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A PYROLYSIS-GAS CHROMATOGRAPHIC STUDY OF ORGANIC MATTER FROM SNAKE RIVER FLAKE-TYPE PLACER GOLD PARTICLES

By

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ABSTRACT

Pyrolysis-gas chromatography (gc) was used to investigate the nature and content of possible organic matter in placer gold from a Snake River site near Grandview, ID. The study supplements and extends scanning electron microscope (SEM) and electron microprobe investigations which have shown that undamaged, partially gold-replaced bacterial populations are present on 1-2% of the placer gold particles from this and other Snake River sites. Because of the maleability of gold, the significance of these features almost certainly extends beyond their low representation in the studied populations of placer gold particles. The primary objective of this study was to determine the presence and amount of organic matter that is incorporated in the interior gold mass of samples of Snake River gold particles--that is, in portions of the gold particles safe from the attack of an oxidizing acid. These data were sought as possible evidence that the observed gold-replaced bacteria and their products, or other organic matter, may be routinely incorporated in Snake River gold particles during their genesis or detrital history.

Pyrograms were generated using samples of HNO_3- or HNO_3- and HF-cleaned gold flakes from the Dixie Ranch Mine, near Grandview, Idaho. Gold samples of ~5 mg contained ~10 parts per million organic matter based on pyrolysis products released at temperatures below the melting point of gold. Treatment of the gold sample with nitric acid was intended to restrict the quantitative estimation of organic matter to that entirely contained within the gold, that is, to a minimum value.

Although some organic matter is associated with HF-soluble minerals, most is associated with the gold. The pyrolysis products include mainly C_1-C_2 hydrocarbon compounds, but also some organic material up to C_{20}. Because multicarbon chains do not survive temperatures of 250°C (Al Hofstra and Joel Leventhal, USGS, pers. commun., 1995), the gold and its content of organic matter can have undergone little or no metamorphic alteration.

The 10 ppm organic matter associated with Dixie Ranch gold is too small to represent a conserved primary depositional matrix for Snake River gold, yet the 10 ppm amount of organic matter exceeds by nearly 400 times the amount of organic matter that can be attributed to bacteria observed on Snake River gold particle surfaces. Mechanically incorporated bacteria and other amorphous organic debris may account for the excess organic matter.

Appendix 2 develops a model for the chemical replacement of bacterial extracellular polysaccharides by gold.

BACKGROUND STUDIES

Scanning electron microscope (SEM) surveys of flake-type gold particles from the Snake River in southern Idaho have shown that as many as 1-2% of placer gold particles collected from areas between Fort Hall and Boise, ID bear 3-dimensional

surficial forms interpreted as populations of short rod-shaped bacteria (Figs. 1 and 2) that evidently have been chemically replaced by gold (also Watterson, extensive unpublished data). In context, these apparent bacterial forms in gold will be referred to hereafter as "gold-replaced bacteria" or simply "bacteria". Although 1-2% is a small proportion of the whole population of gold particles studied, the extreme maleability of gold suggests that such features--particularly such ubiquitous and evanescent features as bacteria--may be of significance for understanding the origin of flake- or "canlid"-type placer gold particles in the Snake River System.

One exceptional Snake River gold particle, the "Dixie Ranch flake", carries approximately 2000 such gold-replaced bacterial cells. Many of these bacterial forms are preserved at various stages of binary fission (Figs. 1 and 2) which is the common mode of reproduction among rod-shaped bacteria (Stanier and others, 1986). SEM and microprobe element-mapping studies of the Dixie Ranch flake show concentrated, high-carbon areas that match the shape and arrangement of clusters of gold-replaced bacteria (Fig. 3; also Watterson, extensive unpublished data). High-resolution SEM stereoscopic studies of several ruptured gold-replaced cells show bacterial forms that are not solid but consist of a hollow gold shell that ranges in thickness from 60 to 120 nm (Watterson, unpubl. data). Although gram-positive bacterial cell walls are normally 80 nm or less in thickness (Stanier and others, 1986), the average thickness (100 nm or 0.1 μm) and form of the studied specimens suggests that gold has preferentially replaced only the bacterial cell-wall material. The chemical replacement of bacterial cell-wall material with gold has been achieved experimentally by Beveridge and Murray (1976); their report shows a transmission electron microscope (TEM) section through a Bacillus subtilis cell wall replaced by metallic gold. The chemical affinity of bacterial cell-wall material for soluble forms of gold and other metals is well known and has been studied at the level of ultrastructure (Beveridge and Doyle, 1989; Beveridge and Murray, 1976, 1980; Beveridge and others, 1983). Further, thinly gold-coated bacterial cells otherwise indistinguishable from their more numerous naked congeners have been recovered from auriferous Alaskan soils and documented before and after heat-stripping the surface film of gold (Brooks and Watterson, 1992); similar gold-coated bacterial cells have been documented in association with Alaskan placer gold (Watterson, 1994).

Other characteristic morphological features in gold (silica-containing forms are also present) invariably accompany bacterial cells where they occur on Snake River flake-type gold particles. These morphological features have the appearance of initially deformable, short cylindrical strands ~0.2 μm in diameter that connect gold-replaced bacterial cells to the colonized gold surface (Fig. 1, arrows). Although these secretions usually take the form of unnoticable "attachment pads" hidden beneath the bacterial cell, they may be highly variable in length, sometimes

reaching a length of several micrometers, in which case they can have the appearance of extruded calking or toothpaste (Fig. 1, arrows).

A review of the literature on mechanisms of microbial attachment to surfaces suggests that these connecting structures are gold-replaced residues of extracellular attachment or "holdfast" secretions. TEM and SEM photographs of polysaccharide holdfast structures and material are shown in Costerton and others, (1978); Bitton and Marshall, (1980, p. 128-130, 161, 263, 264, 383, 410, 412, and 420); and Atlas and Bartha (1981; p. 274 and 304). The latter two SEM photographs show bacteria and holdfast attachments of approximately the same proportions as those shown in Fig. 1. A superlative comparison to Fig. 1, however, can be made with a large photograph shown by Kevin Marshall (1992, p. 265); here a variety of identical "condensed extracellular polymeric substances" are shown connecting rod-shaped bacteria (of the same relative proportions as those in Fig. 1) to each other and to a glass surface.

Sessile bacteria invariably utilize some such form of attachment to establish and maintain their hold on submerged surfaces (Geesey and others, 1978), although among some groups mechanisms in addition to polysaccharide holdfasts may be involved. Contact with submerged surfaces may in fact stimulate exopolysaccharide synthesis by bacteria (Vandevivere and Kirchman, 1993).

The relevant structures in gold that are associated with and appear to have originated from now gold-replaced bacteria are hereafter referred to as "holdfasts", "holdfast structures" or "holdfast material". The residue of holdfast material that adheres to the surface following the loss of a bacterial cell often resembles and has been likened to a tree stump (W.H. Raymond, USGS, pers. commun., 1994); areas on gold surfaces populated by the remnants of such gold-replaced holdfast residues have similarly been likened to "stumpfields".

The potential importance of evidence for gold-replaced bacterial holdfast structures in this study (Fig. 1), is linked to three observations: (1) "stumpfields" of gold-replaced holdfast material (areas containing or appearing to consist largely of gold-replaced holdfast debris) generally extend far beyond areas occupied by gold-replaced bacterial cells; (2) stumpfields of gold-replaced holdfast material, evidently less fragile than gold-replaced bacterial cells, can often be identified in the absence of gold-replaced bacterial cells; thus (3) surface regions of gold particles typified by stumpfields of gold-replaced holdfast material may signify a far more voluminous gold-replaced biological residue on Snake River gold particles than the remaining, now gold-replaced, bacterial cells from which they evidently originated.

It appears that the observed gold-replaced bacterial cells may add gold to the surface of a gold particle; that can be seen in Figs. 1 and 2 where gold-replaced bacterial cells have been flattened against or otherwise partially incorporated into the

adjacent gold surface. Many instances of gold-replaced bacterial cells partially flattened into adjacent gold surfaces have been documented elsewhere (Watterson, extensive unpublished data).

These observations raise fundamental questions about the origin of the observed gold-replaced bacterial cells and their associated gold-replaced holdfast structures in relation to the gold particles on which they reside. Are they, like microscopic barnacles, simply passengers that have become metallized by gold solubilized from neighboring gold particles or perhaps from the very gold particle to which they are attached? Or do bacteria and their associated debris play an accretionary role in the genesis of the gold particles, adding soluble gold from the environment to the gold particle? Do a number of processes occur? If so, is one process more important than the others?

These questions are not answerable by morphological studies alone. The present study was initiated to determine the amount and type of organic matter present in gold particles from one Snake River site. We wished to learn if such data could be related to morphological and spectral data obtained from Snake River gold particles that carry gold-replaced bacteria. Thus, representative gold particles from the Dixie Ranch Mine were analyzed by flash and stepwise pyrolysis-gas chromatography.

MATERIALS AND PROCEDURES

Water and chemicals used were reagent grade. Unsieved, fine so-called "canlid" or flake-type placer gold particles were purchased from Mr. Larry Mashburn, owner of the Dixie Ranch Mine Company near Grandview, ID., where gold particles are routinely recovered on a Diester table in connection with a sand and gravel operation. Gold particles from this site have been described by Desborough and others (1988).

Because of the possible presence of natural organic matter on gold surfaces or adventitious organic matter that may have been added during concentration, panning, and handling, the samples were subjected to rigorous cleaning in nitric acid. The latter procedure restricted pyrolyzed organic matter to that which was indigenous to the gold particles and encapsulated within gold or water-laid silica (dealt with in a separate procedure). Approximately 0.1 g of unsorted gold flakes was immersed in 16N nitric acid overnight, then rinsed in water and acetone. Particles of white and pink quartz sand and non-magnetic black sand were removed by panning in acetone followed by dry panning, the remaining gold was picked reasonably free of sand and amalgam particles under a binocular microscope. The first two ~5-mg samples were taken directly from this batch. For the third 5-mg experiment, gold previously cleaned and sorted (above) was boiled briefly in 16N nitric acid, immersed for six days in 49% HF at 55°C, transferred again briefly to 16N nitric, and finally rinsed three times in acetone.

Pyrolysis-gas chromatograms (pyrograms) were generated on a 1 millivolt Beckman[1] chart recorder using a Perkin Elmer[1] model 900 gas chromatograph equipped with a flame ionization detector and a Pyroprobe 100[1] (Chemical Data Systems) resistance filament pyrolyser. Other experimental details were as noted in Leventhal (1976). Because we were unsure of the amounts of organic matter in these samples, we took precautions to be sure the system was free from any extraneous organic matter, and that the background and sensitivity were optimized. The entire system--pyroprobe coil filament, pyrolysis tubes, injector port, capillary gas chromatographic column, etc.--was taken through several purging cycles at coil temperatures of 600°C, 750°C, 900°C, and 1000°C.

A representative background for the system is shown on Fig 5, labelled as "Blank"; although this is a 600°C step, similar low backgrounds were achieved at higher temperatures. In all experiments the background or blank was less than 0.1 of the signal generated from the sample at the same or comparable temperature, a ratio considered acceptable for low-level pyrolysis experiments of this type. Nominal pyrolysis temperatures refer to temperatures attained by the platinum coil surrounding the quartz sample tube; apparently, the sample does not achieve as high a temperature as the platinum coil. Except for the 1250°C pyrolysis of the third sample, heating was for 10 seconds.

The first sample was pyrolyzed successively at 600°C, 750°C, 900°C, and 997°C. The second sample was pyrolyzed once at 900°C. The third sample was pyrolyzed at 600°C and then at 1250°C in two 10-second heatings. Although the edges of the gold flakes in the last sample fused together where they were in contact, no further indications of melting (such as distortion of the gold flakes or pooling) was observed. The amount of organic matter present in the gold samples was estimated by measuring peak heights, converting their sums to cumulative areas, and referring these areas to areas produced by a standard series of injected methane volumes.

SEM and energy-dispersive x-ray (EDX) analyses referred to in Figs. 1, 2, and 4 were as described in Watterson, 1992.

RESULTS

Following pyrolysis of the first sample, some of the gold flakes were observed to have a sooty appearance on at least one face (Fig. 4). Following pyrolysis of the second sample, counts made using a binocular microscope showed that a minimum of 11% of the pyrolyzed placer gold particles in the second sample had a sooty appearance on at least one side. Light microscope and SEM inspection showed that the "sooty faces" were invariably associated with a thin layer of fine silicious material. No gold flakes bearing silicious coatings were found that had not turned

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[1]Brand names used for technical purposes only.

black; among many hundreds of gold particles inspected, "sooty faces" were found to be coeval with thin silicious coatings. The possibility that organic matter was associated with this silicious material resulted in retesting a third sample from the same batch following HF-dissolution of the silicious material.

Gas chromatograms are shown in Fig. 5. Cumulative estimates of organic matter volatilized from the three gold samples are shown in Table 1.

The first sample (Fig. 5) shows maximum pyrolysis products following heating at 750°C and a diminution of pyrolysis products at higher temperatures. Despite differences in pyrolysis conditions for comparable runs, (one 10-second heating at 900°C for the two HNO_3-cleaned samples and two consecutive 10-second heatings at 1250°C for the HNO_3- and HF-cleaned sample), comparison of the two chromatograms indicated that C_5+ organic matter was associated with both the gold and the associated HF-soluble minerals. Based on fluid-inclusion studies, the presence of C_5+ pyrolysis fragments suggests that the organic matter associated with Dixie Ranch gold had not been heated to >200°C.

The highest system blank recorded prior to a pyrolysis run was 2×10^{-9} g C. Cumulative totals for organic matter from the three gold samples were 20×10^{-9}, 40×10^{-9}, and 21×10^{-9} g C (Table 1). Subtracting the maximum blank and averaging these results gives an average value of 25×10^{-9} g C / 5×10^{-3} g Au or 5 ppm pyrolysis products. Pyrolysis leaves at least half of the initial organic matter immobilized as carbon, according to the standard carbonization/disproportionation reaction typical of high-temperature pyrolysis:

$$-(CH_2)_{2n}- \xrightarrow{\Delta} -(C)_n- + nCH_4.$$

The pyrograms thus indicate that the gold samples contain an average of about 10 ppm organic matter. Assuming the organic matter has a density of 1.0 g/ml, this amount of organic matter would occupy about 0.02 percent of the overall volume of the gold (at a density of 19 g/ml).

Based on SEM observations of the frequency of gold-replaced bacteria on flake-type gold particles surveyed from several sites along the Snake River in southern Idaho, a maximum estimate for the amount of organic matter contributed by intact, gold-replaced surficial bacteria to an average gold sample would be ~0.026 ppm (see Appendix 1). It may be noted that SEM surveys of gold particles from the Dixie Ranch site indicate a rather lower frequency of gold-replaced surficial bacteria than the 1-2% estimated as representative of Snake River sites surveyed. In any case, the amount of organic matter present in Dixie Ranch gold exceeds the estimated contribution of observed gold-replaced bacterial cells by ~385 times (10 ppm / 0.026 ppm).

Based on previous pyrolysis-gc experiments and other organic matter characterization (Hofstra and Leventhal, 1987; Leventhal and Hofstra 1990; Leventhal and others 1975, 1987a, 1987b; Leventhal 1976, 1981, 1990), the presence of pyrolysis products

up to the C_{20} range in molecular weight is representative of unmetamorphosed organic matter, i.e., organic matter that has experienced no heating events above 250 °C. Considering the small total quantity of organic matter tested, the distinct presence of molecules in the C_{20} range suggests that the gold samples had probably not experienced temperatures as high as 100°C.

DISCUSSION

We have not found any previously published information in the literature on the organic contents of natural gold. The further absence of studies of gold-mineralized organic matter has prompted us to refer to a possible natural analog, petrified wood and its content of retained organic matter.

The quality of detail shown by gold-replaced bacteria on Snake River gold particles compares well with the finest SEM preparations that can be made in the laboratory from living specimens. The snapshot-like fidelity of these forms--which show actively dividing, holdfast-secreting bacteria (Figs. 1 and 2)--suggests that their chemical fixation in gold must have taken place fairly rapidly.

The duration of the initial killing event may be related to the number of metallized holdfast structures that are present in the absence of bacterial cells--if it is assumed that these holdfast structures represent a chemically interrupted attachment. Under most conditions, such attachments, once formed, tend to be irreversible (Marshall and Bitton, 1980). A killing time shorter than the time required for a colonizing cell to achieve firm attachment could possibly account for many such isolated and unoccupied holdfast structures. Alternatively, the excess of metallized holdfast structures over metallized cells may relate to the relative efficiency with which these structures are metallized by gold. In either case, the extensive, unoccupied "stumpfield" areas on the Dixie Ranch and other Snake River gold particles may relate to the duration of the killing event.

It is additionally possible that these bacteria have some mechanism for detaching from surfaces in a toxic situation. Tso and Adler (1974) showed that E. coli exhibit negative chemotaxis in response to concentrations of certain metals. Conjecture along this line is clouded, however, by the unknown tenacity of the bacterial attachments and the fact that the motility of bacteria is highly sensitive to inhibition by trace amounts of heavy metal ions (Adler and Templeton, 1967). The ratio of metallized "stumpfield" areas to cells may indeed have nothing to do with their preservation in gold.

Despite the uncertainties, it seems likely that the duration of the killing/fossilizing event is on the scale of a few hours, if not a few minutes. In addition to the high level of biological detail, the exclusively cryptocrystalline form of gold

on the surface of these placer gold particles is consistent with rapid rather than prolonged gold deposition.

The geochemical requirements for such a rapid pulse of dissolved gold at first appeared baffling. However, despite the widespread occurrence and study of petrified wood, the geochemical mechanisms that induce wood petrifaction involve some of these same baffling features.

For instance, silicified plant parts often show no physical distortion or compression, an indication that petrifaction occurs relatively rapidly; yet the amount of silica in groundwater (70-100 parts per million) is so small that silicification must proceed with extreme efficiency (Barghoorn, 1977, p.49). Environmental concentrations of dissolved gold are far lower than dissolved silica. Natural waters in mineralized areas (McHugh, 1988) and even water extracted from gold-bearing soils (Severson and others, 1986), average only about 0.1 ppb dissolved gold. It is difficult to think of a solution this dilute as potentially "mineralizing". Yet, at a concentration of 0.1 ppb the amount of dissolved gold required to mineralize a single bacterium of the size shown in Fig. 1 or 2 (a mass of gold equal to 2.5×10^{-12} g) is contained in 0.025 ml of water, the size of a small raindrop (Appendix 1). There is enough dissolved gold in one ml of water containing 0.1 ppb gold to mineralize 65 such bacterial cells. The mineralizing capacity of such small volumes of water in mineralized soil may be consistent with the chemical replacement of bacteria with gold in soil during the moist unfrozen conditions most conducive to bacterial growth. However, the potential for chemical interaction at particle surfaces in soil may be significantly enhanced when dissolved gold and other solutes become concentrated in unfrozen water films during freezing and/or drying (Watterson, 1985).

Inasmuch as bacterial cell wall peptidoglycans, bacterial capsules, holdfasts, and slimes, and the cellulose of woody materials are all variant polysaccharides with common functional groups, it may be that soluble gold complexes invade and mineralize bacterial cell walls and polysaccharide slimes in much the same way that silicic acid solutions invade and mineralize wood. Plant tissue fossilized in calcite, phosphate minerals, pyrite, hematite, and other less common minerals has been observed (Barghoorn, 1977).

Hydrogen bonding between the hydroxyl functional groups in cellulose and silicic acid [$Si(OH)_4$] has been proposed as the probable mechanism for wood silicification during the process of petrifaction (Sigleo, 1978a; Leo and Barghoorn, 1976). Metals tend to form bonds with electron-donating groups in order to fill their outer electron shell, and the most effective electron donor group associated with acidic capsule and slime polysaccharides is the carboxyl residue (Geesey and Jang, 1989). Weak electron donors are also present on acidic and neutral polysaccharides in the form of oxygen atoms associated with the ether bond and hydroxyl residues on the sugar subunits (Martell, 1971). Beveridge and Jack (1982) have demonstrated that carboxylate

groups are the primary site of metal binding in the peptidoglycan of Bacillus subtilis cell walls.

Pyrolysis-gas chromatography was chosen for this study because it is a sensitive means of investigating complex geochemical organic material. Although under certain conditions the method can provide "fingerprints" of individual species of bacteria (Meuzelaar and Veld, 1972), no attempt was made to apply the present data to such an analysis.

The percentage by weight of organic matter retained in silicified wood may range from "not detectable" (Sigleo, 1978b) to more than 15% (Barghoorn, 1977). However, the amount of organic matter retained in silicified wood may have more to do with its loss during diagenesis than with initial silicification (Cf. Sigleo, 1978b). In the surficial environment, a gold matrix, on the other hand, could presumably serve as an indefinite trap for hermetically enclosed organic matter because of the dense atomic packing of the gold lattice. At temperatures below 100°C, a perfect gold lattice with interatomic spaces of ~0.46A should retain even H_2 with a mean diameter of 1.2A. Imperfections in the gold lattice could perhaps lead to minor losses of hydrogen and other small organic molecules, particularly at elevated temperatures. But apart from mechanical disruption, there appears little reason to expect a significant loss of any organic matter fully encapsulated in gold at surface temperatures.

If bacterial polysaccharides or other organic matter were quantitatively retained during a gold-mineralizing event, the amount of retained organic matter would be in direct proportion to the original density of the organic matrix mineralized. Whether or not this can happen, it is useful to calculate an upper reasonable content of organic matter in gold assuming that organic matter could somehow be dispersed within a gold matrix.

To model a theoretical gold particle that entrains organic matter (i.e., extracellular polysaccharides), we will make the assumption that soluble gold complexes have invaded and metallized, but quantitatively retained the organic content of several concentrations of bacterial slime. The range of densities of organic matter in 0.1, 0.2, 0.5, 1.0, 2.0, and 5.0 percent solutions of bacterial extracellular polysaccharides would reasonably represent the full range of polysaccharide densities from dilute dissolved slime to partially dehydrated capsular polymers, a 1% solution representing average bacterial slime (Wilkinson, 1958). If the water in the above organic solutions was replaced by gold without loss of the organic matter, then on a weight/weight basis (neglecting small changes in the density of the gold sample) such a series of gold samples would contain 53, 105, 263, 526, and 1,053 ppm organic matter, respectively (calculation not shown).

The reported content of organic matter in bulk Dixie Ranch gold, 10 ppm, thus does not reflect quantitative retention of the equivalent organic matter contained in a bacterial slime, even at a 1:10 dilution.

Consistent with SEM and microprobe observations, three alternative conclusions are suggested concerning a content of 10 ppm organic matter in Dixie Ranch placer gold particles. (1) Not all of the organic matter was released from the gold in the pyrolysis-gc studies. (2) All of the organic matter was released from the gold during pyrolysis, but gold-replaced bacteria and their associated stumpfield areas, which may contain organic matter, are limited surface features of the gold particles. (3) Little or no residual organic matter is associated with the stumpfield areas (this appears to be consistent with element-mapping studies completed to date); in which case the excess of organic matter may indicate a much larger contribution to the gold by gold-replaced bacterial cells or other organic matter than estimated on the basis of observed gold-replaced bacteria.

On the model of petrified wood, in which the original organic matter may be largely or entirely absent, it may be that gold-replaced polysaccharide holdfast structures likewise retain little if any of their original organic matter. This conjecture is supported by consideration (Appendix 2) of an ultrastructural model of bacterial extracellular polysaccharides. In any case, the pre-mineralization presence of extensive bacterial holdfast structures appears to follow from their morphological representation in gold, which is well attested in SEM studies of the surface topography of Snake River gold particles.

The small size of interstices in the gold lattice relative to the diameter of methane (0.46 angstroms and 2.74 angstroms, respectively) suggest that gold could retain pockets of organic matter at pyrolysis temperatures below the melting point of gold. However, at pyrolysis temperatures, organic matter reacts to form CH_4 and H_2 gases that will exert high pressure on the enclosing gold. Because the maleability of gold increases significantly with temperature, it is unlikely that these gases would be efficiently retained. In sample #1 (Fig. 5), the relative yield of gases at 750°C, 900°C, and 997°C suggests that the majority of organic matter was released from this sample by the time it reached 750°C.

Imperfections in the gold lattice, folding, mineral inclusions, etc., would also facilitate the escape of pyrolysis products at submelting temperatures. The general softening of gold at submelting temperatures could also permit the release of organic matter in association with steam explosions.

In summary, a small quantity of pyrolysis products (5 ppm) from relatively unmetamorphosed organic matter was released from Snake River flake-type placer gold particles following rigorous cleaning procedures destructive of organic matter and silicious debris. It may be noted that the reported quantity of organic matter in Dixie Ranch gold is a minimum value. Treatment of the gold samples with an oxidizing acid has eliminated not only any organic matter contaminating the surface of these particles, but also, perhaps, some internal organic matter communicating with the surface of these high-surface-area gold particles. Any error

caused by the nitric acid treatment would be small and would favor the present interpretation.

The apparent 10 ppm organic matter content of these gold particles is only about 2 percent of the amount of organic matter that would be expected if bacterial holdfast material had served as a chief depositional matrix for (and had been retained in) the gold. This quantity of organic matter, therefore, does not provide direct evidence for an organic depositional matrix for Snake River gold. The 10 ppm organic matter contained in the gold, however, exceeds by nearly 400 times the amount attributed to observed populations of intact, partially gold-replaced bacterial cells observed on Snake River gold particles. The additional organic matter may derive from bacteria or other morphologically indistinct organic matter mechanically or chemically incorporated in the gold.

Appendix 2 discusses the ultrastructure of bacterial polysaccharides in relation to their possible chemical replacement by gold.

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APPENDIX 1

A calculation of the amount of organic matter expected in Dixie Ranch gold based on the Dixie Ranch flake (outlines shown on Figs. 2 and 3) and the estimated maximum frequency of bacteria on gold flakes from the Dixie Ranch Mine.

Summary: approximately 0.026 ppm organic matter can be accounted for on the basis of observed surface bacteria. The 10 ppm organic matter content of Dixie Ranch gold estimated by pyrolysis products is thus 385 times higher than would be expected on the basis of observed surface bacteria.

Dixie Ranch flake: dimensions; x = 60 μm (60 x 10^{-4} cm or 0.006 cm); y = 136 μm (136 x 10^{-4} cm or 0.0136 cm); z = 7 μm (7 x 10^{-4} cm or 0.0007 cm); volume = 5.71 x 10^{-8} cm^3. At the density of gold, 19 g/cm^3, the Dixie Ranch flake weighs 1.085 x 10^{-6} g.

Dimensions of an average fossil bacterium: 1 μm x 0.476 μm or 10^{-4} cm x 0.476 x 10^{-4} cm; approximating to a cylinder, volume = length x π r^2 10^{-4} cm x $\pi(0.238 \times 10^{-4}\ cm)^2$ = 1.78 x 10^{-13} cm^3. Assuming that the gold-replaced cell wall averages ~0.1 μm in thickness, the approximate internal volume (organic content) of such a bacterium would be 0.8 x 10^{-4} cm x π x $(0.138 \times 10^{-4}\ cm)^2$ = 4.8 x 10^{-14} cm^3.

The amount of gold in a single bacterium would approximate 19 g/cm^3 x [(1.78 - 0.48) x 10^{-13} cm^3 = 2.5 x 10^{-12} g. In water containing 0.1 ppb dissolved gold, this amount of gold would be contained in 2.5 x 10^{-12} g Au / 0.1 x 10^{-9} g ml^{-1} = 0.025 ml of water, the volume of a small raindrop.

If the internal volume of an average gold-replaced bacterium on the Dixie Ranch flake is 4.8 x 10^{-14} cm^3, assuming 30% dry weight (Lehninger, 1982, p. 53), the weight of organic matter in one bacterium would be 1.4 x 10^{-14} g.

On one side of the Dixie Ranch flake, there are approximately 2000 bacteria (2024 by count). Their total weight of residual organic matter would be about 2000 x 1.4 x 10^{-14} = 2.8 x 10^{-11} g. Not counting bacteria that may be on the side that cannot be observed, surface bacteria would contribute 2.8 x 10^{-11} g of organic matter to a gold flake weighing about 1.085 x 10^{-6} g. The ratio of organic matter to gold would be 2.8 x 10^{-11} g / 1.085 x 10^{-6} g = 26 x 10^{-6} g of organic matter per gram of gold, so the Dixie Ranch flake contains a minimum of 26 ppm organic matter.

On the basis of the calculated organic content of the Dixie Ranch flake and a rough estimate of the frequency of similar bacterial features on gold flakes from the same site (at a maximum, one gold flake in fifty may contain 100 surface bacteria), bulk gold from this site might be expected to contain a maximum 26 / (50x20=1000) = 0.026 ppm organic matter, making the empirical 10 ppm organic matter figure 10 / 0.026 = 385 times higher than expected based on observed bacterial cells.

APPENDIX 2 by J.R. Watterson

This appendix provides an additional review of physical and chemical parameters relevant to the conjecture that bacterial polysaccharide holdfast material may be chemically replacable by gold without retaining representative quantities of the original organic matter.

A summary of conclusions. Bacterial (slime) capsules and other polysaccharide structures have been shown to consist of highly penetrable, open-structured, three-dimensional networks of cellulose-like polyglucose fibers. According to the proposed model, which conforms to established biochemical models, chemical reaction between positively charged gold ions and polyglucose fibers would result in the depolymerization of polyglucose fibers concurrent with the reduction of ionic gold. The open structure of the polysaccharide network would conceivably permit broken glucose and polyglucose fragments to diffuse away from a progressively metallized edifice.

Contrary to initial expectation, it thus appears that the physical and chemical structure of bacterial polysaccharides may permit their chemical replacement by gold without concurrently entraining significant organic matter.

The hypothesis with which we began the pyrolysis-gc study was that the ground mass of some, possibly most, Snake River flake-type placer gold particles consists of gold secondarily deposited in the form of morphologically identifiable bacterial extracellular polysaccharide, principally intact bacterial holdfasts or holdfast debris. It was supposed that the above hypothesis would hinge on the presence, in Dixie Ranch gold, of an amount of organic matter commensurate with that contained in equivalent volumes of holdfast material.

Evidence for the secondary nature of this gold consists of SEM photographs and low-voltage, 100 second-count EDX analyses that show gold-replaced bacteria attached to the surface (albeit of a limited number of gold particles recovered between Ft. Hall and Boise, ID) by recognizable gold-replaced "holdfast" secretions (Fig. 1). As in Fig. 1, areas adjacent to gold-replaced bacteria are often interpretable as accumulations of holdfast debris that have been chemically replaced by gold and thereafter mechanically compacted. The surface extent and by inference the volume of such gold-replaced holdfast material greatly exceeds the total volume of gold-replaced bacterial cells on all examined gold particles. The least-compacted debris contains forms indistinguishable from nearby holdfast structures that are yet attached to gold-replaced bacteria. Other closely examined gold particles have been interpreted as consisting of compacted gold-replaced holdfast debris of this sort, i.e, of "stumpfields", with or without associated gold-replaced bacteria.

The large ratio of such "stumpfield" areas to areas occupied by gold-replaced bacteria suggests that the hollow, often precariously attached gold-replaced bacterial cells are more susceptible to loss or obliteration than the holdfast material.

The greater areas of holdfast material may additionally suggest the toxicity of conditions under which they were laid down. Gold concentrations or other physico-chemical conditions capable of initiating the chemical invasion and replacement of a holdfast secretion with gold would be lethal or potentially so to colonizing bacteria. Intact gold-replaced bacterial cells may be exceptional relics of a geochemical process in which bacterial cells attempting to colonize a gold particle are routinely killed or driven off by the local chemical environment.

Assuming that most or all of the organic content of the Dixie Ranch gold is represented in the pyrolysis fragments detailed in Table 1, the pyrolysis experiments indicate that organic matter in amounts approximating the original postulated mass of polysaccharides (the present volume of the gold) is not now present in the gold. Does this mean that gold replacement of bacterial polysaccharides (for which there is visible evidence) did not take place?

It has been suggested in the text that by analogy to certain petrified woods that retain little or no organic matter, gold-replaced bacterial holdfast structures may likewise retain little if any of their original organic matter. Their association with carbon-containing gold-replaced bacterial forms suggests that gold-replaced holdfast structures are authentic replacement structures even in the absence of the original organic matter.

How likely is it that a bacterial extracellular polysaccharide could become metallized in such a way as to retain its original shape and yet not retain most of its original organic matter?

Friedman and others (1968) investigated the ultrastructure of the zoogloeal matrix or polysaccharide capsule formed by Zoegloea ramigera, a common, rod-shaped, flock-forming pseudomonad. Their description of extracellular polysaccharide capsule structure has been verified for other flock-forming bacterial secretions (Brown and Lester, 1979) and may be reasonably applied to the holdfast structures discussed here.

On the basis of infrared absorption spectra, Friedman and others (1968) concluded that the capsule polysaccharides of Z. ramigera consist primarily, if not exclusively, of glucose subunits with primarily hydroxyl and aldehyde or ionized carboxyl functional groups. The polymer was not susceptible to hydrolysis by either α- or ß-amylase but was significantly hydrolysed by cellulase in comparison to carboxymethylcellulose controls, suggesting a polymer resembling cellulose containing 1,4 ß glycosidic bonds (Fig. 6B); glucose was the only hydrolysis product detected (Friedman and others, 1968) In a TEM study of thin sections through quick-frozen purified matrix material, the latter workers concluded that individual "fibrous" polymer strands measured 2 to 6 nm in diameter.

If the subunits of these fibrous strands consist, as indicated, of linear polyglucose polymers on the model of cellulose (Fig. 6B) in which a cross-sectional bundle of three polyglucose subunit strands would approximate 1 nm in diameter (estimated from the data of Pauling, 1959), then the individual fibrous polysaccharide strands could consist of as a few as 9 (3 bundles of 3) and many as 63 (7 bundles of 9) linear polyglucose substrands. The TEM photographs of Friedman and others (1968) suggest that the zoogloeal matrix can be visualized, for convenience, as a three-dimensional fishnet with 50 nm open spaces between the webbing strands. An average polysaccharide strand making up the net is 4 nm in diameter and consists of a bundle of 36 polyglucose substrands.

It is reasonable to expect that the polysaccharide network would contract and become more closely knit during dehydration and that it would inflate with hydration, maximizing the distance between strands. Water within the interstices of the polymer matrix would contain dissolved glucose and polyglucose fragments that could also tend to reduce inorganic gold complexes (and those of other positively charged transition metal ions such as Hg^{++}, Cu^{++}, and Ag^{+}).

What is the density of functional groups on such a 4 nm-diameter polysaccharide strand? A 1-nm length of a building-block polyglucose substrand would contain about three glucose molecules (cf. Fig. 6 B). With a view to coordination or oxidation-reduction reactions, each glucose unit or hexose ring can be assigned two hydroxyl groups and an aldehyde or carboxyl group (Fig. 6 B), depending on whether the ether bonds part between the 1,2 or the 2,3 carbon atoms, respectively. For every nanometer of polysaccharide stand, there are 3 x 2 x 36 = 216 hydroxyl groups and, potentially, 3 x 36 = 108 terminal aldehyde or carboxyl groups.

How penetrable would the three-dimensional polysaccharide net be to organic gold complexes, colloids, etc.? Based on the discussion of structure in Stevenson (1982, 259-261), unfolded fulvic acid "molecules" (Fig. 6 A) are 1-2 nm in their longest dimension; humic acid "molecules" are on the order of 5-10 nm. Most inorganic gold complexes identified as important in the zone of weathering (Lakin and others, 1974), including their hydration spheres, are probably no more than a nanometer in diameter. In short, all of the natural chemical forms of gold appear to be small in comparison to the open spaces in bacterial extracellular polysaccharides. Most true gold colloids are smaller than 60 nm (Alexander, 1937, p. 7), and would be able to penetrate the open spaces of bacterial extracellular polysaccharides.

As noted above, the diameter of a holdfast structure is only about 200 nm. On the basis of the above model, a diffusing moiety would need to negotiate as few as five polysaccharide strands to traverse the diameter of a holdfast structure. Even if holdfast polysaccharides are somewhat more tightly knit than our model based on Z. ramigera, it would appear that the distance across a holdfast structure is small in relation to the size of

the open passages within its polysaccharide network. On the basis of size comparison, 200 nm-diameter holdfasts appear to be remarkably open structures penetrable by the largest humic complexes.

Although a large (10 nm) humic acid "molecule" may contain a few dozen hydroxyl and carboxyl groups, were it to encounter an average 4 nm-diameter polysaccharide strand, it would be within about 4 nm of 2160 hydroxyl groups and 1080 available terminal aldehyde or carboxyl groups. Fulvic acids have been found to be more efficient than humic acids as metal complexing agents, probably because of their relatively higher content of acidic functional groups (COOH), which determine the stability of such metal complexes (Stevenson, 1982, p. 348-50).

The stability of gold-fulvates, which may thus be the strongest complexes in this class, depends on coordination to at most a dozen hydroxyl and carboxyl groups combined (Fig. 6 A). On the basis that the relative stability of gold-complex formation in a competing fulvate-polysaccharide system would depend on the density of carboxylate groups (Stevenson, 1982, p. 348) the probability seems good that Au^{+++} ions complexed to fulvic acid could be lost to the far higher density of carboxylate groups available in a polysaccharide strand.

What is emerging from this exercise is an informal physical and chemical model of our polysaccharide holdfast stalk. We have shown the open nature of the material and the apparent likelihood that chemical complexes of whatever sort would have ready access to the interior of 200 nm-diameter holdfasts. What would happen to the polymer fabric were it saturated with previously complexed Au^{+} or Au^{+++} ions?

The bonding sites on the glucose polymer most attractive to gold or any other oxidant (Lehninger, 1982, p. 282-4) would be the carboxylate group centering on the #1 carbon atom in each hexose ring. Because this functional group includes the bridging oxygen in the 1,4 ß glycosidic bond, the inevitable result of interaction between ionic gold and a polysaccharide strand would be polymer and strand breakage wherever sufficient electrons from carboxyl (glycosidic) bonds were transferred to reducing gold ions. Polymer disruption would occur through the rupture of the ether bonds in the hexose ring at the 1,2 and/or 2,3 positions and through the rupture of the 1,4 ß glycosidic bonds (cf. Fig. 6 B). Clusters of positively-charged metallic gold atoms could be ionically attached to structurally intact polysaccharide strands by means of the terminal carboxyls of broken substrands and perhaps physically held by adjacent unbroken substrands.

The picture that develops, in modelling the chemical saturation of a Z. ramigera-type extracellular polysaccharide with gold ions, is one in which gold would simultaneously replace and destroy polysaccharide strands, leaving only glucose and polyglucose fragments to diffuse away. Because of the chemical accessibility of all parts of the holdfast network, it seems reasonable that portions of the network could be replaced by gold almost simultaneously.

If this chemical scenario is correct, a transient metallic facsimile of the three-dimensional polymer net would come into being as gold chemically replaces the polymer strands. Loss of any organic polymer not replaced by gold initially would presumably occur over time. A three-dimensional gold net at this scale would be highly fragile, being made up of 4 nm-diameter gold filiments a mere dozen gold atoms thick; however, it would have a large surface area highly conducive to chemical infilling with additional gold. With additional infilling, the presented surface area would diminish and cease to be more attractive than adjacent areas for the deposition of secondary gold.

Until mechanically damaged, such gold-replaced holdfast structures would retain their outward shapes, as observed in Fig. 1, yet entrain little or no organic matter. More significantly, such a chemical replacement process would reconcile the relative absence of organic matter in Snake River gold with the wide distribution of gold-replaced bacterial holdfast structures observable on these gold particles.

SUGGESTIONS FOR FURTHER RESEARCH

It may not be possible to "simulate" the growth of secondary placer gold particles; such an effort would at best produce facsimiles of a natural product. It should be possible, however, to test what may be the most important step in the accretion of Snake River flake-type gold particles--the capacity of gold as various naturally occurring complexes to chemically replace bacterial extracellular polysaccharides.

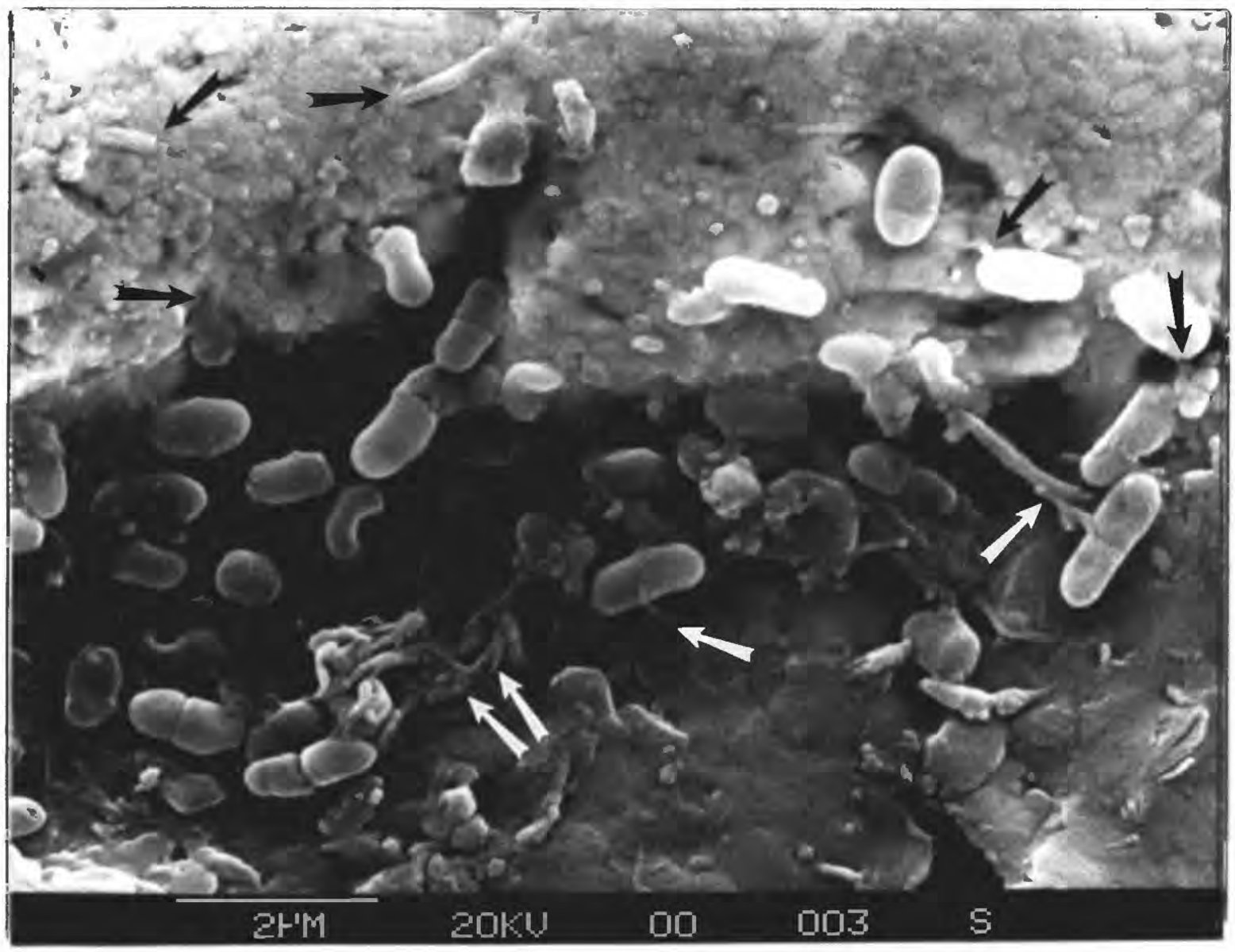
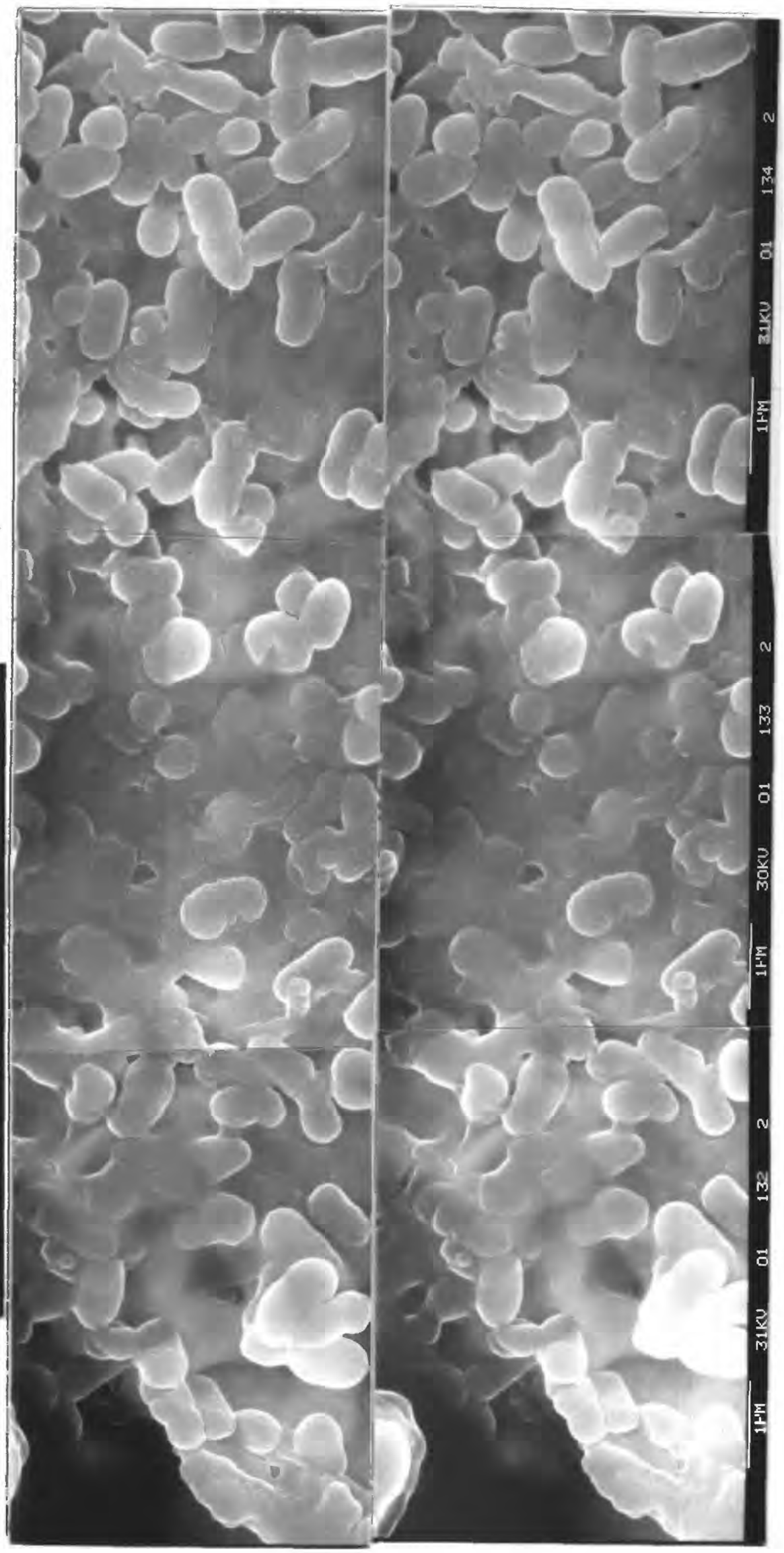


Figure 1. Short rod-shaped bacteria and associated secretion debris found preserved in gold on surface of a 0.1 mm Snake River gold particle. 0.2 μm-diameter strands (arrows) are interpreted as "holdfasts" which bacteria secrete to anchor themselves to submerged surfaces. X-ray analyses of bacterial cells, "holdfasts", and background area (upper left) vary between 97% gold/3% silver and ~100% gold. Note that much of gold background area resembles "holdfast" debris. SEM preparation included boiling in nitric acid and sputter coating with copper.

Figure 2. SEM stereomicrographs at 40° and 50° of a rectangular area (arrow) of the Dixie Ranch gold flake. In EDX analysis the area shown is indistinguishable from 99.99% gold. Note gold-replaced cells at all stages of incorporation in the placer gold particle.

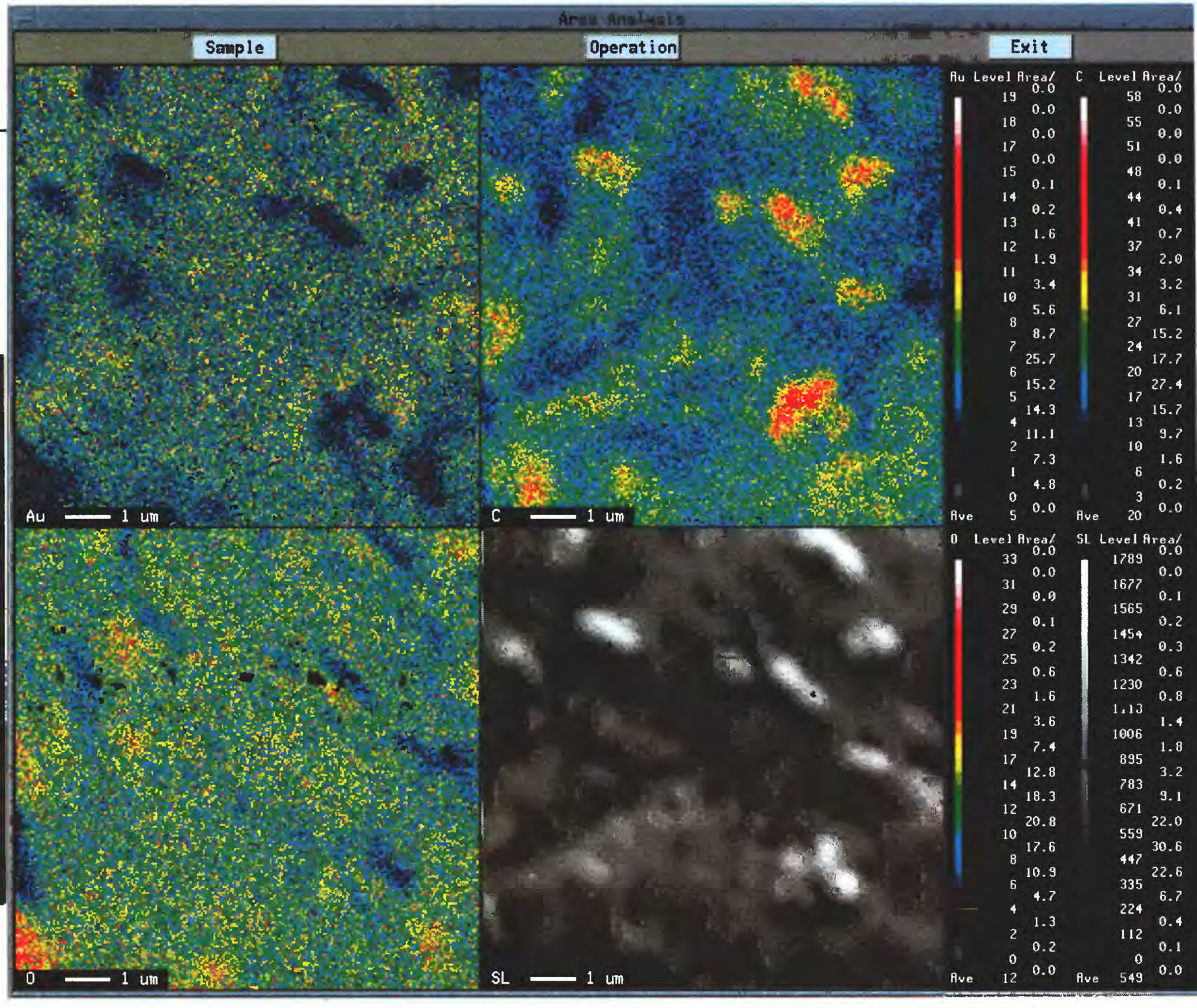
Dixie Ranch
gold particle



1.0 µm

Figure 3. Low-voltage micro-probe (EDS) linescans for relative gold, carbon, and oxygen content of a 100 μm^2 area (arrow) of the "Dixie Ranch" gold flake. High-carbon (low-gold) areas (C) match locations of gold-mineralized bacteria (SL).

Dixie Ranch gold particle



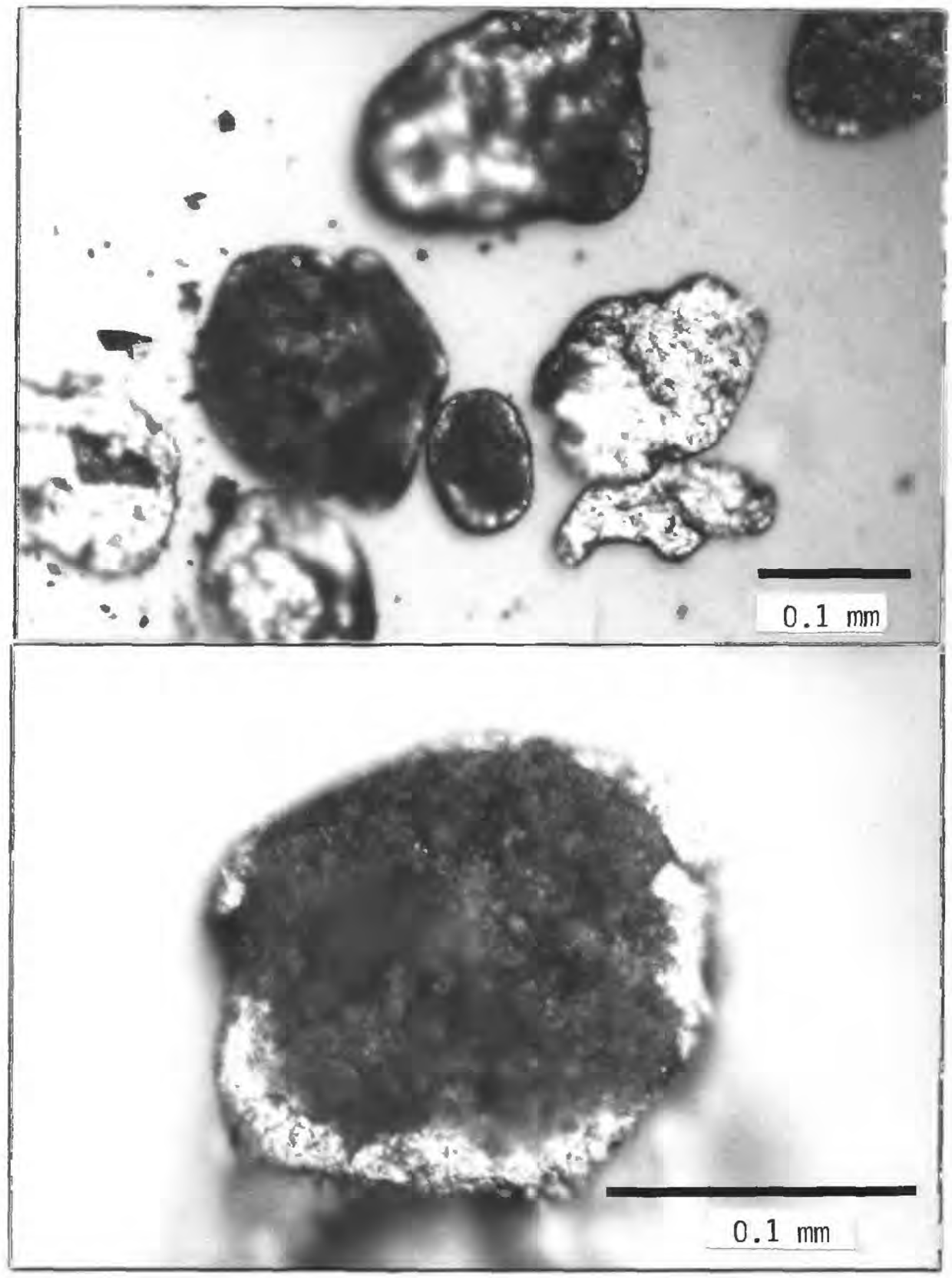


Figure 4. "Sooty-faced" Dixie Ranch placer gold particles following pyrolysis. Dark material showed only traces of carbon in 10 kv, 100-second EDX analyses. At 200x and 400x.

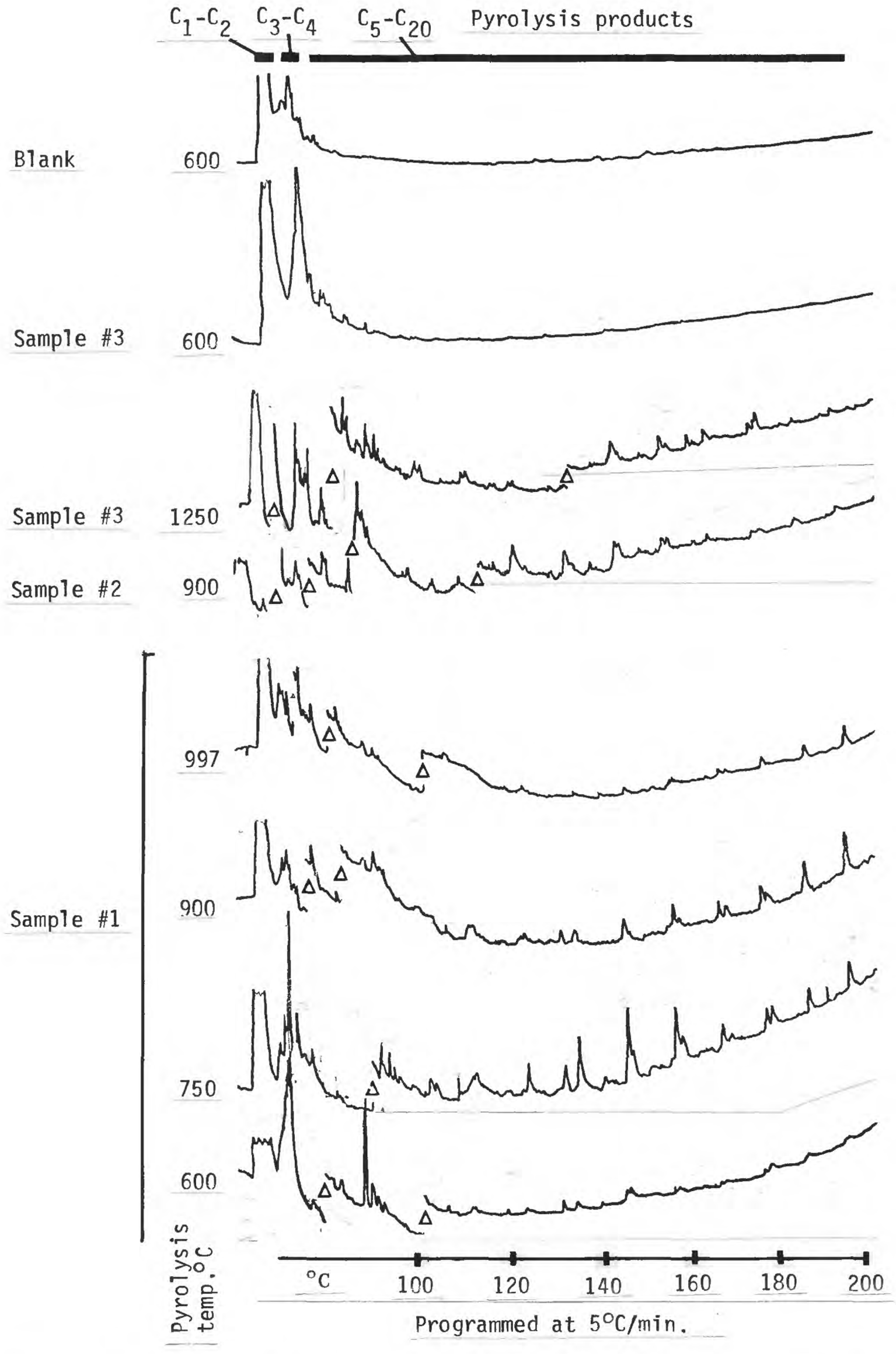
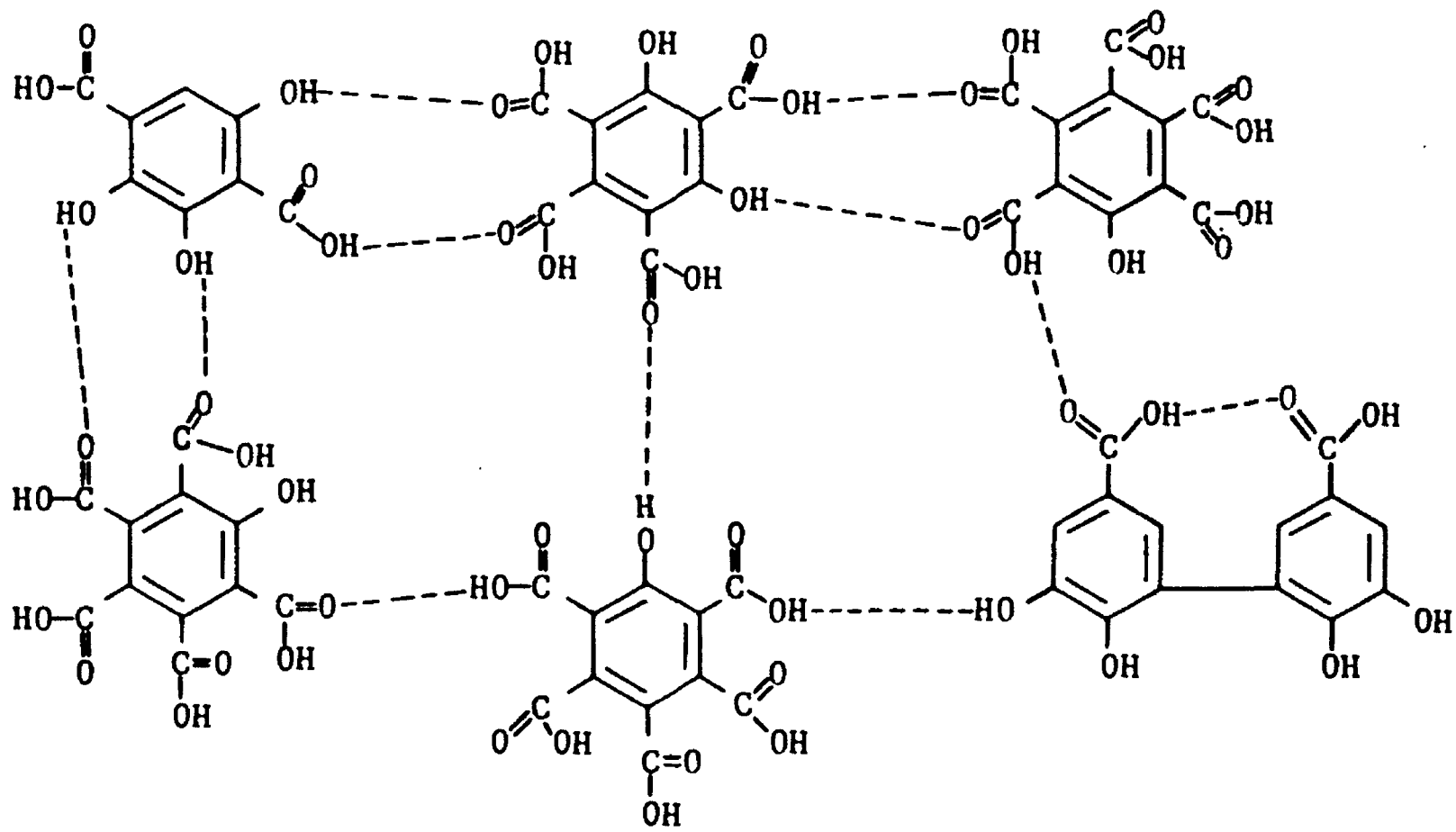
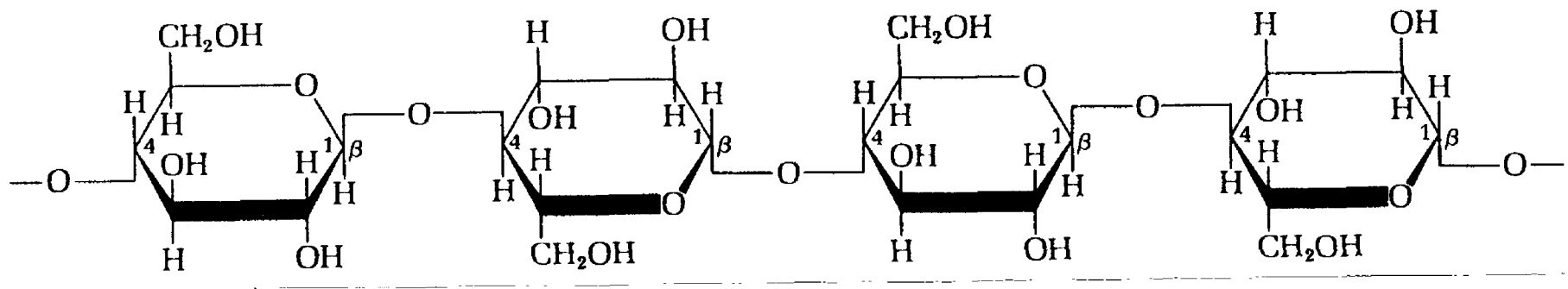


Figure 5. Stacked pyrograms. Line breaks (△) = scale changes. Far left peak = C_1-C_2 molecules; C_3-C_4 peak ignored because of temp./flow-rate interference; evenly spaced peaks toward right side = incrementally heavier C_5-C_{20} normal alkanes and alkenes.



(A)



(B)

Figure 6. (A) One of the chemical structures proposed for fulvic acid (Stevenson, 1982). (B) Cellulose chain with D-glucose units in 1,4 ß linkage (Lehninger, 1982), a structure considered similar to Zoegloea ramigera capsular (extracellular) polysaccharides (Friedman and others, 1968).

Table 1. Pyrolysis products of three 5-mg Snake River placer gold samples

Sample no. and pyrolysis temperature	C_1-C_2 g C	C_5+ g C
Sample #1		
600°C	4×10^{-9}	1×10^{-10}
750°C	5×10^{-9}	15×10^{-10}
900°C	4×10^{-9}	2×10^{-10}
997°C	5×10^{-9}	1×10^{-10}
	18×10^{-9}	19×10^{-10}
		sum= 20×10^{-9}
		net= 18×10^{-9}
		net/5mg= 3.6 ppm
Sample #2		
900°C	40×10^{-9}	3×10^{-10}
		sum= 40×10^{-9}
		net= 38×10^{-9}
		net/5mg= 7.6 ppm
Sample #3		
600°C	2×10^{-10}	1×10^{-10}
1250°C	20×10^{-9}	1×10^{-9}
	20×10^{-9}	1×10^{-9}
		sum= 21×10^{-9}
		net= 19×10^{-9}
		net/5mg= 3.8 ppm
		AVERAGE = 5 PPM
Blank	$<2 \times 10^{-9}$	$<2 \times 10^{-10}$