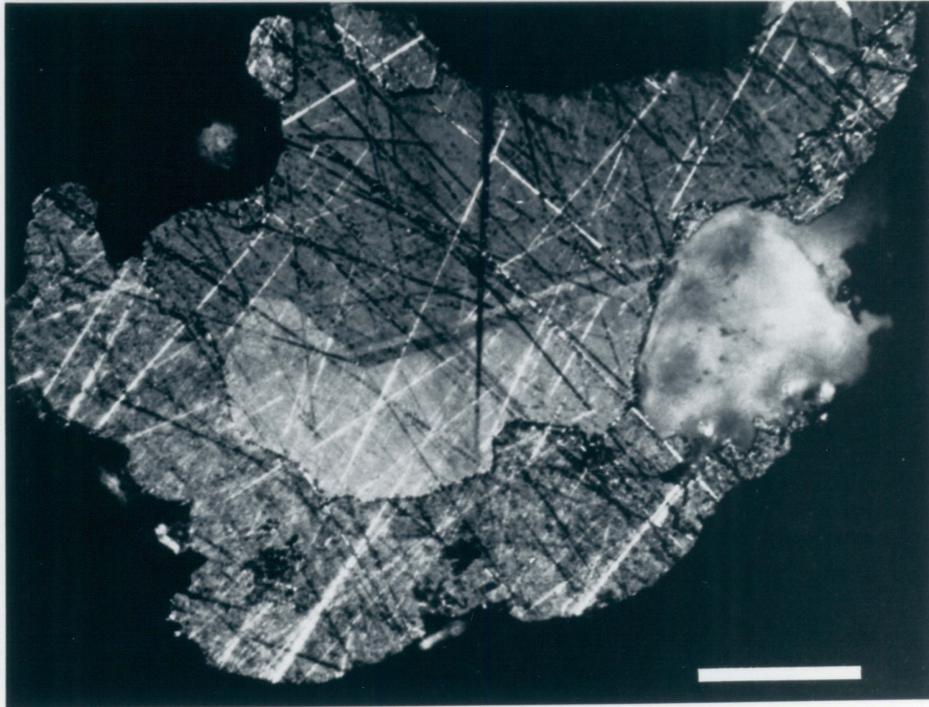
The formation of large gold nuggets via agglomeration of smaller placer gold grains has frequently been hypothesized. Yeend's 1975 work on the experimental abrasion of detrital gold particles, however, shows that mechanical working of gold mixed with clastic silicates (similar to those encountered in stream channels) promotes the breakdown of individual nuggets into numerous smaller particles. The results were similar for five different sets of experimental conditions which employed wet and dry tumbling, differing grain sizes, and differing lithologies of the tumbling medium. The results of panning at progressive points downstream on Brush Creek support Yeend's conclusions, as all the grains found downstream were much smaller ( $\sim 0.02$  mm) compared to the average size of those at the headwaters of the creek ( $\sim 0.1 - 0.2$  mm). Cross sections through the largest grains observed in this study show no signs of mechanically adhered subgrains, either when polished, or when polished and etched. The etching did, however, reveal relatively delicate lath shaped twin-like features in several grains. These features occasionally extend to grain margins and display no evidence of mechanical abrasion or distortion (Fig. 17). The fineness of the lode derived cores of the gold grains found in Brush Creek range from 549 to 849. If such grains were agglomerated to form a nugget, it should contain a patchwork of subgrains of notably different compositions. Examination of the largest gold grains ( $\sim 1.5$  mm) from Brush Creek shows quite the opposite in that they all

FIG. 17. Reflected light photographs of etched polished sections of two placer gold grains from the Lilesville quadrangle, NC, (a) grain number NC85L86-8 shows delicate twin-like features adjacent to the grain boundary (scale bar = 100  $\mu\text{m}$ ), (b) grain number NC85L86-5 shows the same feature very well. The darker, irregular zone around the bottom of this grain is a well developed gold enriched rim, as are the spotty areas on the top and right side of the grain (scale bar = 100  $\mu\text{m}$ ).

**a**



**b**



have cores of uniform fineness. Thus the larger grain cores appear too texturally homogeneous to have been formed by the agglomeration of smaller grains. Based on the above lines of evidence, the formation of large nuggets by agglomeration of smaller grains is not responsible for the largest grains examined in this study.

### (3) Secondary Growth by Chemical Processes

The gold-enriched rims and euhedral surficial gold crystals examined in this study appear to be the only results of extended exposure to stream and sediment waters upon liberation from the host rock. The euhedral gold crystals are most likely the result of secondary enrichment, and the gold-enriched rims are formed by secondary enrichment, electrolytic refining, or a combination of the two processes. The stated phenomena are all constructive processes, effecting an overall enlargement of the gold grain, except for electrolytic refining (assuming it is the sole process). It is possible that gold-enriched rims are incipient cases of large nugget formation, and if the gold grains remained in the soil or stream sediments long enough, some might grow to the remarkable sizes reported from the Reed deposit. The validity of this idea could be tested by analysis of large gold grains. If they formed by the overgrowth process, their fineness should be comparable to those of the commonly found gold-enriched rims.

## CONCLUSIONS

In depth examination of the physical and chemical properties of placer gold grains from several localities in the southeastern U.S. yields significant information concerning post-liberation alteration processes. Newly liberated gold grains are most often irregularly shaped, but as a result of stream transport they become semi-spherical, wafer- and finally flake-shaped. Their surfaces evolve from smooth and clean to pitted, hackly, and eventually to lobate textured surfaces. Grain size declines with increasing distance of transport. Density measurements of nine of the examined gold grains show that such data will not predict the exact fineness of the gold grain, but the technique can be used to set upper limits on the fineness of the grain and provide a "rule of thumb" estimator of the fineness.

Sectioning of the grains revealed rim-preferred patterns of mineral inclusion distribution, and the occurrence of nearly pure gold rims around the outer edges of approximately 80% of the placer gold grains. These rims have very sharp boundaries with the inner cores of lower fineness, and are the result of alterations that were incurred in the stream or sediments. The rims are generally thickest on flake shaped grains and thinnest or absent on irregular grains, pointing to a relationship between morphology and rim development.

Mercury-contamination of placer gold is a common occurrence in numerous areas and results in the formation of Au-Ag-Hg intermetallic amalgams on the surfaces of the gold grains. The amalgam compositions approach an experimentally determined curve of maximum Hg-content for low temperatures over the range of 550-1000 fine. Contamination by mercury results in several surface features, probably the most significant of which is euhedral crystals of differing crystal systems, that attain 35  $\mu\text{m}$  in maximum

dimension. Several of the Au-Ag-Hg crystals grown in the laboratory appear isometric, thus indicating the need for caution in identifying "supergene gold crystals" on the basis of morphology alone.

Several proposed mechanisms of gold-enriched rim development were evaluated on the basis of observational evidence and theoretical calculations. Leaching of silver from the margins of gold grains was dismissed because there is no means by which the solutions could physically extract the silver from more than the outer few Ångstroms of the electrum grain surface. Diffusion of silver through the electrum to make it available to solution was also dismissed on the basis of extremely slow diffusion rates at low temperatures. The possibility of gold dissolution and reprecipitation by means of aqueous complexes appears to be possible if sufficient  $\text{CN}^-$  and  $\text{S}^{2-}$  concentrations can form in normal stream and sediment waters.  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{HS}^-$ ,  $\text{SO}_4^{2-}$  are also potentially capable of significant gold transport provided they have sufficient metastable persistence. Sharp redox boundaries such as at the stream water/sediment interface are the most likely initiators of reprecipitation. Electrolytic refining of placer electrum grains is a very credible process, as the required conditions are present in stream environments and the textures observed match those reported from controlled hydrometallurgical experiments. A combination of electrolytic refining and precipitation of aqueous, complexed gold from sources other than the electrolytic cell could explain the formation of the gold-enriched rims as well as the surface textures on electrum grains.

The formation of large nuggets by agglomeration of smaller grains and nuggets is disputed by the characteristics observed, and the possibility of the large nuggets being remnants of completely eroded deposits has no supportive evidence. Secondary enrichment is therefore proposed as the most likely origin of the numerous large nuggets discovered in the southeastern United States.

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