Canadian Mineralogist
Vol. 28, pp. 207-228 (1990)

GOLD-RICH RIM FORMATION ON ELECTRUM GRAINS IN PLACERS

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ABSTRACT

Grains of placer gold from several localities in the southeastern United States exhibit a high-purity gold rim. The individual rims on the various grains range from <1 to 60 μm in thickness and have silver contents of 3.3 to 0 wt.% (average of 0.9 wt.%), even though the core compositions range from 45.1 to 2.8 wt.% silver. This gold rimming most likely is responsible for the commonly cited cases of gold from placer deposits assaying at higher values of fineness than the gold in the corresponding source lode. A gold-rich rim apparently forms by precipitation of gold from the surrounding solution, because simple leaching of silver from the electrum surface is an ineffective mechanism for the enrichment of gold. Diffusion of silver to the surface of a placer gold grain to expose it to oxidizing meteoric waters, and thus create a diffusion-enhanced leaching process, proceeds far too slowly to produce the observed natural rim thicknesses; furthermore, this mechanism fails to produce the sharp gradients in concentration observed in natural grains. Comparison of the complexation efficacies of 49 different ligands indicates CN^-, OH^-, NH_3, Cl^-, I^-, Br^-, and HS^- to be the ligands most capable (in decreasing order) of transporting gold in ordinary stream environments. Self-electrorefining of placer electrum grains is a likely process of forming gold-rich rims and probably operates in tandem with dissolution–precipitation (cementation) to produce the observed phenomena.

Keywords: gold (Au), silver (Ag), secondary gold enrichment, $Au(CN)_2^-$, electrum, gold rims, gold transport, electrorefining, aqueous complexes, gold-species thermodynamics.

SOMMAIRE

À plusieurs endroits dans le sud-est des Etats-Unis, les particules d'électrum des graviers aurifères montrent une bordure en or très pur. Ces bordures peuvent atteindre 60 μm en épaisseur, et contiennent entre 3.3 et 0% en poids d'Ag (en moyenne, 0.9%), malgré le fait que le noyau de ces particules en contient de 45.1 à 2.8%. La présence d'un tel liseré d'or serait responsable de la teneur accrue en or des particules d'électrum des graviers aurifères, comparées à leurs sources minéralisées. La bordure se forme par précipitation de l'or à partir des solutions environnantes; un simple lessivage de l'argent de la surface des particules d'électrum est inefficace comme mécanisme d'enrichissement. La diffusion d'atomes d'Ag vers la surface d'un grain d'or dans un sable, pour les mettre en contact avec l'eau météorique oxygénée, et ainsi créer un mécanisme de lessivage qui dépend de la diffusion, procède beaucoup trop lentement pour expliquer les épaisseurs observées. De plus, ce mécanisme ne peut expliquer la présence de gradients abrupts en composition. Une comparaison de l'efficacité relative de complexation de 49 ligands différents montre que CN^-, OH^-, NH_3, Cl^-, I^-, Br^- et HS^- (en ordre décroissant) pourraient transporter l'or dans un tel milieu. Un processus d'autoélectro-affinage des grains d'électrum dans un gravier serait impliqué dans l'origine de ces bordures, et agirait avec un phénomène de dissolution et précipitation (cimentation) pour produire les liserés.

(Traduit par la Rédaction)

Mots-clés: or (Au), argent (Ag), enrichissement secondaire en or, $Au(CN)_2^-$, électrum, bordures d'or, transfert de l'or, électro-affinage, complexes aqueux, thermodynamique des complexes aurifères.

INTRODUCTION

Gold, since before recorded history, has been the most prized of mineral possessions. Because of its great value, economic concentrations of gold can be physically small in size and can contain as little as 1–3 ppm gold so dispersed that the deposits are difficult to locate and recognize. Consequently, most of the great gold rushes of history, and indeed many recent discoveries, resulted not from initial location of primary gold-bearing deposits, but rather from the detection and recovery of placer gold, which was concentrated in streams after erosion of the source lode deposits. In many areas, only the placer deposits have proven to be economical to exploit. In 1497, Ulrich Rulein von Kalbe stated that "The gold generated in river sand is the purest and most exalted kind because its matter is most thoroughly refined by the flow and counterflow of the water and also because of the characteristics of the location where such gold is found, that is, the orientation of the river in which such placer gold is made" [translation by Sisco & Smith (1949)]. Since at least as early as von Kalbe's time, reports have indicated that the gold in placer deposits is generally purer than that in the lode deposits from which the placers were derived (Lindgren 1911, Boericke 1936, Emmons 1937, Mackay 1944, Fisher 1945, Koshman & Yugay 1972, Mann 1984). The purity of gold is expressed in terms of fineness, which is the concentration of gold in an alloy (in wt.%) divided by the concentrations of gold and silver, the quantity then multiplied by 1000.

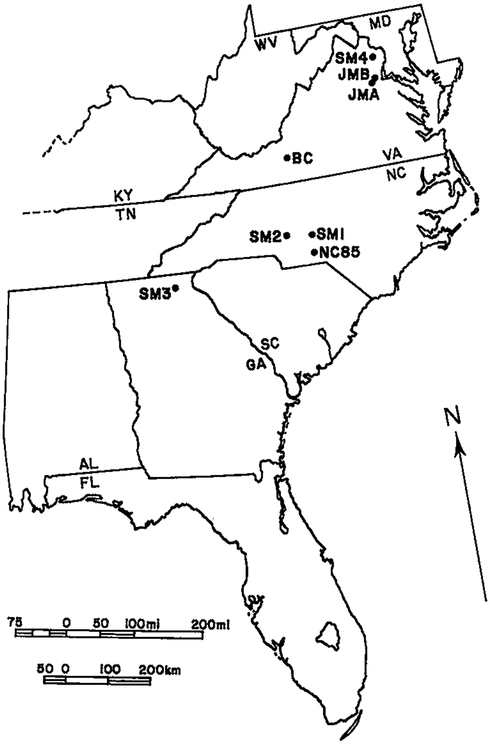

FIG. 1. Sample localities of the gold from this investigation (from north to south): SM4 Manassas quadrangle, Virginia; JMB Storck quadrangle, Virginia; JMA Chancellorsville quadrangle, Virginia; BC Brush Creek, Virginia; SM2 Cabarrus County, North Carolina; SM1 Montgomery County, North Carolina; NC85 Lilesville quadrangle, North Carolina; SM3 White County, Georgia.

Grains of lode and placer gold are very rarely pure. They invariably contain significant amounts of silver, and occasionally minor 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 that contains more than 20% silver is generally referred to as electrum, but there is considerable variation in this arbitrarily set compositional definition. In this study, "electrum" will be used only as a qualitative term to emphasize the fact that at least minor silver is present in the alloy. Craig & Rimstidt (1985) compiled analytical data for nearly 6500 samples of natural gold, and found that virtually all the samples fall in the range of 500 to 1000 fine, with the mode at approximately 920 fine.

The present study examines the nature of placer gold grains from some localities in the southeastern United States and evaluates the processes that may contribute to the formation of the gold-rich rim found on many of these grains. Inasmuch as the processes active in this study area are representative of those operating in most other localities, the conclusions of this study are believed to have general applicability.

The samples examined in this study were obtained from several localities in the southeastern United States (Fig. 1), an area with a moist, temperate climate and oak–hickory-predominant forests. Extensive weathering has occurred in the area owing to prolonged subaerial exposure and a current annual precipitation of 100–200 cm. These environmental conditions subject the gold grains to substantial chemical attack, with local variations manifested in differing water and gold chemistries, and the extent of human influences. All streams from which samples for this study were collected have streambeds that contain mud to pebble- or cobble-sized sediment, and generally abundant organic matter (hence a relatively low Eh) in the finer sediment fractions. Gold grains from Brush Creek in southwest Virginia received the most attention.

CHARACTERISTICS OF THE GRAINS OF PLACER GOLD

The morphology of the grains is influenced by numerous factors, including character of the original lode particles, stream energetics, nature of the stream channel material, time spent in the stream, distance of transport, and chemistry of the stream water. More than 300 gold grains from Brush Creek were closely examined to identify relationships between morphology and some of these parameters. The grains were divided into the following five general morphological groups: irregular (~41%, spherical to semispherical (~33%), wafer-shaped (width-to-thickness ratio ≤5) (~14%), flake-shaped (width-to-thickness ratio ≥5) (~11%), and cylindrical (~1%). The grains recovered from Brush Creek during this study range in size from less than 0.01 mm to 2 mm (maximum dimension); weights range from less than 0.01 to nearly 10 mg.

The surficial features of many of the gold grains were investigated under reflected light and by scanning electron microscopy. Although the surficial textures represent a wide and probably continuous spectrum, they have been broadly classified into the six types shown and described in Figure 2. The general relationships between grain morphologies and surface textures are quantified in Figure 3. The most prevalent correlation exists between irregular grain morphologies and smooth, unpitted surfaces. Many of the other relationships are not as universal, but a general diagonal trend of compatible morphologies and surface textures can be seen from the upper left to the lower right of Figure 3, where a good

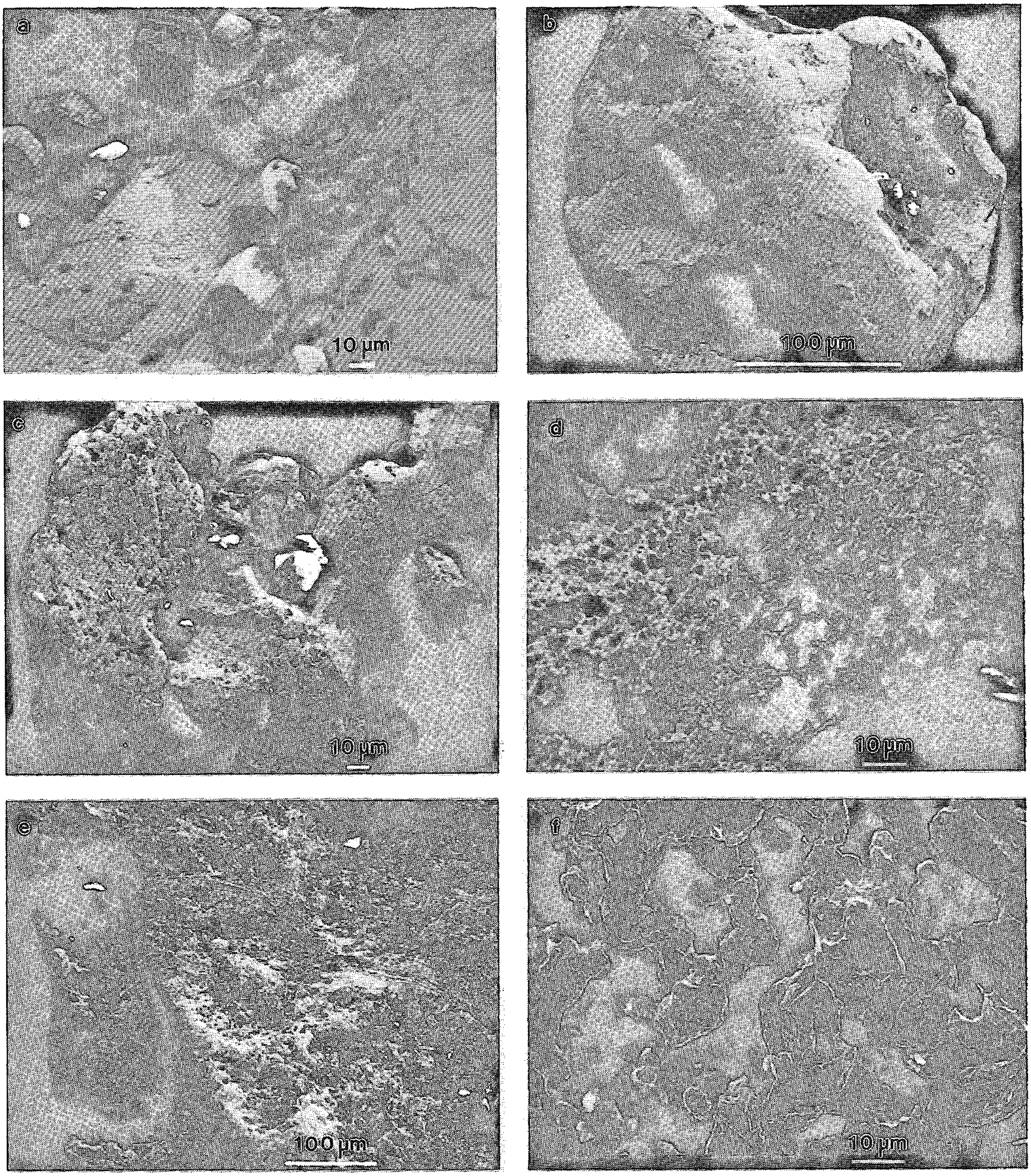

FIG. 2. SEM photomicrographs of the six most readily identifiable textures observed in this study. (a) Euhedral isometric electrum crystals on solid, fairly flat substrates of electrum. (b) Well-rounded, smooth surfaces with little if any evidence of chemical attack. (c) Smoothly rounded grains with pitted surfaces. (d) Smoothly rounded surfaces with large pits containing branching-coral type features. (e) Hackly, friable-looking texture similar to that of foundry slag or weathered, gritty sandstone. (f) Irregular, lobate or bulbous, "stromatolite-like" texture with occasionally stepped but usually smooth individual lobe surfaces.

correlation exists between flake-shaped grains and lobate to hackly or grainy surface-textures.

An apparent relationship exists between grain size, grain shape, and distance of transport for the gold grains from Brush Creek. Near the headwaters of the creek, where the lode deposit is located, irregu-

% of the morphological group % of the surface texture group		GRAIN MORPHOLOGIES				
		Irregular (~41%)	Spherical (~33%)	Cylindrical (~1%)	Wafer (~14%)	Flake (~11%)
SURFACE TEXTURES	Smooth unpitted (~36%)	70-80% >90%	10-20% 6-10%	insufficient data <2%	3-6% <2%	<2% <2%
	Smooth pitted (~32%)	15-25% 30-40%	60-70% 55-65%	insufficient data <2%	8-12% 3-6%	3-6% <2%
	Pitted with branching-coral type features (~15%)	3-6% 3-6%	10-20% 50-60%	insufficient data <2%	30-40% 30-40%	15-25% 3-6%
	Hackly to grainy (~10%)	<2% <2%	3-6% 10-20%	insufficient data <2%	30-40% 30-40%	30-40% 45-55%
	Irregular lobate (~7%)	<2% <2%	<2% 8-12%	insufficient data <2%	10-20% 25-35%	35-45% 55-65%

FIG. 3. Correlation diagram indicating the predominance of relationships between morphologies of electrum grains and surface textures. The value in the upper-right corner of each box indicates the percentage of grains (with the particular morphology given at the top of the column), which possess the surface texture listed to the left. Similarly, the value in the lower left corner of each box indicates the percentage of grains (with the particular surface texture given to the left), which possess the morphology listed at the top of the column.

larly shaped grains up to 1 mm are not uncommon, and the grains average about 0.2 mm in maximum dimension. Downstream 19 km, the average size of the gold grains is less than 0.1 mm. Grain morphology evolves in a predictable trend from the original irregular form through to semispherical and wafer-like, ultimately yielding flake shapes.

Compositional inhomogeneity within the placer gold grains at Brush Creek has been known since as early as 1882, when Fontaine noted: "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."

Additional note of the rims on grains from Brush

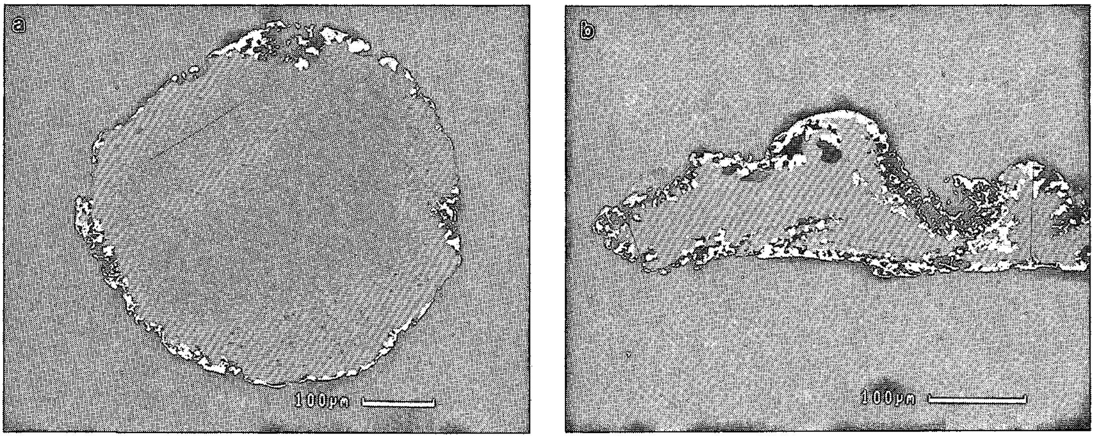

FIG. 4. Back-scattered electron images of two placer gold grains from Brush Creek, Virginia. (a) Grain number BC 2–6, showing partially complete formation of a gold-rich rim (brightest, high-electron-yield areas), with preferential development in and around embayments and pits on the surface. (b) Grain number BC 2–15, showing a much more highly developed gold-rich rim with many voids (lobate texture).

Creek was made by Solberg & Craig (1981); we have subsequently found that most of the grains of placer gold from Brush Creek exhibit some degree of gold-rich rim development, as illustrated in Figure 4. Electron-probe microanalysis of 29 randomly chosen and representative grains from Brush Creek (Table 1) indicates a compositional range of core electrum from 549 to 849 fine. This range is quite large relative to those of other localities considered in this study (Table 1), and other southeastern U.S. localities (Craig *et al.* 1980). Microprobe analysis of the gold-rich rim on grains from all the sample localities shows that 95% of the rims have compositions of ≥985 fine. The remaining 5% of the rims range between 967 and 985 fine (Table 1). It should be noted that some of the optically distinct rims that analyze at finenesses lower than about 995 may actually be purer, because the analytical volume of excitation may overlap or penetrate lower-fineness core electrum. When viewed in cross section, these rims are not uniform in thickness, but vary from <1 to 60 µm. The boundary between the individual cores and rims generally is sharp, and is especially striking in reflected light if the surface has been lightly etched using a potassium cyanide plus ammonium persulfate solution. Grains with an incomplete rim tend to have gold-rich "pockets" wherein the enrichment areas occur in small embayments on the grain surfaces (Fig. 4a). In other cases, the rim is so fully pervasive that it completely encloses the core (Fig. 4b). These pervasive rims commonly exhibit a "swiss cheese" texture, in which numerous small rounded voids are found in the gold-rich rim.

A few distinct relationships were observed between the character and prevalence of gold-rich rims and the morphologies of the gold grains. Firstly, polished sections of gold in vein quartz show no signs of development of a gold-rich rim (Driscoll *et al.* 1990), implying that the rim forms after liberation from the host rock. Furthermore, irregularly shaped grains of placer gold (relatively new to the stream environment) exhibit little or no development of a gold-rich rim. Flat, well-worn, flake-shaped grains, on the other hand, exhibit the most extensive development of a gold-rich rim. Spherical, semispherical, and wafer-shaped grain morphologies show intermediate degrees of rim development.

The surface features observed by scanning electron microscopy also show a general relationship to rim development. There is an increasing progression in the degree of rim development corresponding to the following respective surface textures: smooth, smooth pitted, pitted with branching features, irregular hackly, and lobate (Figs. 2b–f). The "euhedral crystals on gold substrate" texture was observed on one grain only, #SM105364; these crystals and their underlying substrate both have fineness values between 807 and 820. This compositional homogeneity suggests that the crystals are most likely residual lode-gold crystals, as all indications suggest that gold remobilized in the weathering environment in this study area results in virtually pure gold precipitates.

Consideration of these observations permits the recognition of a sequential trend (Fig. 5) that relates formation of the gold-rich rim to the morphology, surface texture, and distance of transport of the placer gold grain. Most of the observed morphologies and surface textures can be roughly correlated into this trend of increasing development of a rim

TABLE 1. CHEMICAL AND PHYSICAL DATA CONCERNING PLACER ELECTRUM GRAINS

Grain Number(1)	Size (mm)(2)	Mass (mg)	Shape(3)	Fineness	
				Core(4)	Rim(4)
BC 1-1 (5)	0.18	0.04	S	727-729 (2)	985-995 (3)
BC 1-2	0.25	0.06	W	580-596 (4)	~983-990 (4)
BC 1-3	0.30	0.02	I	655 (1)	987 (1)
BC 2-1	1.10	4.09	S	~604-614 (4)	988-989 (2)
BC 2-2	1.20	3.87	W	577-~579 (2)	~992-993 (2)
BC 2-3	1.30	4.73	I	570-~578 (3)	~977 (1)
BC 2-4	1.40	1.21	F	664-~667 (3)	987-~988 (2)
BC 2-5	0.65	N.M. (6)	W	693-716 (2)	980-987 (2)
BC 2-6	0.50	N.M.	S	553 (1)	996 (1)
BC 2-7	0.95	N.M.	F	677-684 (2)	992 (1)
BC 2-8	0.60	N.M.	I	558-562 (2)	990 (1)
BC 2-9	0.55	N.M.	W	650 (1)	992-~997 (3)
BC 2-10	0.50	N.M.	S	633-644 (2)	985 (1)
BC 2-11	0.55	N.M.	F	593 (1)	976-982 (2)
BC 2-12	0.60	N.M.	I	668 (1)	967-969 (2)
BC 2-13	0.55	N.M.	W	591 (1)	987 (1)
BC 2-14	0.55	N.M.	S	549 (1)	988 (1)
BC 2-15	0.80	N.M.	F	625-639 (2)	~985-994 (3)
BC 2-16	0.60	N.M.	I	685 (1)	988 (1)
BC 2-17	0.50	N.M.	W	554 (1)	991 (1)
BC 2-18	0.70	N.M.	S	555 (1)	991 (1)
BC 2-19	0.60	N.M.	F	562 (1)	987 (1)
BC 2-20	0.65	N.M.	I	781 (1)	995 (1)
BC 2-26	0.60	N.M.	I	554 (1)	993 (1)
BC 2-27	0.47	N.M.	W	685 (1)	997 (1)
BC 3-1	0.70	0.84	S	608 (1)	997 (1)
BC 4-1	0.50	0.26	W	713 (1)	~994-997 (2)
BC 5-1	0.90	0.65	F	849 (1)	991 (1)
BC 7-1	0.20	0.02	I	776 (1)	989 (1)
NC85L86-1 (7)	1.15	N.M.	F	874 (1)	992 (1)
NC85L86-2	1.45	N.M.	F	948 (2)	993 (1)
NC85L86-3	1.10	N.M.	I	~953-955 (2)	N.D. (8)
NC85L86-4	0.50	N.M.	S	957-~958 (2)	N.D.
NC85L86-5	1.25	N.M.	F	866 (1)	995 (1)
NC85L86-6	0.70	N.M.	S	862 (1)	992 (1)
NC85L86-7	1.20	N.M.	W	994 (1)	N.D.
NC85L86-8	0.90	N.M.	I	945 (1)	999 (1)
NC85L86-9	1.00	N.M.	S	869 (1)	991-998 (2)
NC85L86-10	1.15	N.M.	F	966 (1)	N.D.
NC85L86-11	0.65	N.M.	S	881 (1)	~996-997 (3)
NC85L86-12	0.75	N.M.	I	805-~839 (2)	N.D.
NC85L86-13	0.85	N.M.	I	961 (1)	998 (1)
NC85L86-14	0.65	N.M.	S	941-943 (2)	999 (1)
NC85L86-15	0.70	N.M.	S	972 (2)	998 (1)
NC85L86-16	0.55	N.M.	S	977 (2)	N.D.
NC85L86-17	0.65	N.M.	W	947 (1)	996 (1)
NC85L86-18	0.60	N.M.	I	947 (1)	N.D.
NC85L86-19	0.45	N.M.	I	836-850 (2)	N.D.
JMA 1 (9)	3.35	8.58	R	957-959 (3)	N.D.
JMA 2	4.35	19.90	R	947-949 (3)	N.D.
JMA 3	3.10	27.53	I	944-946 (3)	985 (1)
JMA 4	5.05	81.39	I	970-971 (3)	999 (1)
JMB 1 (10)	3.15	21.21	I	820-822 (4)	~996-998 (3)
JMB 5	1.95	14.92	W	939 (1)	997-~999 (2)
SM C-126 (11)	3.95	88.45	S	1000 (2)	1000 (1)
SM 67994 (12)	5.45	231.68	W	863-864 (3)	987-996 (3)
SM 96982 (13)	8.20	464.25	I	961 (2)	992-1000 (3)
SM 97398-1 (14)	0.80	0.95	C	809-812 (3)	N.D.
SM 97398-2	2.55	1.96	C	816-818 (3)	N.D.
SM 97398-3	3.00	3.46	C	818 (1)	~992-993 (2)
SM 105364 (15)	0.75	3.52	T	807-820 (6)	N.D.

with time spent in the stream. The above relationship suggests that the physical characteristics of placer grains can give clues about the potential presence and nature of a gold-rich rim without going through lengthy sample preparations.

The contact between the gold-rich rim and the lower-fineness core in the grains from Brush Creek is very sharp and well defined, facilitating immediate recognition of the rim, even where it may be thin and irregular (Fig. 4a). The rim–core boundary in grains from most other localities is equally sharp, though generally less apparent owing to the higher average fineness of their core electrum. The compositional characteristics of two representative rims as determined by electron-microprobe traverses are shown in Figure 6. These traverses were especially useful in the quantification of the steep compositional gradients in such rimmed grains.

The compositions of coexisting rim–core pairs in this study, as well as from other sources (data on 681 grains from 32 localities) are presented in Figure 7. The average core composition is roughly equivalent to that given by Craig & Rimstidt (1985) for gold grains from all over the world. This similarity, and the fact that all of these grains have a gold-rich rim, suggest that there is no strong relationship between the composition of the core and the potential for rim development. The plotted rim–core compositional pairs from Brush Creek (solid circles in Fig. 7) illustrate the unusual composition of this gold. The scatter of rim compositions shown in Figure 7 also indicates that there is no real relationship between the purity of the gold-rich rim and the composition of the underlying electrum core.

Mineral inclusions observed in the gold grains from Brush Creek are primarily present in the rim. The occasional mineral inclusions found within core electrum 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 complex silicates (*e.g.*, amphiboles and pyroxenes), as they usually contain substantial amounts of Si, Al, Fe, and Ti ± subordinate K and Ca, as determined by energy-dispersion X-ray (EDX) analysis. Roughly 20% of the inclusions in the rim are believed to be iron oxides

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(1) Grains with "JM" prefix were generously donated by Mr. J. R. McCloud of Fredericksburg, VA. Grains starting with "SM" are on loan from the United States National Museum of Natural History and are identified with USNMNH sample numbers following the "SM".

(2) Values determined by means of optical estimation.

(3) Shape abbreviations: S=sphere, W=wafer, I=irregular, F=flake, R=rod, C=crystalline, T=thin plate.

(4) 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 >4%.

(5) "BC"-grains = placer gold, Brush Creek, VA.

(6) "N.M." = not measured.

(7) "NC"-grains = paleo-placer gold, Lilesville quad., NC.

(8) "N.D." = not detected.

(9) "JMA"-grains = placer gold, Chancellorsville quad., VA.

(10) "JMB"-grains = placer gold, Storck quad., VA.

(11) SM C-126 = placer gold (?) from unknown locality in NC.

(12) SM 67994 = gold from the Eldorado Mine, Montgomery Co., NC that is well worn and rounded suggesting stream transport in its history.

(13) SM 96982 = placer gold, Silver Creek, Cabarrus Co., NC.

(14) SM 97398 (1-3) = worn crystals, Dugas Gold Mine, White Co., GA.

(15) SM 105364 = placer gold, Bull Run, Fairfax Co., VA.

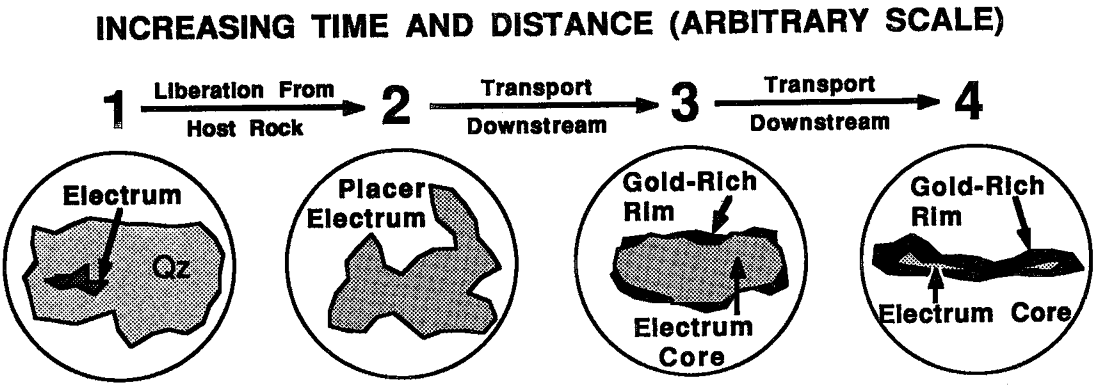

FIG. 5. Schematic illustration depicting the chemical and mechanical alterations experienced by grains of placer gold as they are transported downstream. The figure in each circle is representative of a sample's appearance in polished section. The following characteristics are typical for each grain's particular stage of development: (1) unrimmed gold grain in mineralized quartz vein, (2) irregularly shaped grain of placer gold with little or no evidence of gold-rich rimming, (3) spherical to wafer-shaped grain of placer gold with spotty to intense development of gold-rich rimming, (4) flake-shaped grain of placer gold with thick, very well-developed gold-rich rim.

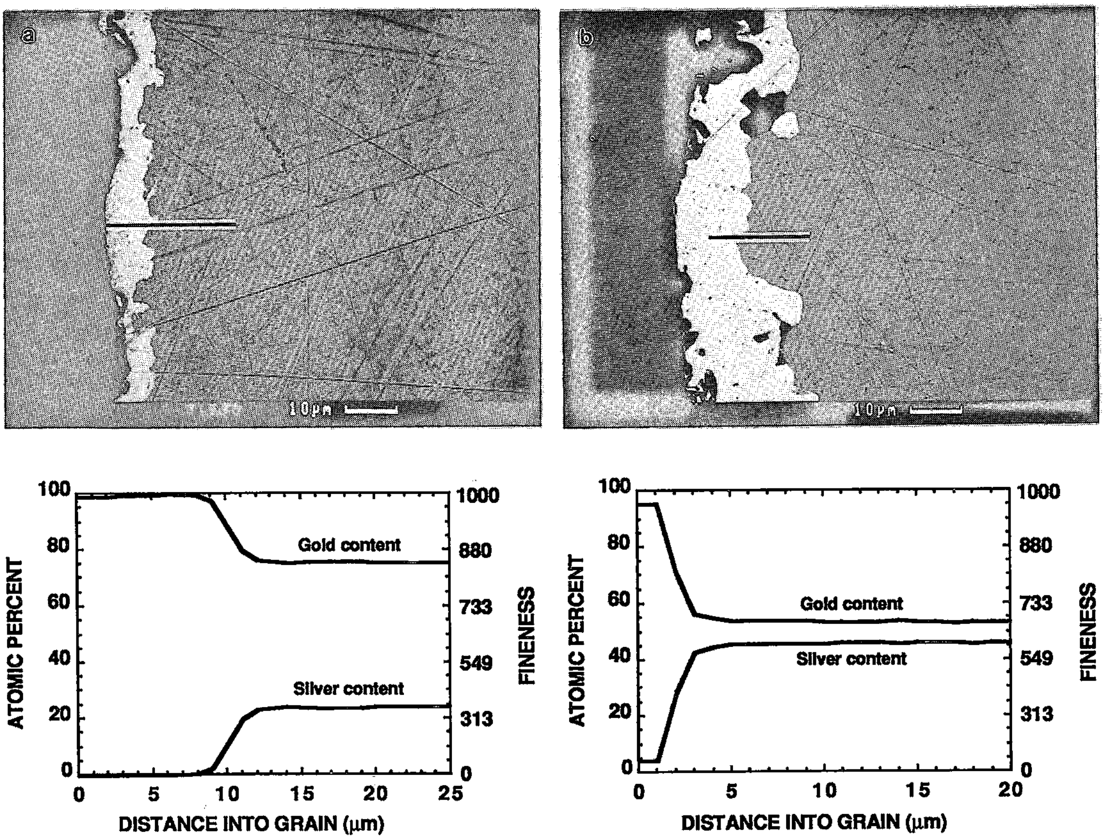

FIG. 6. Illustration of the compositions of placer gold grains. (a) Back-scattered electron (BSE) image of a portion of the polished section of grain number BC 5-1 along with a plot of the change in major-element chemistry determined by electron-microprobe analysis along the traverse path indicated by the black-on-white horizontal line on the BSE image. (b) BSE image of a portion of the polished section of grain number BC 2-7 along with a plot of the change in major-element chemistry determined by electron-microprobe analysis along the traverse path indicated by the black-on-white horizontal line on the BSE image.

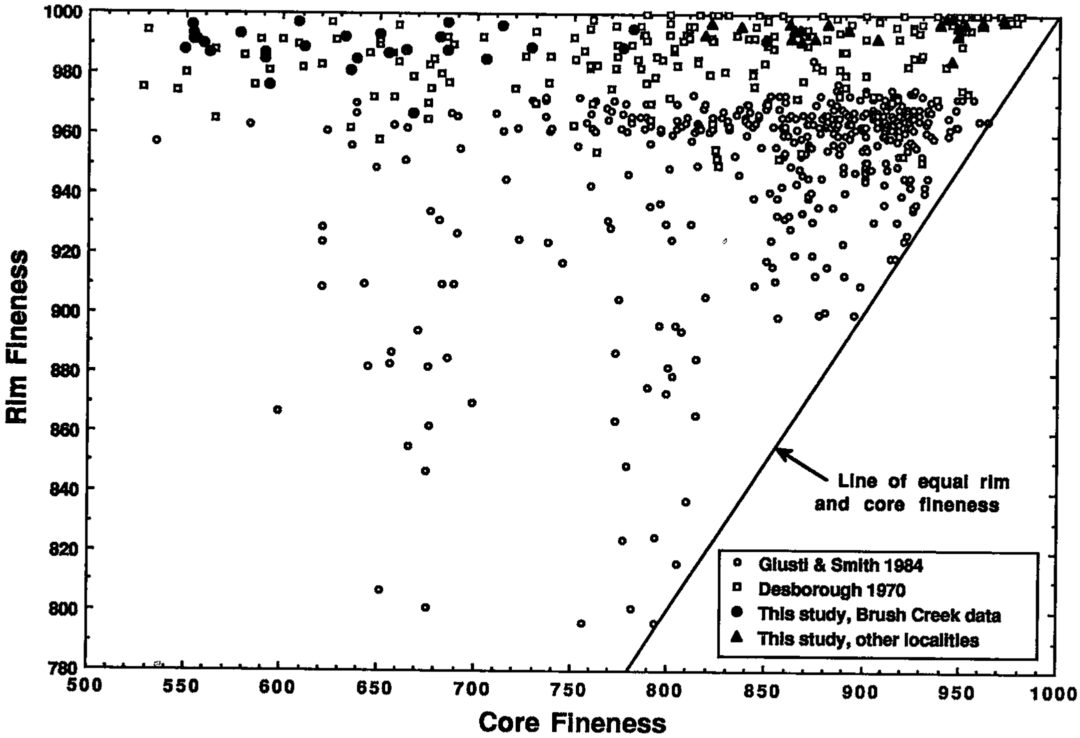

FIG. 7. Scatter plot of rim *versus* core compositions of placer electrum grains with gold-rich rims from Brush Creek (filled circles), other localities in this study (filled triangles), Desborough (1970) (open squares), and Giusti & Smith (1984) (open circles).

and hydroxides, as iron is the only major element indicated by EDX analysis. Placer gold grains from the other localities commonly have more mineral inclusions than at Brush Creek, but usually show similar inclusion mineralogy and size distributions with respect to rim and core. Inclusions in the core electrum of all the grains from this study seem to be primary, relict phases, as described by Driscoll *et al.* (1990), whereas those in the rim probably have been injected into the ductile, high-purity gold by mechanical working, or have been incorporated during a process of chemical growth.

DISCUSSION

Introduction

Several explanations have been proposed to account for gold-rich rimming, which gives rise to gold grains in placer deposits having higher average fineness than the grains in their parent lode deposits. The three principal models of rim formation considered here are: (1) preferential dissolution of silver from placer grains during weathering and transport, (2) precipitation of gold onto placer grains from oxidizing, Au-bearing stream water as it encounters more reducing conditions (cementation), and (3) a self-electrorefining process where the electrum at the grain–solution interface dissolves, and the gold immediately precipitates back onto the surface of the placer grain.

Preferential dissolution of silver

The most commonly invoked mechanism for the development of gold-rich rims is a process of 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). These studies indicate that a model based on the preferential dissolution of silver is chemically reasonable; however, such a model fails to explain how silver atoms from deeper than the outer few ångströms of the grain can come into contact with the solution. 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 mechanism, however, is probably ineffectual, as Fontana (1986) commented on an analogous system wherein the "dezincification" of brass results in a copper-rich coating: "A strong argument against [zinc being dissolved, leaving vacant sites in the brass lattice structure] is that dezincification to appreciable depths would be impossible or extremely slow because of difficulty of diffusion of solution and ions through a labyrinth of small vacant sites". In addition, during the commercial refining of electrum, sufficient porosity for selective leaching of silver from electrum is only developed through a process known as "inquartation". Inquartation involves the dilution of molten natural electrum with two to four times its weight of silver. The need for inquartation is explained by Bowdish (1983): "When alloyed with less than about three times its own weight of silver, gold will also protect the silver from attack by nitric acid solutions." Placer gold with a core fineness as high as 972 has been observed to develop a distinct rim of 998 fineness (Table 1, Fig. 7); such a small difference in silver content would afford very little increased porosity along which a leaching solution could encroach. Finally, grains with high silver contents in the core electrum do not in general develop a thicker or more prolific rim.

Another mechanism for the removal of silver from the core of an electrum grain is that of silver diffusion from the interior of the grain to the surface, where it can dissolve. This was tested by modeling diffusion profiles formed at 25°C in grains of the following compositions: $Au_{60}Ag_{40}$, $Au_{75}Ag_{25}$ and $Au_{90}Ag_{10}$ (equivalent to finenesses of 733, 846 and 943, respectively). These calculations are based on a model of non-steady-state diffusion in a semi-infinite medium presented in Darken & Gurry (1953, pp. 441-445). In accordance with this model's requisite boundary-conditions, the instantaneous and constant concentration of silver at the surface of an electrum grain is taken as zero, and the initial concentration at the semi-infinite distance remains fixed at the values stated above. The tracer diffusion coefficients of silver in $Au_{60}Au_{40}$, $Au_{75}Au_{25}$ and $Au_{90}Au_{10}$ at 25°C were extrapolated from the data of Mallard *et al.* (1963) as 1.36×10^{-32}, 3.39×10^{-32} and 1.05×10^{-31} cm^2/s, respectively. The more recent diffusion-coefficient data of Cook & Hilliard (1969) were not used even though they may be slightly more accurate, as they do not change our conclusions, and also cannot be easily adjusted to any desired composition of electrum, as can those of Mallard *et al.* (1963).

Diffusion profiles (Fig. 8) calculated for reasonable periods of geologic time show that silver diffuses much too slowly in such alloys to deplete silver from more than about the outer 2-3 Å of the gold grain. In fact, the number of years necessary to produce a gold rim roughly equal in thickness to natural rims (~8 μm) (Fig. 8b) is between 10^{17} and 10^{18} years (about one million times the age of the universe). Furthermore, this mechanism is incapable of yielding the extremely sharp rim–core contact observed in natural grains.

Thus, the only conceivable means by which selective silver dissolution could produce a significant gold-rich rim would involve repeated cycles of ångström-level leaching of silver followed by mechanical deformation (leading to re-exposure of

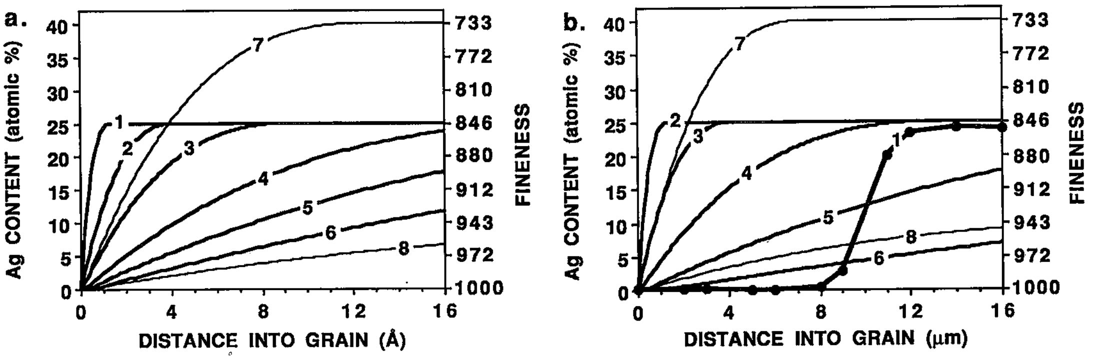

FIG. 8. Observed natural gradients of silver and calculated diffusion profiles of silver in gold. (a) Calculated diffusion profiles of silver in $Au_{75}Ag_{25}$ for the geologically reasonable time periods of 1, 10, 50, 300, 1000, and 3000 Ma (heavy black lines 1-6, respectively) and the diffusion profiles of silver in $Au_{60}Ag_{40}$ and $Au_{90}Ag_{10}$ after 300 Ma (fine lines 7 and 8, respectively). (b) Observed natural gradient in silver concentration in grain number BC 5-1, as determined by electron-microprobe analyses along a traverse (heaviest black line, #1); calculated diffusion-profiles of silver in $Au_{75}Ag_{25}$ for time periods of 10^{14}, 10^{15}, 10^{16}, 10^{17}, and 10^{18} years, necessary to simulate the natural gradient in Ag concentration (heavy black lines 2-6, respectively); and, for comparison of the effect of composition, the diffusion profiles of silver in $Au_{60}Ag_{40}$ and $Au_{90}Ag_{10}$ after 10^{16} years (fine lines 7 and 8, respectively).

TABLE 2. DISSOLUTION REACTIONS FOR METALLIC GOLD

LIGAND	$\Delta G^{\circ}_{f(cmx)}$(1)	REACTION	log K	S_C(2)	Ref.(3)
		TRIVALENT GOLD COMPLEXES			
		NO LIGANDS			
N.A.(4)	433.5	$Au(s) + 0.75O_2 + 3H^+ = Au^{3+} + 1.5H_2O$	-11.47	N.A.	FL
		ONE LIGAND			
Cl^-	239.3	$Au(s) + 0.75O_2 + 3H^+ + Cl^- = AuCl^{2+} + 1.5H_2O$	-0.45	11.83	BL
OH^-	184.9	$Au(s) + 0.75O_2 + 2H^+ = AuOH^{2+} + 0.5H_2O$	-9.47	N.A.	BL
		TWO LIGANDS			
Cl^-	70.7	$Au(s) + 0.75O_2 + 3H^+ + 2Cl^- = AuCl_2^+ + 1.5H_2O$	6.10	2.64	BL
SO_4^{2-}	-1090.4	$Au(s) + 0.75O_2 + 3H^+ + 2SO_4^{2-} = Au(SO_4)_2^- + 1.5H_2O$	-5.37	8.38	MFL
OH^-	-63.6	$Au(s) + 0.75O_2 + H^+ + 0.5H_2O = Au(OH)_2^+$	-7.47	N.A.	BL
		THREE LIGANDS			
Cl^-	-83.3	$Au(s) + 0.75O_2 + 3H^+ + 3Cl^- = AuCl_3(aq) + 1.5H_2O$	10.08	0.43	BL
OH^-, Cl^-	-148.4	$Au(s) + 0.75O_2 + 2H^+ + 2Cl^- = AuOHCl_2(aq) + 0.5H_2O$	2.95	1.22	AL
OH^-, FA^{2-}	-----(5)	$Au(s) + 0.75O_2 + H^+ + 0.5H_2O + FA^{2-} = Au(OH)_2FA^-$	1.33	-1.94	KBL
OH^-, Cl^-	-217.3	$Au(s) + 0.75O_2 + H^+ + 0.5H_2O + Cl^- = Au(OH)_2Cl(aq)$	-3.54	2.93	AL
OH^-	-283.4	$Au(s) + 0.75O_2 + 1.5H_2O = Au(OH)_3(aq)$	-10.51	N.A.	L
		FOUR LIGANDS			
CN^-	172.4	$Au(s) + 0.75O_2 + 3H^+ + 4CN^- = Au(CN)_4^- + 1.5H_2O$	69.53	-14.54	JL
NH_3	-11.92	$Au(s) + 0.75O_2 + 3H^+ + 4NH_3 = Au(NH_3)_4^{3+} + 1.5H_2O$	47.98	-9.15	IL
I^-	-45.0	$Au(s) + 0.75O_2 + 3H^+ + 4I^- = AuI_4^- + 1.5H_2O$	36.21	-6.21	HL
SCN^-	561.6	$Au(s) + 0.75O_2 + 3H^+ + 4SCN^- = Au(SCN)_4^- + 1.5H_2O$	31.05	-4.92	L
Br^-	-167.3	$Au(s) + 0.75O_2 + 3H^+ + 4Br^- = AuBr_4^- + 1.5H_2O$	20.92	-2.38	L
Cl^-	-235.1	$Au(s) + 0.75O_2 + 3H^+ + 4Cl^- = AuCl_4^- + 1.5H_2O$	13.70	-0.58	L
OH^-, Cl^-	-293.6	$Au(s) + 0.75O_2 + 2H^+ + 3Cl^- = AuOHCl_3^- + 0.5H_2O$	5.38	0.00	AL
OH^-, Br^-	-333.7	$Au(s) + 0.75O_2 + H^+ + 0.5H_2O + 2Br^- = Au(OH)_2Br_2^-$	3.42	-2.02	CL
OH^-, Cl^-	-349.7	$Au(s) + 0.75O_2 + H^+ + 0.5H_2O + 2Cl^- = Au(OH)_2Cl_2^-$	-3.35	1.36	AL
OH^-, Cl^-	-403.7	$Au(s) + 0.75O_2 + 1.5H_2O + Cl^- = Au(OH)_3Cl^-$	-12.42	5.81	AL
OH^-	-455.4	$Au(s) + 0.75O_2 + 2.5H_2O = Au(OH)_4^- + H^+$	-21.91	N.A.	L
OH^-, Br^-	-251.9	$Au(s) + 0.75O_2 + 1.5H_2O + Br^- = Au(OH)_3Br^-$	-34.23	27.61	CL
		FIVE LIGANDS			
SCN^-	654.5	$Au(s) + 0.75O_2 + 3H^+ + 5SCN^- = Au(SCN)_5^{2-} + 1.5H_2O$	31.01	-3.93	L
OH^-	-616.5	$Au(s) + 0.75O_2 + 3.5H_2O = Au(OH)_5^{2-} + 2H^+$	-35.24	N.A.	L
		SIX LIGANDS			
SCN^-	747.0	$Au(s) + 0.75O_2 + 3H^+ + 6SCN^- = Au(SCN)_6^{3-} + 1.5H_2O$	31.05	-3.28	L
OH^-	-763.2	$Au(s) + 0.75O_2 + 4.5H_2O = Au(OH)_6^{3-} + 3H^+$	-51.08	N.A.	L

TABLE 2 (cont'd). DISSOLUTION REACTIONS FOR METALLIC GOLD

LIGAND	$\Delta G^{\circ}_{f(cmx)}$(1)	REACTION	log K	S_C(2)	Ref.(3)
MONOVALENT GOLD COMPLEXES					
NO LIGANDS					
N.A.(4)	163.6	$Au(s) + 0.25O_2 + H^+ = Au^+ + 0.5H_2O$	-7.17	N.A.	EL
ONE LIGAND					
S^{2-}	21.6	$Au(s) + 0.25O_2 + HS^- = AuS^- + 0.5H_2O$	19.82	-22.22	MEL
HS^-	35.6	$Au(s) + 0.25O_2 + H^+ + HS^- = AuHS(aq) + 0.5H_2O$	17.37	-19.77	GL
SO_3^{2-}	-393.3	$Au(s) + 0.25O_2 + H^+ + SO_3^{2-} = AuSO_3^- + 0.5H_2O$	5.16	-7.56	BL
$S_2O_3^{2-}$	-418.4	$Au(s) + 0.25O_2 + H^+ + S_2O_3^{2-} = AuS_2O_3^- + 0.5H_2O$	3.25	-5.65	BL
Cl^-	5.0	$Au(s) + 0.25O_2 + H^+ + Cl^- = AuCl_{(aq)} + 0.5H_2O$	-2.38	-0.02	BL
OH^-	-54.4	$Au(s) + 0.25O_2 + 0.5H_2O = Au(OH)(aq)$	-10.52	N.A.	BL
TWO LIGANDS					
CN^-	285.8	$Au(s) + 0.25O_2 + H^+ + 2CN^- = Au(CN)_2^- + 0.5H_2O$	31.82	-17.11	L
$CS(NH_2)_2$	----- (6)	$Au(s) + 0.25O_2 + H^+ + 2CS(NH_2)_2 = Au[CS(NH_2)_2]_2^+ + 0.5H_2O$	27.91	-15.16	HL
HS^-	15.7	$Au(s) + 0.25O_2 + H^+ + 2HS^- = Au(HS)_2^- + 0.5H_2O$	22.97	-12.68	GL
SO_3^{2-}	-962.3	$Au(s) + 0.25O_2 + H^+ + 2SO_3^{2-} = Au(SO_3)_2^{3-} + 0.5H_2O$	19.61	-11.01	BL
$S_2O_3^{2-}$	-1030.2	$Au(s) + 0.25O_2 + H^+ + 2S_2O_3^{2-} = Au(S_2O_3)_2^{3-} + 0.5H_2O$	18.90	-10.65	JL
NH_3	1.3	$Au(s) + 0.25O_2 + H^+ + 2NH_3 = Au(NH_3)_2^+ + 0.5H_2O$	11.97	-7.19	IL
I^-	-47.6	$Au(s) + 0.25O_2 + H^+ + 2I^- = AuI_2^- + 0.5H_2O$	11.76	-7.08	HL
SCN^-	251.9	$Au(s) + 0.25O_2 + H^+ + 2SCN^- = Au(SCN)_2^- + 0.5H_2O$	9.84	-6.12	L
Br^-	-115.0	$Au(s) + 0.25O_2 + H^+ + 2Br^- = AuBr_2^- + 0.5H_2O$	5.21	-3.81	L
Cl^-	-151.1	$Au(s) + 0.25O_2 + H^+ + 2Cl^- = AuCl_2^- + 0.5H_2O$	1.98	-2.19	L
OH^-, Br^-	-199.9	$Au(s) + 0.25O_2 + 0.5H_2O + Br^- = AuOHBr^-$	-3.25	-5.15	DL
OH^-, Cl^-	-215.2	$Au(s) + 0.25O_2 + 0.5H_2O + Cl^- = AuOHCl^-$	-5.35	-3.05	DL
OH^-	-275.4	$Au(s) + 0.25O_2 + 1.5H_2O = Au(OH)_2^- + H^+$	-13.34	N.A.	DL
DI-GOLD COMPLEXES					
HS^-, S^{2-}	21.0	$2Au(s) + 0.5O_2 + H^+ + 3HS^- = Au_2(HS)_2S^{2-} + H_2O$	45.64	-15.72	MEL
S^{2-}	116.8	$2Au(s) + 0.5O_2 + 2HS^- = Au_2S_2^{2-} + H_2O$	26.75	-17.13	GL

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(1) Standard state free energy of formation of the gold complex or free gold ion, given in kJ/mol for 25°C and 1 bar.

(2) S_C = Strength of complex = the logarithm of the activity of the ligand in equilibrium with the corresponding aqueous gold-complex solution ($P(O_2) = 0.2$ atm, pH = 6), yielding 0.1-ppb of gold.

(3) References: A - Baes & Mesmer 1976, B - Baranova & Ryzhenko 1981, C - Bjerrum 1971, D - IUPAC 1982, E - Johnson et al. 1978, F - Latimer 1952, G - Renders & Seward 1989, H - Schmid 1985, I - Skibsted & Bjerrum 1974, J - Skibsted & Bjerrum 1977, K - Varshal et al. 1984, L - Wagman et al. 1982, M - Webster 1986.

(4) N.A. = not applicable.

(5) FA = Fulvic acid - stoichiometry unknown, therefore ΔG_f undeterminable.

(6) No ΔG_f available for the complex or free ligand.

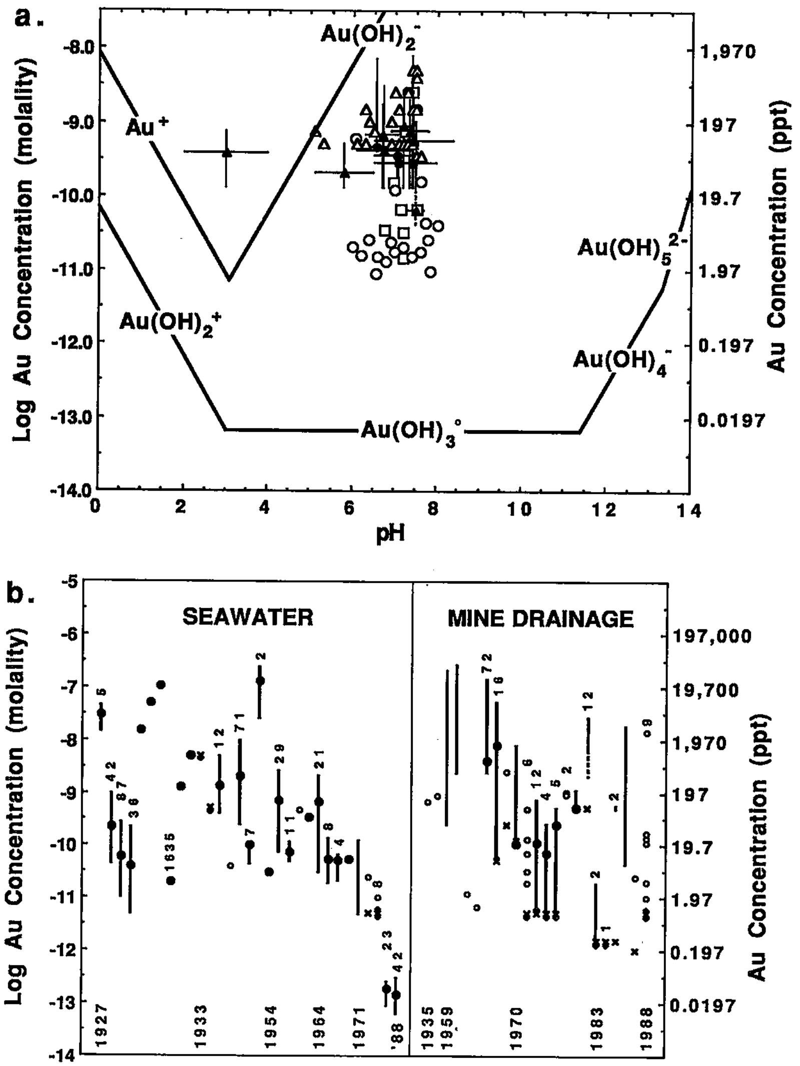
fresh electrum). This mechanism is, however, in no way supported by the textures of the observed surfaces.

Cementation

Despite its chemical inertness, gold is transported in significant quantities as aqueous complexes at high temperatures to form hydrothermal deposits. At low temperatures, gold is much less soluble, yet can be complexed by a host of ligands (Table 2). Depending on the concentrations of such ligands, and ambient conditions of Eh and pH, several of the ligands appear to be capable of transporting significant amounts of gold in the supergene environment. The following observations have been offered as evidence for low-temperature aqueous transport of gold: (1) placer gold grains with smooth, well-formed crystal faces (Warren 1982, Craig & Callahan 1990), (2) high-purity gold crystals and dendrites on iron oxides in laterites (Mann 1984, Freyssinet *et al.* 1989), (3) gold impregnations of originally carbonaceous matter (Wilson 1984), and (4) secondarily enriched concentrations of gold associated with recently deposited iron hydroxides (Lesure 1971).

At least two detailed accounts suggest that there has been secondary enrichment of gold in deposits in the southeastern United States. Lesure (1971) reported on secondary enrichment at the Calhoun mine in Lumpkin County, Georgia, where significant concentrations of gold (2.9 ppm) occur in fresh limonite coatings of the walls of an adit. Cook (1987) compiled a series of historical accounts of gold mines of Georgia and Alabama, which document large accumulations of coarse gold in quartz veins just at the water table. These same veins commonly show a significant decrease in particle size and grade of gold below the water table.

The calculated equilibrium solubility of gold in



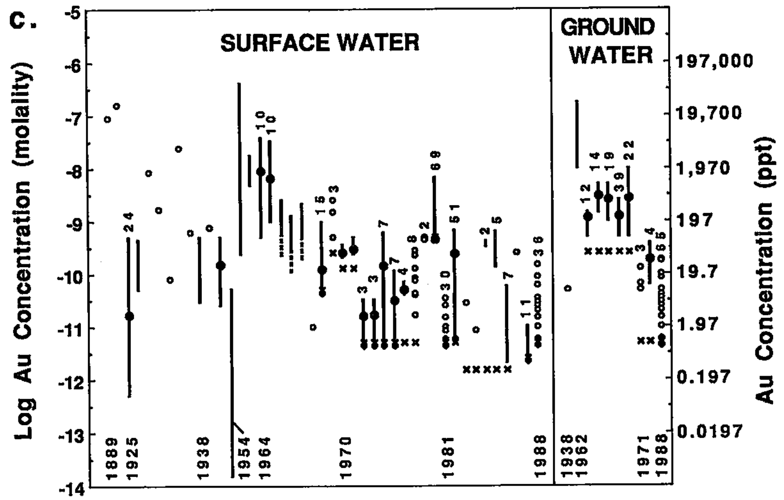


FIG. 9. Gold concentration plots. (a) Log Au concentration (molality and ppt) *versus* pH for gold–hydroxide complexes and free gold ions [where $P(O_2) = 0.2$] in the absence of other ligands. The predominant univalent gold species (indicated by the upper two bold connecting straight-line segments) from low to high pH are Au^{1+} and $Au(OH)_2^-$, with the concentration of the neutral AuOH° complex constant at $10^{-11.42}m$. The predominant trivalent gold species (indicated by the lower four, bold, connecting, straight-line segments) from low to high pH include: $Au(OH)_2^+$, $Au(OH)_3^\circ$, $Au(OH)_4^-$, and $Au(OH)_5^{2-}$. Plotted circles represent measured natural gold concentrations of stream waters, whereas triangles represent groundwaters, and squares represent mine waters; open symbols are for data which included specific concentration–pH pairs, whereas solid symbols and their associated range bars are for data which specified only ranges of pH and concentration. (b) Log Au concentration (molality and ppt) *versus* the year of determination for seawater and mine drainage; dates along bottom axis indicate the first, last, and several intermediate dates for the corresponding Au-concentration determinations. Symbols used to plot concentration data are as follows: small open circle: single concentration value, large solid circle: average concentration value for a number of analyses, x: limit of detection, x ("x" with solid lower quadrant): sample(s) with no gold detected, x ("x" with solid upper quadrant): sample(s) with a trace of gold detected, solid bar: range of reported gold concentrations, dashed bar: range with no lower limit specified, numerals above bars, open circles, and solid circles: number of individual analyses within the set. Each set of concentrations generally represents analyses from a particular locality, except for several of the seawater data sets, and some grouped sets of individual analyses. (c) Log Au concentration (molality and ppt) *versus* the year of determination for surface water and groundwater. Conventions in part (c) are the same as for part (b). Reported values of gold concentration have declined over time, probably as a result of improved analytical techniques and the greater care taken in preconcentration steps to fully filter the solutions to remove fine particulate matter and colloidal gold. It should be noted that virtually all of the measurements shown on this figure were made on samples from regions where gold deposits occur, or where gold was being explored for and expected to occur (except of course, for seawater samples). Data for Figures 9a–c were taken from the following sources and tabulations within them: Borovitskiy *et al.* 1966, Brooks *et al.* 1981, Chernyayev *et al.* 1969, Crocket 1978, Goleva *et al.* 1970, Gosling *et al.* 1971, Hall *et al.* 1986, Hamilton *et al.* 1983, Jones 1970, Kaspar *et al.* 1972, Koide *et al.* 1988, Lomonosov *et al.* 1985, McHugh 1988, Turekian 1968, Turner & Ikramuddin 1982, Volkov & Shakhbazova 1975.

pure water as a function of pH is shown by the bold lines in Figure 9a, constructed for $P(O_2) = 0.2$ atm. At the near-neutral pH values found in most stream waters, the equilibrium concentration of gold ions and hydroxy complexes would be expected to range from ~0.04 ppb at pH 4.5 to ~12 ppb at pH 7.0. These values are considerably higher than the ones reported in the literature for various types of natural solutions (plotted points and ranges in Fig. 9), probably as a result of slow kinetics of dissolution or, more likely, insufficient interaction of solution and gold-bearing sediment. Gold–hydroxy complexes, therefore, may or may not be important in accounting for the total dissolved contents of gold in natural systems, depending upon the relative influences and contributions of the other gold-complexing ligands.

Table 2 lists 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 activity of the ligand in equilibrium with metallic gold and a corresponding gold-complexed solution [pH = 6.0, $P(O_2) = 0.2$ atm.] yielding 0.1 ppb gold. Note that an S_C value refers to the concentration of a free ligand remaining after gold complexation; it does not refer to the total concentration of the ligand. The smaller the value of S_C, therefore, the more effective the ligand is at complexing gold. A concentration of dissolved gold of 0.1 ppb was chosen for the S_C parameter, as it represents the middle to upper range of recent determinations of the dissolved gold content of various natural environments (Figs. 9a–c). This concentration is assumed to be a reasonable estimate of the minimum value at which sufficient transport occurs to yield the products commonly ascribed to secondary enrichment of gold (Lesure 1971).

The value of S_C can thus be used as a "yardstick" to eliminate from consideration all complexing agents that could in no way be capable of producing significant supergene transport of gold. Ligands with values of S_C greater than -1.65 (= 100 × the average concentration of the most abundant natural ligand, chlorine) are eliminated from further consideration because such ligand concentrations are virtually never observed in typical, fresh surface waters or shallow groundwaters, where gold grains with gold-rich rims are frequently found. Gold–hydroxy complexes were chosen for further consideration if they are capable of yielding concentrations greater than 1×10^{-11} *m* (1.97 ppt) at normal values of pH for streams, since the S_C parameter does not apply to these complexes. Because solutions in these environments are normally quite dilute, all activity coefficients were assumed to equal one. Several of the ligands listed in Table 2 are metastable in solutions with an Eh buffered by equilibrium with $P(O_2) = 0.2$ atm, but since their metastable persistence is not quantitatively known, they have been assumed to be completely stable for the "S_C" consideration. The choices of pH and Eh are consistent with values commonly found in fresh surface waters (Baas Becking *et al.* 1960). As can be seen from Table 2, 28 of the gold complexes have S_C values that indicate they are at least strong enough to warrant a more thorough evaluation. The only thermodynamic data available for complex organic ligands that might dissolve gold pertain to fulvic acid (Table 2), and although the concept of gold dissolution by micro-organisms and complex organic molecules has been substantiated by various sources (Lakin *et al.* 1974, Mineyev 1976), sparse thermodynamic data prevent a further quantitative evaluation of them. Colloidal and very fine particulate gold in natural waters also is possible, but the results of workers who have considered this problem (Goleva *et al.* 1970, Gosling *et al.* 1971, Lomonosov *et al.* 1985) are not in agreement over their importance. Clearly, there is a great need for further work in this field.

Of the ligands that can form strong Au complexes, only a few occur at sufficient concentrations in natural waters to produce significant transport of gold. The average concentration of each ligand forming a complex with an S_C value from Table 2 of -1.65 or more was estimated for stream waters and slow-moving sediment solutions from literature data. These data were then used in combination with the equilibrium constants given in Table 2 to calculate the expected concentrations of the gold complexes in equilibrium with elemental gold (Table 3). The concentrations of gold complexes given in Table 3 were calculated using both mass-action and mass-balance considerations. The pH value of 6.0 used in calculations for both stream water and sediment solution (Table 3) was estimated from the extensive compilation of field measurements by Baas Becking *et al.* (1960). The activity of dissolved oxygen used for the stream water in calculations in Table 3 is that for air–water equilibrium. The value of $a(O_2)$ in organic-matter-rich sediment solutions was estimated to be 2.51×10^{-69} (Barnes 1979), by assuming that the solution exists at the H_2S–SO_4^{2-} boundary at $\Sigma S = 0.001$ *m* and 25°C. Stream sediments tend to develop a sharp redox boundary where H_2S exists just below the stream bed - stream water interface, whereas SO_4^{2-} predominates in the stream water.

The CN^- concentration used for stream waters in Table 3 (3.84×10^{-8} *m* or 1.0 μg/L) 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 stated that "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 (0.04 mg/kg) being easily set free." Accordingly, the CN^- concentration used in Table 3 for stream sediments was 40 μg/L (1.54×10^{-6} *m*).

Various studies indicate a wide variety of natural sources of cyanide, including certain plants (Lakin *et al.* 1974, Hughes 1981, Leduc 1981, Warren 1982), and algae (Vennesland *et al.* 1981). Seigler (1981) described 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, monocotyledonous and dicotyledonous angiosperms, fungi, bacteria, and several insects. Altogether, cyanide is produced by more than 2050 plant species. Krutz (1981) noted that man-made sources of cyanide, such as steel and galvanic industries, fertilizers, and domestic sewage, can elevate the cyanide content of streams to levels as high as 200 μg/L. The same respective estimates were used for the concentrations of SCN^- as for CN^- in Table 3, as it was assumed that cyanide would be present in similar concentrations whether or not the solutions were sufficiently sulfur-rich to convert the CN^- to SCN^-.

TABLE 3. PREDICTED GOLD-COMPLEX CONCENTRATIONS

Au-complex(1)	$\log[\text{lig}]_{sw}$(2)	$\log[\text{cmx}]_{sw}$(3)	$\log[\text{lig}]_{rs}$(4)	$\log[\text{cmx}]_{rs}$(5)	Ref.(6)
TRIVALENT GOLD COMPLEXES					
FOUR LIGANDS					
$Au(CN)_4^-$	-7.42	-8.02	-5.81	-23.16	DFA
$Au(NH_3)_4^{3+}$	-8.51	-9.11	-8.51	-55.49	BGA
AuI_4^-	-7.42	-14.14	-7.42	-62.91	CA
$Au(OH)_2Br_2^-$	-8.00, -6.35	-17.96	-8.00, -6.35	-66.73	CA
$Au(SCN)_4^-$	-7.42	-19.29	-5.81	-61.64	DA
$AuBr_4^-$	-6.35	-25.15	-6.35	-73.93	CA
FIVE LIGANDS					
$Au(SCN)_5^{2-}$	-7.42	-26.74	-5.81	-67.49	DA
SIX LIGANDS					
$Au(SCN)_6^{3-}$	-7.42	-34.12	-5.81	-73.26	DA
MONOVALENT GOLD COMPLEXES					
ONE LIGAND					
AuS^-	——(7)	——	-7.99	-11.32	EFA
$AuHS_{(aq)}$	——	——	-7.99	-13.77	EFA
$AuSO_3^-$	——	——	-13.25	-31.24	EFA
$AuS_2O_3^-$	——	——	-13.47	-33.37	EFA
TWO LIGANDS					
$Au(CN)_2^-$	-7.42	-7.72	-5.81	-6.11	CEA
$Au(OH)_2^-$	-8.00	-8.23	-8.00	-24.49	A
$AuOHCl^-$	-8.00, -3.65	-9.89	-8.00, -3.65	-26.15	C
AuI_2^-	-7.42	-9.97	-7.42	-26.23	CA
$AuOHBr^-$	-8.00, -6.35	-10.50	-8.00, -6.35	-26.75	CA
$Au(SCN)_2^-$	-7.42	-11.88	-5.81	-28.14	DA
$Au(NH_3)_2^+$	-8.51	-11.93	-8.51	-28.19	BGA
$AuCl_2^-$	-3.65	-12.21	-3.65	-28.47	CA
$AuBr_2^-$	-6.35	-14.38	-6.35	-30.64	CA
$Au(HS)_2^-$	——	——	-7.99	-16.16	EFA
$Au(SO_3)_2^{3-}$	——	——	-13.25	-30.04	EFA
$Au(S_2O_3)_2^{3-}$	——	——	-13.47	-31.19	EFA
DI-GOLD COMPLEXES					
$Au_2(HS)_2S^{2-}$	——	——	-7.99	-18.62	EFA
$Au_2S_2^{2-}$	——	——	-7.99	-23.53	EFA

(1) Concentration data is not predicted for $Au(OH)_2FA^-$ or $Au[CS(NH_2)_2]_2^+$, even though their "S_C" parameters from Table 2 are greater than -1.65, because concentration data for the ligands in natural systems are not available.

(2) $\log[\text{lig}]_{sw}$ = log activity (≈ concentration) of the ligand in average stream waters.

(3) $\log[\text{cmx}]_{sw}$ = log activity (≈ concentration) of the Au-complex in average stream waters.

(4) $\log[\text{lig}]_{rs}$ = log activity (≈ concentration) of the ligand in average reducing solutions in organic-matter-rich sediments.

(5) $\log[\text{cmx}]_{rs}$ = log activity (≈ conc.) of the Au-complex in average reducing solutions in organic-matter-rich sediments.

(6) References: A - Barnes 1979; B - Feth 1966; C - Fuge 1978a,b,c; D - Krutz 1981; E - Pan 1981; F - Wagman et al. 1982; G - Wlotzka 1978.

(7) Reduced sulfur species are not stable in aerated stream waters. Although they may be released from organic-matter-rich sediments and persist metastably in the stream waters, there are no reports of measurable concentrations of S^{2-}, HS^-, SO_3^{2-}, or $S_2O_3^{2-}$ in unpolluted stream waters.

The NH_3 concentration used in Table 3 was determined using a *pK* value of -9.25 for the reaction $NH_4^+ = NH_3 + H^+$, and by assuming that the "ammonia" concentrations of natural waters (reported inconsistently as either NH_3 or NH_4^+) actually represents the total of both species. The number of measured natural concentrations is not large, but a range of ~5 ppb to ~5,000 ppb appears to be common for ocean water, river water, rain water, and groundwater. River water and groundwater tend to have concentrations in the middle to upper portion of this range, but as a conservative estimate, 100 ppb was chosen as the total ammonia concentration, yielding an activity of NH_3 for use in Table 3 equal to 3.12×10^{-9} *m*.

The concentrations of the HS^-, $S_2O_3^{2-}$, and SO_3^{2-} ligands in sediment solutions were calculated by assuming chemical equilibrium with H_2S for the appropriate Eh and pH conditions of stream sediments. The H_2S concentration value used for these calculations was taken from Pan (1981), who measured the concentration of this species in a neutral paddy soil that was adjusted to different pH values. The reported concentrations are likely to be close to those found in water-logged stream sediments containing some organic matter. This approach is likely to underestimate the concentrations of the sulfoxy ligands, as these species are formed by partial oxidation of H_2S and may persist metastably at higher concentrations (Giggenbach 1974, Hoffman 1977). The discovery of numerous small crystals of copper sulfide growing on the surfaces of recent 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 have two basic types of morphology, roughly

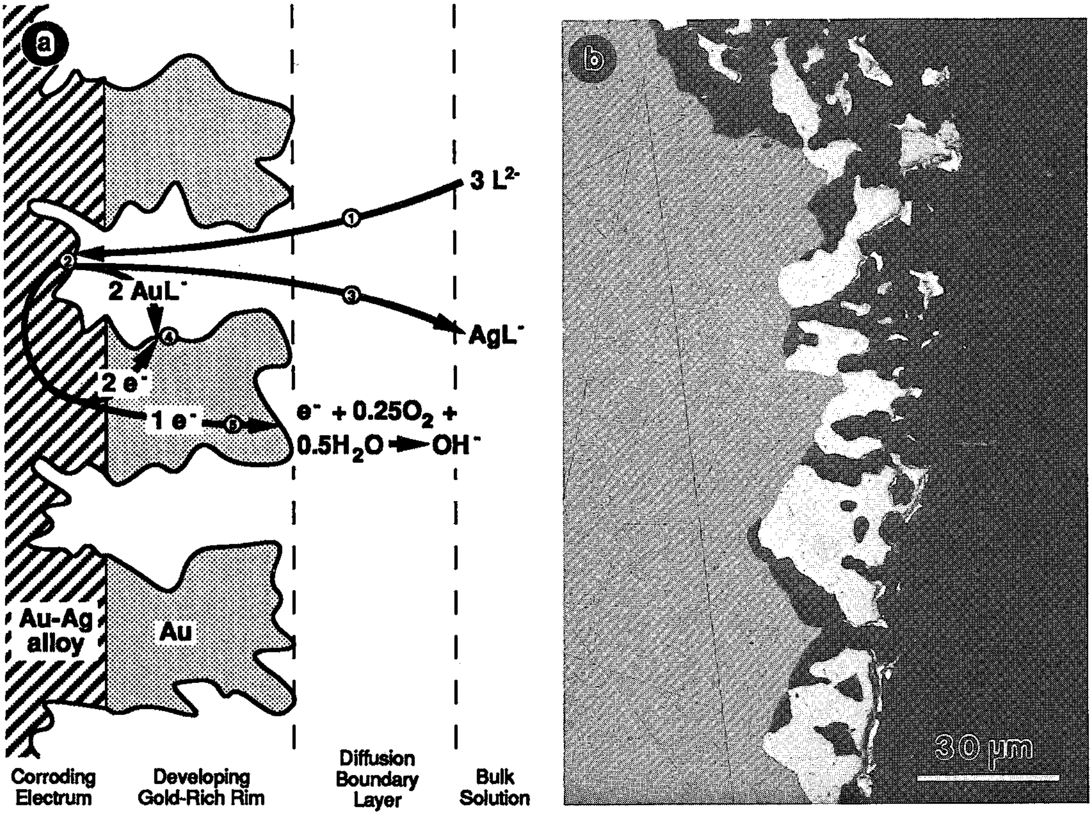


FIG. 10. Self-electrorefining model for the formation of a gold-rich rim. (a) Schematic illustration of the self-electrorefining process occurring on the surface of a placer electrum grain entailing the following steps (see corresponding small circled numerals on diagram): (1) transport of Au- and Ag-complexing ligands (L^{2-}) to the corroding surface of the electrum, (2) dissolution of the electrum by the complexing agents, with coincident liberation of three electrons (e^-), (3) loss of the more soluble Ag-complex to the bulk solution, (4) dissociation of the Au-complex by reaction with the free electrons at the pure gold surface bringing about the precipitation of pure gold, (5) consumption of extra free electrons through reduction of O_2 and H_2O to OH^- (diagram patterned after Fig. 1 of Strickland & Lawson 1973). (b) Back-scattered electron image of a polished placer gold grain from Brush Creek showing a gold-rich rim (brightest, high-electron-yield areas), with textural features nearly identical to those seen in the schematic of part (a).

orthogonal prisms and trigonal to hexagonal plates, the latter being more common. The hexagonal plates are believed to be covellite, and the orthogonal crystals, chalcocite. Based on the log $a(S_2)$ *versus* log $a(O_2)$ diagram for copper (Garrels & Christ 1965, p. 160), covellite is only stable at log $a(S_2)$ greater than about -21.0 [log $a(S^{2-}) = -33.2$]. These estimates are consistent with those given by Pan (1981).

The concentrations of the gold complexes are generally much higher for stream waters than for the sediment solutions, because the more oxidizing conditions in the stream waters promote oxidation of elemental gold to gold ions. The most likely complexes for significant transport of gold in oxidizing stream waters indicated by Table 3 are $Au(CN)_2^-$, $Au(OH)_2^-$, $Au(NH_3)_4^{3+}$, $AuOHCl^-$, $AuOHBr^-$ and $Au(I)_2^-$, whereas in the stream-sediment solutions $Au(CN)_2^-$ and $Au(HS)_2^-$ are potentially important, although $Au(CN)_2^-$ is by far predominant. These complexes are the main ones likely to yield concentrations of dissolved gold in typical fresh waters, near or above the upper limit of natural measured concentrations (Fig. 9).

Table 3 indicates that cyanide is by far the most effective complexing agent of gold in both oxidizing and reducing conditions; unfortunately, the small number of measured CN^- concentrations in natural waters makes it difficult to obtain a reliable estimate of its average concentration.

Thiosulfate has been credited as a likely transporter of gold in acidic, oxidizing sulfide ore deposits (Goleva *et al.* 1970, Stoffregen 1986). Table 3 indicates that this ligand is not especially important in normal stream waters, however, where total sulfur activity is considerably lower and Eh–pH conditions are markedly different.

Precipitation of gold complexes from solution takes place by the reduction of the Au^{1+} or Au^{3+} ions as they encounter solutions with a lower Eh. A steep redox boundary exists at the interface between stream waters and organic-matter-rich stream sediments. In Brush Creek, for example, crystals of copper sulfide grew on coin surfaces only one or two centimeters below oxidizing stream waters. This redox boundary is a very likely site of gold precipitation. Sharp redox boundaries also occur at the water table, and the large gold nuggets found down to, but not below, the water table in the southeastern United States (Cook 1987) may have grown at such a redox boundary.

The precipitation of aqueous gold complexes was examined by Mann (1984) and Stoffregen (1986). The precipitation mechanism suggested by Mann (1984) uses Fe^{2+} as a reducing agent. The Fe^{2+} ion, liberated from weathering rocks, migrates in solution until it encounters and releases its available electron to a gold complex. This reaction simultaneously precipitates native gold and ferric hydroxide:

$$Au(CN)_2^- + Fe^{2+} + 2H_2O = Au^0 + FeOOH + 2HCN + H^+.$$

Strong evidence supporting this type of process is provided by the common occurrence of iron hydroxide coatings on many of the recovered placer grains, and the presence of iron hydroxide inclusions in the gold-rich rims, as noted above. There are also numerous reports of the common and intimate association of the two phases (Desborough 1970, Lesure 1971, Mann 1984, Wilson 1984, DiLabio *et al.* 1985, Freyssinet *et al.* 1989). A precipitative origin for gold-rich rims is furthermore supported by the fact that the textures observed on natural grains are commonly indistinguishable from those textures resulting from the hydrometallurgical process of cementation (Fig. 10). Strickland & Lawson (1973) described "cementation" as: "...the electrochemical precipitation of a metal, usually from an aqueous solution of its salts, by a more electropositive metal." In the present case, however, the cementation process is driven by the oxidation of ferrous iron, rather than by the oxidation of a solid metal substrate.

Self-electrorefining

Electrorefining is a hydrometallurgical process in which a multicomponent alloy is electrochemically dissolved, with the subsequent precipitation of a generally pure phase of the most noble dissolved metal. The driving force for this process is an electrochemical potential. This potential can be brought about in two ways: (1) with a battery, (2) as a result of the electromotive force (EMF) between two dissimilar metals in a solution whose Eh is higher than that in which the starting alloy is stable. Our concerns are with natural systems, where batteries are not involved, and so the term "self-electrorefining" will hereafter be used to refer to electrorefining brought about by the second process listed above.

Fontana's (1986) description of the dezincification corrosion process shows that the dissolution of the brass requires oxidizing solution conditions and that the EMF formed by the copper–brass couple causes pure copper to precipitate. According to Fontana (1986): "The commonly accepted mechanism consists of three steps, as follows: (1) the brass dissolves, (2) the zinc ions stay in solution, and (3) the copper plates back on." For our concerns then, dezincification is a form of self-electrorefining, even though it involves man-made materials, because it proceeds without an external source of power.

Mann (1984) performed electrochemical experiments, which showed that in 0.03 *m* HCl - 1 *m* NaCl solutions, a distinct increase in Au–Ag alloy stability occurs with increasing fineness as measured against a pure gold electrode, demonstrating lower reduction potentials for lower fineness alloys.

Mann's (1984) results with synthetic alloys indicate that placer electrum grains can oxidize, releasing dissolved Ag and Au into solution (Fig. 10a). Once in solution, the less electropositive (and now isolated or "refined") dissolved Au species accepts the available electrons at the gold-rich areas on the electrum surface, and immediately precipitates to yield the textures described below. The more easily oxidized silver is washed away. The resulting electrolytic reaction is self-perpetuating as a result of the EMF between the gold-rich areas and the unrefined electrum. This process does not require a sharp Eh gradient to precipitate a gold-rich rim, just an ambient solution that is oxidizing enough to initiate dissolution of the primary electrum. This process would be accelerated by the presence of ligands such as CN^- , OH^-, NH_3, Cl^-, I^- Br^-, or HS^-; as they increase the solubility of the electrum components. Rudimentary forms of this idea were suggested more than 50 years ago by Fisher (1935).

The electrorefining process frequently produces surfaces bearing lobate protrusions of the deposited metal (crystalline growths also have been reported). These protrusions form because the surface of the more electropositive metal must maintain sites that remain exposed to the aqueous medium so that dissolution and subsequent charge-transfer can occur; hence "channelways" develop between the growing metal deposits on the surface (Fig. 10). The branching-coral texture of Figure 2 and the magnified view of the lobate gold-rich rimming of Figure 4a (shown in Fig. 10b) are strikingly similar to the schematic representations of cementation textures in Strickland & Lawson (1973) (after which Fig. 10a is patterned), and suggest that these rims were formed by precipitation from an electrorefining process. The size of the protrusions and the ratio of gold-coated surface area to surface area of the dissolving electrum core are highly variable on natural placer grains, as would be expected for grains of differing fineness of the core electrum in solutions of differing ambient composition (yielding variable reaction rates and availabilities of gold for precipitation). We do believe, however, that the same basic processes are responsible for the range of microtextures observed in the gold-rich rims.

Gold-rich rims and their associated surface textures appear to be the only likely products of extended exposure of electrum grains to stream and sediment waters. Gold-rich rims are very common on placer gold grains from the streams throughout the present study area, as well as from other localities that we, and other investigators (Desborough 1970, Giusti & Smith 1984, Freyssinet *et al.* 1989), have sampled. These rims appear to form by electrorefining where sharp Eh gradients do not exist (in flowing stream water), and by cementation where sharp Eh gradients do exist (*e.g.*, the interface between fine, organic-matter-rich sediment and oxidizing stream water, or at the water table). Where gold precipitation resulting from an Eh gradient is the dominant process, it is possible that the gold-rich rim is an incipient stage of a large "grown" nugget; thus gold grains that happen to reside in a soil horizon at the water table, for example, might grow to the remarkable and enigmatic sizes reported from various areas in the southeastern United States (Crayon 1857). The validity of this idea could be tested by analysis of large gold nuggets. If they formed by an overgrowth process, the fineness of the outer portion of such grains should be very close to 1000.

CONCLUSIONS

Gold grains undergo both physical and chemical changes as they are transported by streams. Newly liberated gold grains are usually irregularly shaped, and as a result of progressive stream transport they become semispherical, wafer-shaped, and finally flake-shaped. Their surfaces evolve from smooth and clean to pitted, hackly, and eventually, to lobate-textured, although variations in the stream's composition, energy and sediment type somewhat modify this general trend. Grain size decreases with increasing distance of transport.

During transport, many grains of placer gold develop an outer rim of nearly pure gold on the more silver-rich electrum core. The rim has a very sharp contact with the core, and appears to be the result of electrochemical processes active in the stream or stream sediments (or both). The rim generally is thickest on flake-shaped (most transported) grains and thinnest or absent on irregular (least transported) grains.

Three proposed mechanisms of gold-rich rim development were evaluated on the basis of observational evidence and theoretical calculations. Selective leaching of silver from the margin of gold grains appears to be impossible, because there is no means by which the solutions can physically extract the silver from more than the outer few ångströms of the grain. Diffusion of silver through the electrum to make the silver available to solution cannot aid this process, owing to the extremely slow rates of diffusion at low temperatures. Gold dissolution, transport, and cementation are steps in a viable process of growth of the gold-rich rims. There are sufficient amounts of CN^-, OH^-, NH_3, Cl^-, I^- Br^-, and HS^- in average stream and sediment solutions to account for the highest gold concentrations reported for streams. Several sulfur-bearing ligands are potentially capable of significant transport of gold, provided they can maintain their concentrations in oxidizing waters through metastable persistence. Some organic complexes also show potential for gold transport; however, there simply are not enough data regarding these species for a quantitative evaluation. Sharp redox boundaries, such as the stream water – sediment interface and the water table, would cause gold precipitation. Self-electrorefining of placer electrum grains is also a process that can produce gold-rich rims. The required conditions are present in most stream environments, and the textures of the gold-rich rims match those reported from controlled hydrometallurgical experiments with other alloys. Thus, a combination of self-electrorefining and cementation can explain the formation of gold-rich rims, as well as observed surface textures on the grains of placer gold.

ACKNOWLEDGEMENTS

The authors express sincere gratitude to Robert F. Martin, Scott A. Wood, and an unnamed referee for their insightful reviews of this manuscript. Samples of placer gold were graciously donated for use in this study by the U.S. Museum of Natural History and Mr. James R. McCloud. This research was supported by the Department of the Interior's Mineral Institutes program administered by the Bureau of Mines under allotment grant number G1184151.

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Received July 5, 1989, revised manuscript accepted February 28, 1990.