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BIOGEOCHEMICAL STUDIES OF GOLD IN A PLACER DEPOSIT, LIVENGOOD, ALASKA

By

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INTRODUCTION

Gold is generally regarded as chemically inert at the earth's surface, and the movement of gold within sediments and soils has long been considered a mechanical process. However, there is evidence for the presence of mobile forms of gold in the surficial environment. Gold has been reported in the parts per billion (ppb) range in plants (Shacklette and others, 1970; Severson and others, 1986; Cohen and others, 1987; Jones and Peterson, 1989) and in the parts per trillion (ppt) range in surface waters (Gosling and others, 1971; McHugh, 1984), indicating that gold is chemically active under ambient temperature and neutral pH conditions (Lakin and others, 1974).

Concentrations of gold are most commonly reported as total gold in soils and sediments, and there is little quantitative information regarding the chemical forms of gold. This information is difficult to obtain because of the generally low concentration of gold in these materials. A sensitive analytical method is necessary to determine gold in a certain fraction of a sample, for example, gold associated with organic material. Partial, sequential extractions are commonly used to determine the mode of occurrence of transition metals (Chao, 1984). Few such extractions are useful for determining gold's modes of occurrence, however, due to the unique properties of gold such as its ionic instability in most solutions. Therefore, controversy still exists over the most common forms of gold, other than elemental, in the surficial environment.

An understanding of gold's geochemistry and mobility in the weathering zone is important to the interpretation of geochemical and biogeochemical surveys. The placement and extent of a geochemical or biogeochemical gold anomaly is strongly influenced by the mobility of gold in a given environment. Knowledge of the chemical behavior of gold at ambient temperatures should be considered essential to the design and evaluation of an exploration survey.

One problem that has plagued both gold exploration and analysis is the "nugget effect." This is the tendency of gold to be present as a few particles in a large amount of matrix. The nugget effect may be minimized by taking very large samples in order to accurately represent the sampled population. By sampling plants or decayed plant material in which gold would not be expected to occur as nuggets, it may be possible to identify gold anomalies more accurately. However, the implementation of a biogeochemical survey requires an extensive knowledge of the factors that influence the gold content of a plant and its relationship to the gold content of the substrate.

A placer gold mining operation in the Tolovana gold district of central Alaska was chosen as a study area to investigate the behavior of gold in the surficial environment. In a preliminary study by Severson and others (1986) on Lillian Creek, several species of plants in this area including labrador tea, alder, and birch, were found to contain anomalously high levels of gold. In the same study, water-extracts of soil samples yielded measurable amounts of gold in the low ppb range. This work suggested that the Lillian Creek gold placer deposit would be an appropriate study area to investigate the mobility of gold in the weathering environment.

Soil and plant samples were collected during the summer of 1988. The samples were analyzed for a variety of chemical constituents in order to determine the distribution, and to some extent, mode of occurrence of gold in natural materials at the placer. Gold in plants and water-extracts of soils are used as a measure of gold activity (Lakin and others, 1974). The abundance and distribution of potential gold-mobilizing agents in the soils, as well as other elements associated with gold in these types of deposits, such as arsenic and antimony, were also investigated. In addition to the analysis of samples from the study site, controlled dissolution experiments were performed in the laboratory to investigate gold's behavior in the surface environment.

The objectives of this study were: (1) to describe the distribution of gold in the soil and two species of native plants; (2) to confirm the existence of mobile forms of gold in the surficial material; and, (3) to suggest probable agents of gold mobilization using the results of both observational and experimental studies.

GOLD GEOCHEMISTRY AND BIOGEOCHEMISTRY

Gold and Inorganic Ligands

Observing gold in soil solutions raises the question of gold mobility in the weathering zone. Due to their high oxidation potentials, the simple ionic forms of gold, Au(I) (+1.68 volts) and Au(III) (+1.50 volts), are not stable in water (Ong and Swanson, 1969). Therefore, gold must be transported as a complex ion or ion pair. To form a complex, gold must first be oxidized to a simple ion, and the strength of the oxidizing agent necessary is dependent upon the stability of gold complex being formed. Lakin and others (1974) have reviewed the stable complexes of gold at 25 °C with a number of inorganic ligands such as chloride, bromide, iodide, cyanide, thiocyanate, and thiosulfate.

Gold is a type B metal ion ("soft" acid) and is therefore more likely to bind to a type B ligand ("soft" base) according to the general rules by Pearson (1973). Although these rules are largely empirical, there is a theoretical basis for the observation: hard acids and bases have a tendency to form bonds that are more ionic in nature, whereas soft acids and bases generally form covalent bonds (Huheey, 1983). Arranged in the order of increasing softness and stability of gold complexes formed, some potential, inorganic gold complexing ligands include (from Renders and Seward, 1989):

Cl- < Br- < SCN- < I -< S203- <CN-

increasing stability--------->

hard<---------->soft

At ambient temperatures, atmospheric oxygen is an adequate oxidizing agent for the formation of gold cyanide (Lakin and others, 1974), but a stronger oxidizing agent, such as manganese dioxide, is required for the formation of gold chloride (Krauskopf, 1951). Lakin and others (1974) reviewed these inorganic ligands and stated that in an oxidizing environment where pH values range from 5 to 8, only thiosulfate, thiocyanate, and cyanide ions are likely to complex with gold.

Gold chloride complexes are cited by Helgeson and Garrels (1968) as the most important inorganic gold-complexing agent in natural aqueous solutions. However, the solubility of gold in the presence of chloride drops sharply with decreasing temperature (Henley, 1973). In view of this temperature dependency and the requirement of a strong oxidizing agent to form gold chloride complexes, except under unusual conditions, these complexes can be expected to play a limited role in gold mobility in the surficial environment. Bromide and iodide complexes of gold are more stable than chloride complexes (Lakin and others, 1974), but bromine and iodine are much less abundant than chloride in soil. According to Vinogradov (1959), the average soil concentration of both bromine and iodine is 5 parts per million (ppm), compared with 100 ppm for chlorine. Base metals such as copper and iron form more stable complexes with bromide and iodide than does gold, and will therefore be competitors for the limited amounts of bromide and iodide present in soils and sediments (Lakin and others, 1974). Except in unusual circumstances, bromide and iodide are unlikely gold complexing agents in the weathering zone.

Several anionic sulfur compounds are potential complexing agents for the transport of gold at 25 °C. Seward (1973, 1982) reported Au(HS)2- to be a stable complex at near-neutral pH values under reducing conditions. However, the weathering zone is generally oxidizing and the thiosulfate ion is more likely to complex gold than biosulfide. Webster (1986) stated that thiosulfate would be relatively stable under the mildly oxidizing conditions present in the phreatic zone, whereas sulfate would be the dominant sulfur species in the more oxidized soils above the water table. The tendency of sulfur to oxidize to sulfate in the soil limits the abundance of compounds such as thiosulfate, which contains sulfur in an intermediate oxidation state. The oxidation of sulfides was shown by Goldhaber (1983) to yield thiosulfate at pH values above 7. Under weakly acidic conditions, thiosulfate was either not formed, or it was oxidized to tetrathionate before it could be detected. Lakin and others (1974) cited both a lack of stability and abundance of this compound as the limiting factors in thiosulfate's gold-mobilizing capabilities. However, considering the relative stability of gold thiosulfate compounds, the possibility of gold transport as a mobile complex with thiosulfate should not be discounted, especially in neutral to alkaline soils with high sulfur concentrations.

Cyanide forms very stable complexes with gold and is a likely agent of gold mobilization in the soil environment (Lakin and others, 1974; Warren, 1982). Shacklette and others (1970) showed that gold cyanide complexes are readily absorbed by plants. However, because cyanide

is dependent upon cyanogenic plants and microorganisms for its synthesis, cyanide is not ubiquitous in soils and sediments. The tendency of cyanide to hydrolize also limits its concentration in soils (Lakin and others, 1974).

Thiocyanate has also been found to form stable gold complexes, but it is readily oxidized by the soil bacteria *Thiobacillus thiocyanoxidans* and, probably is also limited in its abundance in surficial environments (Lakin and others, 1974).

Gold and Soil Organic Matter

The affinity of metals for organic material is well known. High concentrations of metals are often found in organic-rich deposits such as coal and carbonaceous shales. The association of gold with organic material has been noted both in hydrothermal gold deposits (Levitskiy and others, 1983) and in the Witwatersrand paleoplacer (Dexter-Dyer Grosovsky, 1983). Gold is known to form a number of complexes with organic compounds (Johnson and Davis, 1973), some of which may have an influence on gold mobility in the soil environment (Boyle, 1979).

Humic substances are often defined as the soil organic matter which cannot be classified as discrete organic compounds such as amino acids, carbohydrates, or lipids (Stevenson, 1982). Humic substances are defined by Schnitzer (1978) as "dark colored, acidic, predominantly aromatic, hydrophilic, chemically complex, polyelectrolyte-like materials that range in molecular weights from a few hundred to several thousand." Humic substances are broken down into three main categories: humic acids, fulvic acids, and humin. These substances are operationally defined based on their relative solubility in dilute acid and base. Humic acids are alkali soluble, but acid insoluble; fulvic acids are both acid and alkali soluble; and humin is both acid and alkali insoluble (Schnitzer, 1978). Many other properties separate fulvic acids from humic acids: fulvic acids are lighter in color, have a lower molecular weight, contain less carbon and more oxygen, and have more exchange sites per unit weight relative to humic acids (Stevenson, 1982). The greater solubility and exchange capacity make fulvic acid the primary focus of the experimental portion of this study.

Humic acids are thought to play an important role in controlling the availability of both nutrients and toxic substances to plants (Schnitzer, 1978; Stevenson, 1982). Humic acids have also been shown to form strong complexes with base metals, such as copper and iron (Van Dijk, 1971). The ability of humic acids to complex or adsorb gold has been postulated and not proven conclusively. Curtin and others (1970) demonstrated that gold concentrations in organic material leachates to be roughly proportional to color; that is, the darker the leachate, the higher the gold content. Because soil organic matter is credited for imparting a dark color to soils and waters, this observation implies an association between gold and organic substances in gold-bearing soils. Baker (1978) was able to measure up to 330 ppb gold in solution after exposing particulate gold to solutions of humic acid. This represents an enrichment of several thousand times the amount of gold usually found in natural waters (McHugh, 1984). Other authors have cited humic and (or) fulvic acids as possible complexing agents for gold (Freise, 1931; Rashid and Leonard, 1973; Baker, 1978; Boyle, 1979; Fedoseyeva and others, 1985; Severson and others, 1986; Jones and Peterson, 1989). The results of other studies have not always supported the ability of humic substances to complex gold (Fetzer, 1934; Andrade and others, 1988). Ong and Swanson (1969) suggested that humic acids do not form chemical complexes with gold but

instead form a protective, hydrophilic coating around gold colloids, allowing the gold to remain in suspension.

Gold in Plants

Although there are many reports of anomalous levels of gold in plants, very little is known about the physiological processes that control the uptake of gold by vegetation. Controlling factors may include the age and growth rate of a plant, the type of plant tissue of the plant, for example, stems versus leaves, and the uptake physiology of the plant (Berry, 1986). The "uptake physiology" refers to the ability of a plant to exclude, accumulate, or passively adsorb a given element, and is dependent both on the species of plant and the element's concentration in the soil. All of these factors should be taken into account before implementing, and especially interpreting, a biogeochemical survey. Many soil factors also influence elemental abundance in plants. Thornton (1986) cited drainage conditions, pH, chelating agents in the soil, antagonistic and synergistic effects of other elements, and the effects of soil microorganisms (which are poorly understood), as soil factors affecting the uptake of metals by plants.

In a comprehensive study of the ability of plants to absorb various forms of gold, Shacklette and others (1970) concluded that impatiens (*Impatiens holstii*) and garden balsam (*Impatiens balsamina*) are unable to assimilate colloidal gold. This study, which measured the movement of radioactive gold (Au^{198}) through these two plants, tested the ability of both rooted and cut plants to assimilate gold as a complex with chloride, cyanide, bromide, iodide, thiosulfate, and thiocyanate, as well as two different sizes of gold colloids (<0.05 μm and 0.05-0.45 μm). Autoradiographs of the leaves of cut and rooted plants showed that radioactive gold from the colloidal mixtures was not transported to the leaves. The plants with intact roots were able to transport radioactive gold to their leaves from all but the gold chloride and thiosulfate solutions. The leaves of plant cuttings were found to absorb Au^{198} from all of the solutions tested. Only the radioactive gold content of the leaves was investigated in this experiment. Therefore, the amount of gold assimilated by other parts of the plants is unknown.

A similar experiment was performed using nonradioactive gold to determine if the plants would preferentially assimilate Au^{197} from the various solutions (Shacklette and others, 1970). Analysis of stems and leaves by atomic absorption spectroscopy showed that gold was absorbed by plants from all of the solutions in varying amounts. These results suggest either that Au^{198} is not as readily absorbed as Au^{197}, which is unlikely, or that certain solutions of gold are sequestered in the stems and are not transported to the leaves in appreciable amounts. However, autoradiographs of Au^{198} may not be as sensitive in detecting gold as atomic absorption spectroscopy. This experiment did not investigate the absorption of nonradioactive colloidal gold by plants, and therefore the ability of plants to absorb small colloids of Au^{197} remains in question.

The uptake of many metals, including gold, by three species of conifers was investigated by King and others (1984). In this study, lodgepole pine, douglas fir, and engelmann spruce seedlings were planted in pots containing soil and characteristic ore minerals of various types of ore deposits. These seedlings, along with a control group planted only in soil, were moved to a coniferous forest in Jefferson County, Colorado. The pots were placed in the ground so that the surface of the soil in the pots was approximately even with the ground surface. The seedlings

were allowed to grow under natural conditions for seven years. They were then removed from the plot and analyzed for various metals. The results showed that many metals from the ore minerals had been assimilated by the plants. Gold, which was supplied to the plants as gold foil, was found in the ppm range in the ash of roots, leaves, and stems of some of the plants. The highest concentrations of gold were generally found in the roots, but the authors speculate that this may be due to contamination by mineral matter on the outer surfaces of the roots. The findings of this study are significant because they show that metallic gold in the soil may be converted to a form that is available to plants in a relatively short time.

FIELD STUDY

Location

The field study area is located within the Lillian Creek drainage (T. 8 N. R. 5 W., sec. 22) which runs east to west approximately 1.5 km south of Livengood, Alaska. Livengood is located approximately 90 km north-northwest of Fairbanks, Alaska (fig. 1a).

Climate and Topography

The study area is located within the Yukon-Tanana uplands in the interior basin of Alaska where the climate is semiarid, subarctic (Mertie, 1937). The mean annual temperature of Fairbanks is -3.4 °C, and ranges from -54.4 °C to 33.9 °C. Annual precipitation in Fairbanks is 28.7 centimeters, most of which falls in the summer months (Hare and Hay, 1974).

The topography of the area is well described by Mertie (1918):

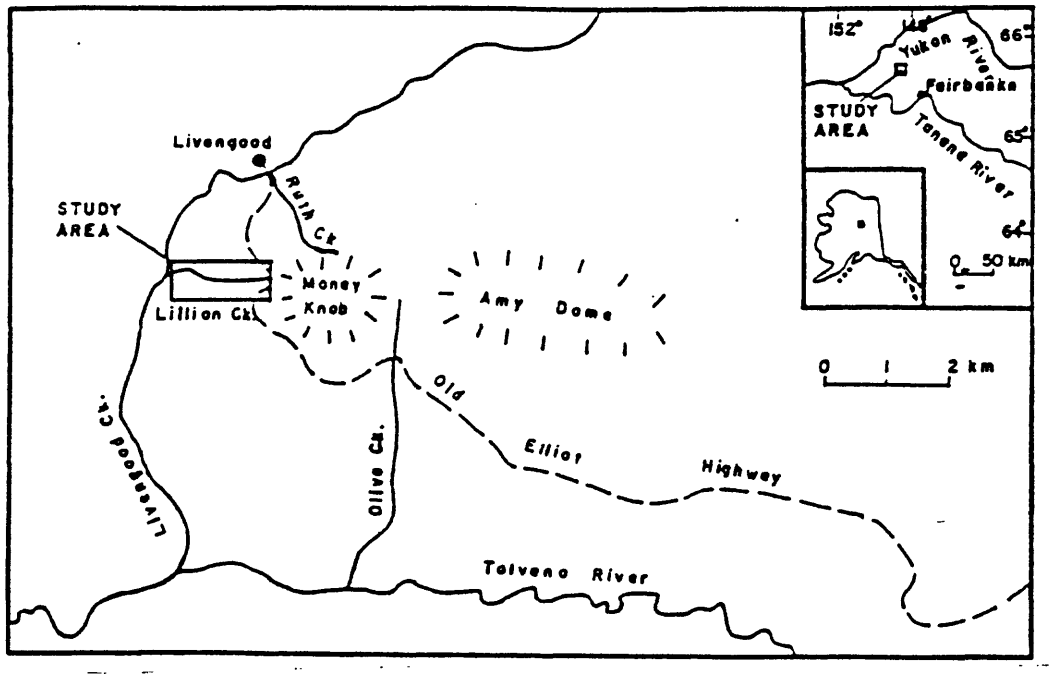
> (p. 222) The Tolovana district is part of the Yukon-Tanana upland. Its topography is characterized by broad, even-topped ridges, which rise to a general elevation of 2,000 feet or higher and from which long, gently sloping spurs descend to the valley floors.
>
> (p. 229) The ridge-tops in the Yukon-Tanana region as a whole are probably the dissected remnants of an old peneplain, in the widest sense of that term...more or less uniform in elevation but sloping shieldlike to the major drainage channels.

The Yukon-Tanana region is located within the zone of discontinuous permafrost (Péwé, 1975). Permafrost areas were noted in the study area, especially on the north sides of the drainages. The south-facing side of the Lillian Creek drainage is less steep than the north-facing side, due to the thawing and solifluction of the unconsolidated material on the south-facing slopes.

Vegetation

Livengood is located within the interior spruce and birch forest region, consisting chiefly of white and black spruce, birch, poplar, and aspen (Sigafoos, 1958). Timberline in the Yukon-Tanana area is 758 m (2,500 ft) above sea level (Mertie, 1937), but trees may be absent to

A.



B.

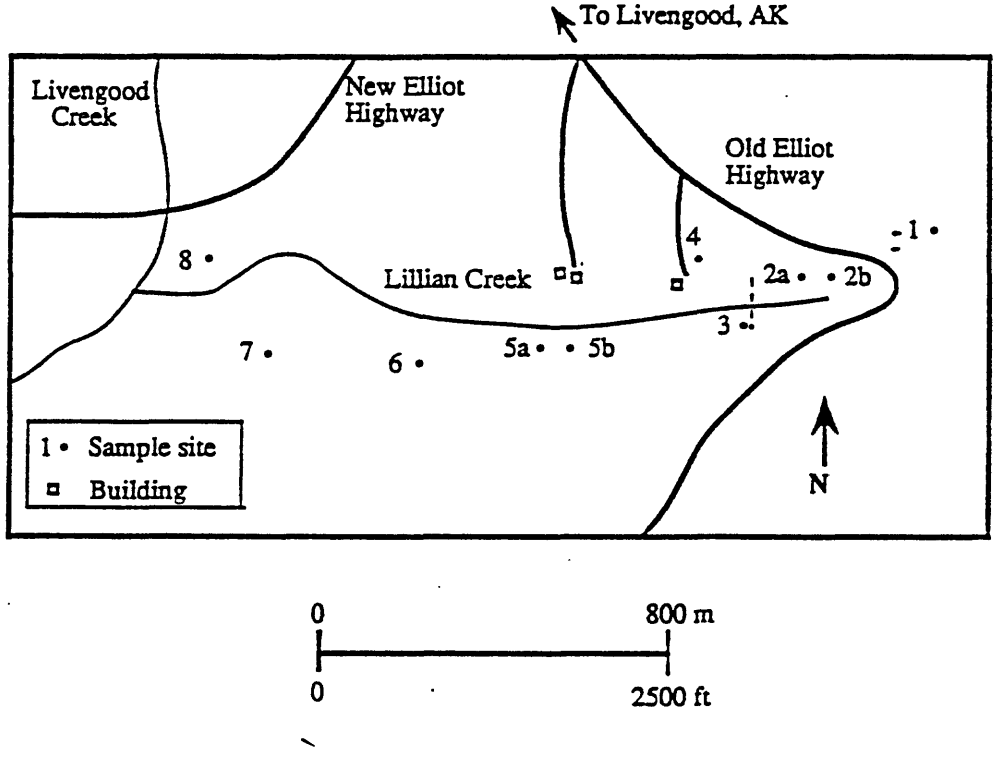


Figure 1.--Location of the study area (1a) and sampling sites (1b). The approximate location of a vein containing 90 ppm Au is shown as a dotted line.

considerably lower altitudes on north-facing slopes (Foster, 1966). Vegetation differs considerably from one side of the Lillian Creek drainage to the other. On the north-facing side of the valley, the vegetation is generally more "tundra-like," and is comprised of lichens, moss, black spruce, blueberry, labrador tea, and alder. Parts of the north-facing slopes are quite open with low-growing plants. The south-facing side of the valley is generally more wooded with birch, white spruce, and alder; the understory contains shrubs such as labrador tea. In the valley bottom, where most of the surficial material has been disturbed at some time by placer operations, alder, willow, grasses, and horsetail are abundant. Labrador tea is generally absent in the recently disturbed areas.

Quaternary Deposits

Overlying the bedrock in the Lillian Creek drainage are deposits of Pleistocene gravel, loess, and organic-rich "muck" which may attain thicknesses of many meters. The gravels probably represent both alluvial deposits ("bench" or abandoned stream channel deposits), and locally-derived solifluction deposits (Mertie, 1918). The latter contain angular clasts, and probably have not been displaced far from the source, or were transported so slowly that essentially no abrasion occurred. This type of deposit, and the gold associated with it, probably account for much of the placer material on the steep upper reaches of the drainage. The alluvial sand and gravel deposits dominate the downstream reaches (Weber and others, 1985).

A large loess bank containing ice lenses is located in the Lillian Creek valley. The original extent of the loess is unknown, due to the removal of much of it by placer operations. Although the central part of Alaska saw only limited alpine glaciation, these loess deposits formed during periods of intense glaciation to the north and south of the study area (Péwé, 1975).

Lenses of fine, organic-rich silt are abundant in the Lillian Creek drainage, and are seen interbedded with the coarser gravels. These deposits are probably loess which accumulated organic material as it slumped into the valley bottom during periods of thawing (Péwé, 1952). Buried layers of poorly decomposed organic material, which are almost free of mineral matter, may represent previous soil 0-horizons that have been covered by solifluction deposits. One exposed soil profile shows the remnants of a burned 0-horizon buried under more recent gravel deposits and the modern soil.

Placer operations have stripped the overburden from much of the valley floor, leaving well-exposed soil profiles and slump material along both sides of the drainage. Mining activity has also uncovered the remains of Quaternary animals such as bison, mammoth, and mastodon.

Bedrock Geology

The bedrock in the Livengood area consists mainly of deformed and metamorphosed Paleozoic sedimentary and igneous rocks. The sedimentary rocks consist of shale, sandstone, conglomerate, and chert of Middle Devonian age (Robinson, 1983). The igneous rocks consist of diorite, gabbro, basalt (greenstone), intermediate volcanics, and serpentinized ultramafic rocks (Foster, 1966; Smith, 1983; Robinson, 1983). This assemblage is cut by Tertiary monzonite dikes.

Fresh exposures of Tertiary monzonite dikes and Middle Devonian shales and sandstones are located near the head of Lillian Creek where the Old Elliot highway switches back across the drainage. These rocks are extensively sheared and show iron staining from the oxidation of abundant iron sulfides. The sedimentary rocks strike northwest and dip steeply to the northeast. The dikes run roughly parallel to strike in this location (Robinson, 1983). Middle Devonian sedimentary rocks are exposed in other parts of the drainage by the mining operations. In some of these exposures, recumbent folds with axes trending approximately east-west show the overall structural trend.

Mineralization

Placer gold in Lillian Creek is thought to have originated on the ridge which runs between the Tolovana River and Livengood Creek (fig. 1a). Streams draining this ridge are generally gold-bearing, in contrast with other drainages in the area (Mertie, 1918). The ridge consists of two structures, Amy Dome and Money Knob. The larger of the two structures, Amy Dome, is composed of Devonian metadiorite, metabasalt, and serpentinite (Foster, 1966). Money Knob, a small knoll on the western end of Amy Dome, is composed of Devonian sedimentary rocks crosscut by Tertiary monzonite dikes (Robinson, 1983). Gold mineralization in the area is thought to be genetically associated with these dikes (Mertie, 1918; Overbeck, 1920; Foster, 1969). Most of the lode prospects in the past have been localized in Lillian, Ruth, and Olive Creeks, which drain Money Knob (Mertie, 1918; Eakins, 1974). These creeks contain some of the most historically productive placers in the area (Saunders, 1958).

A Tertiary arsenopyrite-stibnite-quartz vein which runs perpendicular to the Lillian Creek drainage was sampled, assayed, and found to contain over 90 ppm gold. Altered Tertiary monzonite dikes exposed in the roadcut contain approximately 1.0 ppm gold (Albanese, 1983a). Some of the Devonian sedimentary rocks were found to contain small amounts of gold, generally 0.1 ppm or less.

Several other economic minerals are found in the sediments of the creeks draining Money Knob (Overbeck, 1920), including magnetite, scheelite, cinnabar, chromite, arsenopyrite, pyrite, and stibnite. Stibnite is restricted to the Lillian Creek drainage. Chemical analyses of stream sediments from this drainage have indicated high levels of arsenic, silver, gold, and antimony (Foster, 1968).

Mining History

Gold was first discovered in the Livengood area in 1914 by Jay Livengood and N.R. Hudson (Brooks, 1916). By 1915 shallow placers were being worked on Lillian Creek and many other creeks in the area. Placer mining by the open-cut method was continuing on Lillian Creek in 1916, and some lode prospects at the head of the creek had been claimed (Mertie, 1918). Gold production for the Livengood area for 1915 through 1917 totaled approximately 100,000 oz, with the vast majority of the gold coming out of Livengood Creek and its tributaries (Saunders, 1958). By 1918, four open-cut operations and a drift mine were being worked on Lillian Creek (Overbeck, 1920). Smith (1933) reported that mining in the Livengood area in 1932 was carried out almost exclusively by the opencut method, and that the largest mining operations were located on tributaries of Livengood Creek, including Lillian Creek. In 1941,

mines in the area closed due to a war-time order halting gold mining, but eight operations had resumed production by 1946 (Saunders, 1958). Total production for the Livengood area as of 1958 is given by Saunders (1958) as 350,000 oz. Presently, two families have claims on Lillian Creek. During the summer of 1988, the upper claim was inactive and the lower claim was operating sporadically.

METHODS

Sample Collection

Eight sampling sites and two duplicate sites (2b and 5b) were selected along the Lillian Creek drainage (fig. 1b). Sampling sites were chosen on the basis of the following criteria: (1) the surficial material had not been disturbed by recent mining activity, (2) a reasonable exposure of the soil profile could be cleared, and (3) at least one of two species of plants, labrador tea (*Ledum palustre* L. subsp. *decumbens* [Ait.] Hult.) or alder (*Alnus incana* [L.] Moench), was present. A clear exposure from surface to bedrock was rarely possible due to the thickness of the overburden or large amounts of slumped material which obscured the contact between bedrock and overburden.

At each sampling site the soil profile was cleared with a shovel to expose a fresh surface. The profile was then divided into horizons based on the physical characteristics of the soil (color and texture) (table 1). Using a stainless steel trowel, composite samples of each horizon (about 1 kg) were collected and put into cloth bags.

Labrador tea and (or) alder samples were collected at each site. Alder was present at every site and labrador tea was present at six of the eight sites. Using stainless steel clippers, the current year's growth of the alder (approximately the distal 15 to 20 cm) was sampled. Both twigs and leaves were included in the sample and later homogenized by milling. The labrador tea was not as abundant as the alder, and the plants were generally small. All the secondary stems and leaves (several years' growth) were sampled. Plant samples (composites of several plants) were collected within a 5-m radius of the soil sampling site. Plant samples were not taken at the duplicate soil sampling sites due to the overlap of the plant sampling area above two closely spaced duplicate sites. During sampling and handling of both plant and soil samples, no jewelry was worn to avoid possible metal contamination. Samples were mailed from the field to the U.S. Geological Survey laboratories in Denver, Colorado.

Sample Preparation

Soil samples were dried in a forced air oven at ambient temperature for about 72 h. They were then disaggregated using a mechanical mortar and pestle and then passed through a 10-mesh (2.00 mm) screen. A riffle splitter was used to obtain a representative split of about 100 g of each sample. This split was ground to -100 mesh (<0.149 mm) with an alumina plate grinder, and then rolled in a mechanical mixer for one hour to ensure sample homogeneity. The grinder, splitter, and screens were carefully cleaned with compressed air between every sample. Both the -10-mesh fraction of the soil and the ground -100-mesh split were retained for chemical analysis.

Table 1. Soil sample and sample site descriptions for samples collected at Lillian Creek, Alaska

Sample no.[1]	Texture	Dry color[2]	Site description
1-0-4	organic/silt	10 YR 2/2	Bedrock: recrystallized siltstone with
1-4-10	silt/gravel	10 YR 5/3	abundant sulfides and iron staining
1-10-40	silt/gravel	10 YR 6/4	Vegetation: predominantly alder and birch
1-40+	sand/gravel	10 YR 6/6	
2a-0-4	organic	10 YR 4/2	Bedrock: saprolitic, thinly fissile shale
2a-4-30	silt/gravel	2.5 Y 6/4	Vegetation: predominantly alder and birch
2a-30-34	organic (charred)	10 YR 5/3	
2a-34-67	silt/gravel	2.5 Y 6/2	
2a-67-74	clay/shale fragments	2.5 Y 7/2	
2a-74+	saprolitic shale	2.5 Y 6/2	
2b-0-4	organic	10 YR 4/2	Bedrock: same as site 2a
2b-4-30	silt/gravel	2.5 Y 6/4	Vegetation: same as site 2a
2b-30-34	no sample	--	
2b-34-67	silt/gravel	2.5 Y 6/4	
2b-67-74	clay/shale fragments	10 YR 6/4	
2b-74+	no sample	--	
3-0-4	organic	10 YR 4/3	Bedrock: siltstone (below approximately
3-4-19	gravel	10 YR 6/4	5 meters of slump material), sulfide vein in
3-19-24	gravel/clay/organic	2.5 Y 5/2	vicinity
3-24-30	organic/peat	10 YR 4/2	Vegetation: moss, lichens, labrador tea,
3-30-34	no sample	--	blueberries, alders, black spruce
3-34+	organic/clay	10 YR 4/2	
4-0-4	organic	10 YR 3/1	Bedrock: saprolitic, fissile shale
4-4-18	silt/shale fragments	2.5 Y 6/2	Vegetation: alders and labrador tea
5a-0-2	silt/organic	2.5 Y 4/2	Bedrock: dark gray, fissile shale
5a-2-12	silt	2.5 Y 5/2	Vegetation: willow, alder, grass
5a-12+	silt	2.5 Y 5/2	
5b-0-2	silt/organic	2.5 Y 6/2	Bedrock: same as site 5a
5b-2-12	silt	2.5 Y 6/2	Vegetation: same as site 5a
5b-12+	silt	2.5 Y 5/2	
6-0-5	organic	10 YR 4/2	Bedrock: unknown
6-5-14	organic/clay	2.5 Y 5/2	Vegetation: moss, labrador tea, alder, black
6-14-23	peat/wood fragments	10 YR 3/3	spruce
6-23+	clay/organic	10 YR 4/1	
7-0-5	organic	10 YR 3/2	Bedrock: unknown
7-5-9	silt/organic	10 YR 6/4	Vegetation: moss, lichens, alders, bryophytes
7-9-20	clay	2.5 Y 5/2	
7-20+	sand/clay/cobbles	2.5 Y 6/2	
8-0-4	organic	2.5 Y 5/2	Bedrock: unknown
			Vegetation: white spruce, alder, labrador tea

[1]First number represents the sample site; remaining numbers refer to depth of sample, in inches.
Example: 1-0-4: Sample site no. 1, 0-4 inches.

[2]From Munsell Soil Color Chart (1975).

To minimize contamination from mineral material, the plant samples were washed with demineralized water in an ultrasonic cleaner for 90 s, then placed in a plastic sieve and rinsed thoroughly with demineralized water. The washed plants were dried in a forced air oven at room temperature, then ground to -10 mesh in a Wiley Mill, which was thoroughly cleaned with compressed air and acetone between samples. A split of each sample was ashed for 8 h at 450 °C to calculate percent ash. A split of the unashed material was pelleted for instrumental neutron activation analyses (INAA).

Analytical Methods

Soil

All of the soil samples were analyzed for pH, specific conductance, chloride, organic and total carbon, total sulfur, arsenic, antimony, total gold and water-extractable gold, and an additional 44 elements by inductively coupled argon plasma-atomic emission spectrometry (ICAP-AES). Table 2 gives a listing of the approximate limits of determination for pH and the total elements reported. Samples that were found to contain water-extractable gold were also analyzed for soluble organic carbon, total and soluble cyanide, and organic-bound and "loosely bound" gold as defined by Gregoire (1985).

Soil pH was determined following the method of Crock and Severson (1980). Due to the high organic matter content of many of the soils, a 1:3 ratio of unground -10-mesh soil to water was used instead of the standard 1:1 ratio. The suspension was stirred every 10 min for one-half hour, and then allowed to stand for one hour. The pH was then measured using a digital pH meter calibrated with certified pH 4 and 7 buffers. An automatic temperature probe corrected for changes in temperature.

Specific conductance and chloride were determined on a 1:5 soil:water extract. Twenty grams of the -10-mesh sample and 100 mL of demineralized water were measured into a plastic bottle and placed on a shaker table over night. The solution was then passed through a 0.45-µm filter after centrifuging for 15 min at 2,500 rpm. A 0.45-µm filter was chosen because material which passes through a 0.45-µm filter is operationally defined as being "in solution." This definition may include some colloids. The specific conductance of the extracts were analyzed with a specific conductance meter. Water-extractable chloride was determined by ion chromatography (Jackson and others, 1987).

The total organic carbon content of the soil samples was determined using the modified Mebius procedure, a wet-ashing chemical oxygen demand (COD) method (Nelson and Sommers, 1982). Samples which were found to have very high organic carbon content by this method were weighed, ignited in a muffle furnace at 550 °C, and reweighed to calculate loss on ignition. This procedure provides a cross-check of the results of the wet-ashing method for organic-rich samples. Making the assumption that carbon accounts for roughly 50 percent or organic matter by weight, the amount of material lost on ignition in a relatively dry sample should be approximately double the percent by weight of organic carbon in the sample.

Table 2. Listing of approximate limits of determination for pH and elements reported

Analytical method	Medium	Determination limit	Variables
Continuous flow hydride generation	Soil	0.1 ppm	As, Se
	Plant[1]	0.05 ppm	As
Induction coupled plasma	Soil and plant[2,3]	2.0 ppm	Ag, Cd, La, Li, Mo, Ni, Sc, Sr, V, Y
		0.05%	Al, Ca, Fe, K, Mg, Na, P, Ti
		1.0 ppm	Ba, Be, Co, Cr, Cu, Yb
		4.0 ppm	Ce, Ga, Ho, Mn, Nb, Nd, Pb, Th, Zn
		8.0 ppm	Au
		10 ppm	Bi
		20 ppm	Sn
		40 ppm	Ta
		100 ppm	U
Hot-water extract	Soil	0.4 ppm	B
Continuous flow cold vapor	Soil	0.02 ppm	Hg
Water slurry	Soil	0.1 units	pH
Combustion-IR	Soil	0.05%	Total C, S

[1]Determined on dry plant material.
[2]Determined on plant ash.
[3]Sample mass for plants was one-half that for soils, so determination limits are twice those listed for soils.

Total carbon and total sulfur content of the soil samples were determined by using a Leco induction furnace according to the manufacturer's directions (Jackson and others, 1987).

Major, minor, and trace element chemistry (up to 44 elements) of the -100-mesh soil samples were determined by ICP-AES using a multi-acid digestion (Crock and others, 1983). Table 2 lists the limits of determination for most of the methods.

The arsenic and antimony contents of the soil samples were determined by continuous flow, hydride-generation atomic absorption spectroscopy (CFHG-AAS) following a closed vessel multi-acid digestion on the -100-mesh split (Crock and Lichte, 1982).

Total gold content of the soils was determined by performing a hydrobromic acid-bromine solution digestion and MIBK (methyl isobutyl ketone) extraction on the -100-mesh soil samples (Thompson and others, 1968). Following the extraction, the total gold content of the samples was determined by flame atomic absorption spectroscopy (flame-AAS, detection limit, 50 ppb). Samples which were found to contain less than 50 ppb gold by this method were reanalyzed by graphite furnace atomic absorption spectroscopy (GF-AAS, detection limit, 2 ppb).

Water-extractable gold was determined on a duplicate 1:5 soil:water extract. The filtrate was prepared and analyzed according to the GF-AAS method of McHugh (1984). In this method, the filtrate is brought to dryness on a hotplate. A hydrobromic acid-bromine solution is added to the residue, and the sample is gently heated. After cooling, the gold in the HBr-bromine solution is extracted into MIBK, and iron interference is removed as in the total gold method described above. The water-extractable gold is then determined by analyzing the MIBK layer by GF-AAS. Samples containing water-extractable gold were analyzed for "loosely bound" and organic-bound gold after the method of Gregoire (1985). The loosely bound gold is desorbed by treatment with ammonium acetate. Following the desorption of loosely bound gold, the organic-bound gold is extracted by treatment with sodium hypochlorite. All samples were analyzed by GF-AAS (detection limit, 2 ppb).

Soluble organic carbon was determined on selected samples containing water-extractable gold by analyzing the 1:5 soil:water extract for organic carbon. A coulometric carbon analyzer was used for this analysis (Jackson and others, 1987).

Total and soluble cyanide were also determined for selected samples containing water-extractable gold. Total cyanide was determined by the standard reflux distillation method (method #9010, U.S. Environmental Protection Agency, 1986). Soluble cyanide content was determined on the 1:5 soil:water extract by CHEMet cyanide test kit according to the manufacturer's directions.

Elemental Gold

Morphological and textural characteristics of both placer gold and gold recovered from vein material were observed by scanning electron microscope (SEM). The crystallography of selected euhedral crystals from the placer was determined by single-crystal precission

photography. The major element composition of the gold, essentially gold, silver, and silica (as quartz), was determined by electron microprobe analysis.

Plants

The raw, washed plant material was analyzed by induced neutron-activation analysis (INAA) for gold, arsenic, cobalt, chromium, iron, molybdenum, antimony, zinc, and other elements (Cohen and others, 1987). A split of each sample was ashed, and percent ash was calculated. Table 3 lists the limits of determination. After drying the sample at 90 °C, the plant material was ground and a split briquette, irradiated, and the resulting gamma ray spectra measured. One sample, found to contain an elevated level of gold by INAA, was reanalyzed by flame-AA following an acid digestion of the plant ash.

Statistical Methods

To evaluate correlations between plants and soils, the plant data were segregated by species and the soil data were segregated by horizons. This subdivision resulted in small data sets, particularly in the case of the plants, which required special statistical handling in order to define relationships among the data. A nonparametric statistical method, Spearman's coefficient of rank correlation, was chosen for this purpose. Nonparametric statistics are useful in determining associations between variables in small data sets because a normal distribution of the data is not assumed. The level of significance of the test was chosen at 0.05 (95% confidence level). Parametric correlation matrices were used in order to identify relationships in the larger data sets, such as the total soil chemistry. The level of significance of this test was also chosen at 0.05.

RESULTS

Soil Chemistry

The results of the analysis of the soil samples for pH, specific conductance, water-extractable chloride, organic and total carbon, loss-on-ignition, and total sulfur are presented in table 4.

The pH values of the soils range from 4.6 to 8.6, with the majority being below 7.0. The most alkaline samples are those taken at sites 5a and 5b, which are located on a loess bank in the center of the study area.

Specific conductance of the water-extracts ranges from 33 to 340 µS/cm. The highest specific conductance values generally occur in samples with high concentrations of dissolved organic carbon. The soil contains low concentrations of water-extractable chloride. The water extracts contain from 0.1 to 5.8 ppm chloride, with the median value being 0.7 ppm.

Organic carbon of the soil ranges from 0.29 percent to 33.5 percent by weight, with the highest values being present in the 0-horizon and "muck" lenses. Two exceptions to this are the

Table 3. Listing of approximate limits of determination for plant analysis by induced neutron activation analysis

[D.L. = Detection limit as part per billion (ppb or µg/kg), part per million (ppm or µg/g), or percent (%). Analysis by Actlabs, Ancaster, Ontario, Canada by E.L. Hoffman]

Element	D.L.	Element	D.L.
Au	0.1 ppb	Rb	1 ppm
Ag	0.2 ppm	Sb	0.005 ppm
As	0.01 ppm	Sc	0.01 ppm
Ba	5 ppm	Se	0.1 ppm
Br	0.01 ppm	Sr	10 ppm
Ca	0.01 %	Ta	0.05 ppm
Co	0.1 ppm	Th	0.1 ppm
Cr	0.3 ppm	U	0.01 ppm
Cs	0.05 ppm	W	0.05 ppm
Fe	0.005 %	Zn	2 ppm
Hf	0.05 ppm	La	0.01 ppm
Hg	0.05 ppm	Ce	0.1 ppm
Ir	0.1 ppb	Nd	0.3 ppm
K	0.01 %	Sm	0.001 ppm
Mo	0.05 ppm	Eu	0.05 ppm
Na	1 ppm	Tb	0.1 ppm
Ni	2 ppm	Yb	0.005 ppm
		Lu	0.001 ppm

Table 4. A listing of pH, chloride, sulfur, organic and total carbon, loss-on-ignition, and specific conductance data for soil samples collected from Lillian Creek, Alaska

Sample no.[1]	pH	Cl^- [2] ppm	Total S %	Organic C %	Loss-on-ignition %	Total C %	Specific conductivity µS/cm
1-0-4	6.22	3.0	0.17	19.88	40	23.00	210
1-4-10	6.51	0.3	0.07	2.74		1.98	94
1-10-40	6.59	0.3	0.06	0.54		0.52	78
1-40+	6.56	0.3	0.07	0.57		0.4	110
2a-0-4	5.99	3.8	0.15	27.42	55	27.21	320
2a-4-30	5.27	0.4	0.02	1.67		1.69	67
2a-30-34	4.58	1.1	0.03	7.31	15	7.90	100
2a-34-67	5.09	0.2	0.03	0.72		0.49	33
2a-67-74	5.16	0.2	0.02	0.56		0.47	50
2a-74+	5.32	0.2	0.01	1.27		0.41	67
2b-0-4	5.40	5.8	0.12	21.27	43	21.76	310
2b-4-30	5.50	0.5	0.02	0.56		0.79	180
2b-34-67	5.18	0.1	0.02	1.19		0.64	73
2b-67-74	5.22	0.3	0.02	0.78		0.98	53
3-0-4	5.43	3.4	0.17	32.28	64	30.72	100
3-4-19	6.45	0.4	0.03	2.85		3.62	130
3-19-24	5.63	0.4	0.05	6.01		6.62	120
3-24-30	6.56	0.8	0.11	18.94	38	19.24	170
3-34+	6.70	1.3	0.10	17.68	35	18.11	230
4-0-4	4.74	2.9	0.14	33.60	67	33.78	340
4-4-18	7.04	5.4	0.01	0.29		0.45	70
5a-0-2	7.36	2.2	0.03	2.61		3.47	160
5a-2-12	7.23	0.6	0.04	4.04		4.04	130
5a-12+	8.08	1.0	0.03	2.19		2.30	260
5b-0-2	8.33	2.4	0.01	2.46		3.21	190
5b-2-12	8.58	0.4	0.01	1.09		1.33	170
5b-12+	8.29	1.6	0.05	2.19		2.55	290
6-0-5	6.51	1.3	0.08	15.80	32	17.77	280
6-5-14	5.85	0.2	0.02	3.13		3.75	100
6-14-23	5.78	0.6	0.15	29.72	60	29.40	100
6-23+	5.94	0.4	0.04	7.00		7.82	130
7-0-5	4.87	3.6	0.10	21.66	43	20.76	250
7-5-9	5.08	1.3	0.02	2.86		2.86	78
7-9-20	5.77	0.8	0.02	1.90		2.13	84
7-20+	5.98	0.6	0.04	2.07		2.20	170
8-0-4	6.78	1.2	0.10	6.26	12	6.09	140

[1]First number represents the sample site, remaining numbers refer to depth of sample, in inches.
Example: 1-0-4: Sample site no. 1, 0-4 inches.

[2]Concentration in a 100-mL water extract of 20 g of soil.

0-horizon samples from sites 5a and 5b, the loess bank, which have relatively low organic carbon contents (2.61% and 2.46%, respectively). There was very good agreement between the organic carbon content of the samples as determined by the COD method and as estimated by dividing the loss-on-ignition values by two (assuming carbon accounts for roughly 50% of organic matter by weight). The total carbon content of the soil samples is very comparable to the organic carbon values obtained and ranges from 0.40 percent to 33.8 percent. This indicates that very little of the carbon in the soil is present as mineral carbon (carbonate). These data are not surprising for most of the samples, because there are no carbonate rocks in the drainage.

Total sulfur content of the soils is low (0.01% to 0.20%), not surprising because the soils are developed in loess above the pyrite-bearing bedrock. The 0-horizon samples and the organic-rich muck layers have the highest total sulfur content, with samples 5a-0-2 and 5b-0-2 again being the exceptions.

Elevated concentrations of barium, cobalt, chromium, copper, iron, manganese, nickle, vanadium, and zinc were found in many samples as compared with averages seen in soils as given by Rose and others (1979) (table 5). Samples from the upper portion of the drainage, particularly those from sites 2a and 2b, generally have the highest base metal content. Molybdenum was detected in only two samples, both from site 2a. These samples contain elevated concentrations of molybdenum, 9 and 13 ppm. Typically molybdenum in soils averages about 3 ppm (Rose and others, 1979). Silver was present at the limit of determination (2 ppm) in samples 4-0-4 and 2a-30-34.

Arsenic, antimony, and total and water-extractable gold values for the soil samples are given in table 6. Arsenic and antimony are present in elevated concentrations in many of the samples. Arsenic values range from 16 to 6,500 ppm and antimony ranges from 4 to 220 ppm in these soils. Soils typically contain only 8 ppm arsenic and 2 ppm antimony (Rose and others, 1979). The distribution of arsenic follows that of total gold, with the highest values found in the upstream sites. Most of the high values for antimony were obtained at sampling sites 2a and 2b.

All soil samples were found to contain detectable total gold ranging from 2 ppb to 600 ppb with a median of 16 ppb (table 6). The highest gold concentrations were found closer to the head of Lillian Creek, particularly in samples from sites 1, 2b, and 3. The highest gold values at each site were generally found lower in the soil profile, near bedrock (sample 1-40+), or in gravelly horizons (samples 7-20+, 3-4-19, and 3-19-24).

Twenty-three of the soil samples contain small amounts of water-extractable gold, from 0.4 ppb to 10 ppb (table 6). Only three of the 0-horizon samples (from sites 3, 4, and 5b) contain detectable water-extractable gold, whereas most of the underlying horizons contain detectable water-extractable gold.

The soluble organic carbon content of the samples ranged from 21 to 75 mg/L in the extracts (table 7). The distribution of soluble organic carbon closely follows that of total organic carbon.

Table 5. Listing of analytical data for major, minor, and trace element concentrations of soil samples collected near Lillian Creek, Alaska

[ND= not detected]

Sample no.	Al %	Ca %	Fe %	K %	Mg %	Na %	P %	Ti %	Mn ppm	Ag ppm	Ba ppm
1-0-4	3.7	1.4	2.7	0.89	1.7	0.46	0.13	0.13	590	ND	770
1-4-10	6.1	0.74	4.2	1.7	2.1	1	0.07	0.25	580	ND	1,300
1-10-40	6.3	0.6	4.7	1.9	2.1	1.2	0.06	0.22	420	ND	1,500
1-40+	7.1	0.18	5.6	1.4	0.35	2.8	0.03	0.08	230	ND	1,700
2a-0-4	2.7	1.7	2.2	0.85	0.68	0.27	0.13	0.10	2,000	ND	890
2a-4-30	6.4	0.52	4.8	1.9	0.84	0.67	0.07	0.30	460	ND	1,400
2a-30-34	6.8	0.53	3.4	1.8	0.57	0.57	0.07	0.31	370	2	1,400
2a-34-67	7.4	0.05	5.7	2.4	0.51	0.09	0.09	0.36	380	ND	1,700
2a-67-74	7.0	0.06	5.4	1.8	1.1	0.05	0.07	0.26	400	ND	1,400
2a-74+	7.6	0.08	6.2	1.9	1.6	0.05	0.07	0.32	530	ND	1,500
2b-0-4	3.5	1.1	2.7	1.1	0.73	0.36	0.12	0.13	1,500	ND	870
2b-4-30	6.6	0.44	5.4	1.9	0.78	0.6	0.07	0.31	460	ND	1,500
2b-34-67	6.5	0.51	5.0	1.9	0.71	0.67	0.07	0.30	500	ND	1,400
2b-67-74	6.6	0.47	5.4	1.9	0.75	0.64	0.06	0.36	410	ND	1,400
3-0-4	2.7	1.4	1.7	0.77	0.34	0.25	0.14	0.11	220	ND	550
3-4-19	7.4	0.58	4.4	2.5	0.66	0.53	0.07	0.28	2,800	ND	1,900
3-19-24	6.6	0.73	4.3	2.2	0.58	0.52	0.08	0.21	580	ND	1,800
3-24-30	4.8	2.1	2.6	1.5	0.58	0.45	0.07	0.16	740	ND	1,200
3-34+	5.3	2	2.9	1.6	0.66	0.45	0.08	0.18	450	ND	1,400
4-0-4	2.5	1.2	1.5	0.67	0.38	0.25	0.14	0.11	1,800	2	980
4-4-18	6.9	0.24	5.7	1.9	0.86	0.14	0.07	0.30	480	ND	1,600
5a-0-2	6.3	1.9	3.8	1.5	1.2	1.3	0.1	0.37	700	ND	1,000
5a-2-12	6.3	1.8	3.9	1.5	1.1	1.2	0.09	0.36	960	ND	1,100
5a-12+	6.4	2.5	3.9	1.5	1.3	1.4	0.10	0.38	740	ND	1,000
5b-0-2	6.3	2.5	3.9	1.5	1.3	1.4	0.09	0.40	720	ND	1,000
5b-2-12	6.6	2.3	4.0	1.5	1.3	1.5	0.09	0.40	730	ND	1,100
5b-12+	6.3	2.6	3.8	1.5	1.3	1.4	0.1	0.39	720	ND	1,000
6-0-5	3.9	2.0	2.3	0.87	0.95	0.78	0.1	0.19	760	ND	640
6-5-14	5.9	1.3	3.6	1.4	1.0	1.1	0.09	0.32	500	ND	930
6-14-23	2.1	1.9	4.6	0.45	0.51	0.33	0.15	0.1	2,800	ND	680
6-23+	5.5	1.5	3.1	1.3	0.95	1.1	0.1	0.31	640	ND	900
7-0-5	3.6	1.3	1.9	0.87	0.6	0.76	0.08	0.20	630	ND	730
7-5-9	6.2	1.4	3.7	1.4	0.95	1.3	0.07	0.34	540	ND	1,000
7-9-20	6.4	1.5	3.7	1.5	1.0	1.3	0.08	0.36	530	ND	1,100
7-20+	6.2	0.82	3.9	1.8	1.2	0.77	0.09	0.24	960	ND	1,300
8-0-4	6.2	1.7	3.8	1.6	1.2	1.1	0.11	0.32	600	ND	1,100

Table 5. Listing of analytical data for major, minor, and trace element concentrations of soil samples collected near Lillian Creek, Alaska--(Continued)

Sample no.	Be ppm,	Cd ppm	Ce ppm	Co ppm	Cr ppm	Cu ppm	Ga ppm	La ppm	Li ppm	Mo ppm	Nb ppm
1-0-4	2	ND	27	18	150	48	10	17	21	ND	ND
1-4-10	3	ND	71	22	330	30	19	41	35	3	9
1-10-40	4	ND	87	18	320	39	21	50	39	4	11
1-40+	5	9	220	5	17	51	35	120	25	2	28
2a-0-4	1	6	24	14	100	37	8	14	18	3	ND
2a-4-30	3	ND	70	19	260	46	17	41	41	5	10
2a-30-34	2	2	51	9	200	44	20	31	28	4	9
2a-34-67	3	ND	73	26	240	69	19	45	48	13	8
2a-67-74	2	ND	59	29	300	85	18	37	59	9	6
2a-74+	2	ND	58	41	360	76	19	33	70	6	7
2b-0-4	2	3	29	17	130	38	9	17	23	3	ND
2b-4-30	3	ND	66	21	240	49	17	39	45	5	7
2b-34-67	3	ND	65	19	210	40	18	39	42	5	7
2b-67-74	3	ND	63	18	220	48	17	38	43	5	8
3-0-4	ND	ND	21	6	69	21	6	12	14	ND	ND
3-4-19	3	ND	55	36	230	36	20	31	44	ND	6
3-19-24	3	ND	79	19	170	40	18	45	41	2	7
3-24-30	2	ND	31	12	110	36	13	20	29	ND	6
3-34+	2	ND	35	12	130	36	14	24	32	ND	6
4-0-4	ND	4	20	8	70	42	7	12	14	4	ND
4-4-18	2	4	53	32	280	77	17	31	53	7	6
5a-0-2	2	ND	67	17	110	35	15	40	28	ND	7
5a-2-12	2	ND	63	21	130	36	16	38	30	ND	5
5a-12+	2	ND	66	18	110	36	16	40	28	ND	7
5b-0-2	2	ND	66	18	110	34	15	40	28	ND	6
5a-2-12	2	ND	69	18	110	37	16	42	30	ND	8
5b-12+	2	ND	63	18	110	36	15	39	28	ND	9
6-0-5	ND	ND	32	13	74	28	9	19	18	ND	4
6-5-14	2	ND	60	16	130	29	14	35	31	ND	7
6-14-23	ND	ND	27	27	44	44	6	15	10	ND	ND
6-23+	1	ND	50	15	110	29	14	30	27	ND	7
7-0-5	ND	ND	31	9	63	14	10	18	14	ND	5
7-5-9	2	ND	66	17	110	23	15	39	27	ND	8
7-9-20	2	ND	72	15	110	28	15	42	29	ND	8
7-20+	3	ND	78	20	230	41	17	45	39	3	7
8-0-4	2	ND	57	18	110	42	15	34	31	ND	7

Table 5. Listing of analytical data for major, minor, and trace element concentrations of soil samples collected near Lillian Creek, Alaska--(Continued)

Sample no.	Nd ppm	Ni ppm	Pb ppm	Sc ppm	Sr ppm	Th ppm	V ppm	Y ppm	Yb ppm	Zn ppm
1-0-4	16	190	14	9	150	8	94	15	2	100
1-4-10	33	190	18	11	160	12	140	18	2	110
1-10-40	39	200	17	8	150	16	110	22	3	130
1-40+	97	48	9	ND	110	29	12	57	7	120
2a-0-4	12	96	20	7	170	5	110	8	ND	460
2a-4-30	34	120	18	14	150	11	240	17	2	280
2a-30-34	26	65	15	14	120	7	260	15	2	130
2a-34-67	37	200	17	17	75	15	370	17	3	430
2a-67-74	32	210	19	19	56	9	310	14	2	360
2a-74+	30	290	16	23	42	9	300	15	2	350
2b-0-4	16	120	23	8	150	7	140	10	1	90
2b-4-30	33	150	19	16	150	12	250	16	2	330
2b-34-67	32	90	15	14	150	12	260	15	2	250
2b-67-74	31	110	18	14	140	11	260	15	2	290
3-0-4	11	35	7	10	100	4	53	14	1	60
3-4-19	27	97	25	15	120	11	160	16	2	120
3-19-24	38	89	28	12	140	13	120	29	3	140
3-24-30	18	67	18	10	160	7	85	24	2	91
3-34+	19	61	20	10	180	8	93	26	3	89
4-0-4	11	62	16	6	120	ND	96	7	ND	300
4-4-18	29	230	17	20	94	11	330	16	2	610
5a-0-2	31	45	18	14	210	11	130	18	2	95
5a-2-12	32	79	17	14	220	11	140	19	2	130
5a-12+	34	46	14	14	230	11	130	19	2	92
5b-0-2	33	44	14	14	230	11	130	20	2	90
5b-2-12	34	45	15	15	230	11	130	20	2	91
5b-12+	32	44	16	4	230	10	130	19	2	91
6-0-5	15	59	11	9	190	5	76	11	1	89
6-5-14	29	65	13	13	190	10	130	17	2	91
6-14-23	15	66	6	6	130	5	50	13	1	61
6-23+	25	58	12	12	190	8	110	15	2	100
7-0-5	14	30	8	7	140	5	77	8	1	72
7-5-9	32	37	15	13	200	11	130	18	2	80
7-9-20	35	44	16	14	210	11	130	19	2	87
7-20+	37	130	18	13	190	13	180	19	2	170
8-0-4	30	55	17	13	190	10	130	18	2	120

Table 6. A listing of total gold, water-extractable gold, arsenic, and antimony data for soil samples collected from Lillian Creek, Alaska

[ND = not detected]

Sample no.[1]	Total Au ppb	Water-extractable Au ppb	As ppm	Sb ppm
1-0-4	12	ND	400	14
1-4-10	40	0.5	1,300	23
1-10-40	50	1.0	1,200	30
1-40+	600	2.0	6,500	38
2a-0-4	2	ND	460	55
2a-4-30	30	1.0	710	100
2a-30-34	6	ND	290	41
2a-34-67	16	1.5	140	76
2a-67-74	18	ND	150	68
2a-74+	16	10.1	130	62
2b-0-4	20	ND	670	86
2b-4-30	36	0.5	860	220
2b-34-67	24	0.5	590	41
2b-67-74	48	ND	630	51
3-0-4	18	0.8	240	24
3-4-19	100	1.0	1,000	64
3-19-24	100	0.9	1,200	47
3-24-30	50	0.4	310	33
3-34+	46	2.0	380	25
4-0-4	2	0.5	36	8
4-4-18	8	0.5	67	27
5a-0-2	4	ND	40	8
5a-2-12	24	ND	320	38
5a-12+	4	ND	21	4
5b-0-2	2	5.0	19	5
5b-2-12	2	0.5	16	5
5b-12+`	6	0.9	16	7
6-0-5	2	ND	29	6
6-5-14	6	1.5	62	16
6-14-23	2	ND	190	17
6-23+	6	1.4	59	17
7-0-5	4	ND	30	5
7-5-9	4	0.5	46	6
7-9-20	14	0.5	50	11
7-20+	300	3.1	830	160
8-0-4	4	ND	71	13

[1]First number represents the sample site, remaining numbers refer to depth of sample, in inches.
Example: 1-0-4: Sample site no. 1, 0-4 inches.

Table 7. Distribution of gold and organic carbon in the soil samples collected from Lillian Creek, Alaska

[---, not determined]

Sample no	Total Au ppb	Organic-bound Au ppb	Percent of organic-bound gold of total gold	Loosely bound Au ppb	Water extractable Au ppb	Organic C %	Soluble organic C[1] mg/L
1-40+	600	150	25	4	2.0	0.57	34
2a-4-30	30	23	77	1	1.0	1.67	32
2a-34-67	16	12	75	1	1.5	0.72	23
2a-74+	16	13	81	1	10.1	1.27	21
3-4-19	100	40	40	---	1.0	2.85	89
3-34+	46	26	57	1	2.0	17.7	---
5b-0-2	2	2	100	1	5.0	2.46	75
6-5-14	6	5	83	<1	1.5	3.13	67
6-23+	6	1	17	1	1.4	7.00	---
7-20+	300	75	25	---	3.1	2.07	64

[1]Concentration in a 100 mL water extract of 20 g of soil.

Cyanide was not detected in any soil sample analyzed by the total cyanide method (method detection limit 5 ppm). Soluble cyanide was not detected in any of the water extracts of the soils (method detection limit 10 ppb in the extract).

Ten samples were analyzed for organic-bound gold and found to contain from 1 to 150 ppb (table 7). This form of gold makes up a significant portion (up to 80%) of the total gold in all samples analyzed. According to Gregoire (1985), this method may only recover 70 percent of the organic-bound gold in a sample, due to readsorption of gold by the mineral matrix. If this is the case, the gold in half of the samples may be present almost entirely in some organic-associated form.

Eight samples were analyzed for loosely bound gold and found to contain from <0.1 to 4 ppb gold in this form (table 7). Six of the eight samples contained only 1 ppb of loosely bound gold. Sample 1-40+, which contains the greatest amounts of total and organic-bound gold, also contains the greatest amount of loosely bound gold.

Elemental Gold

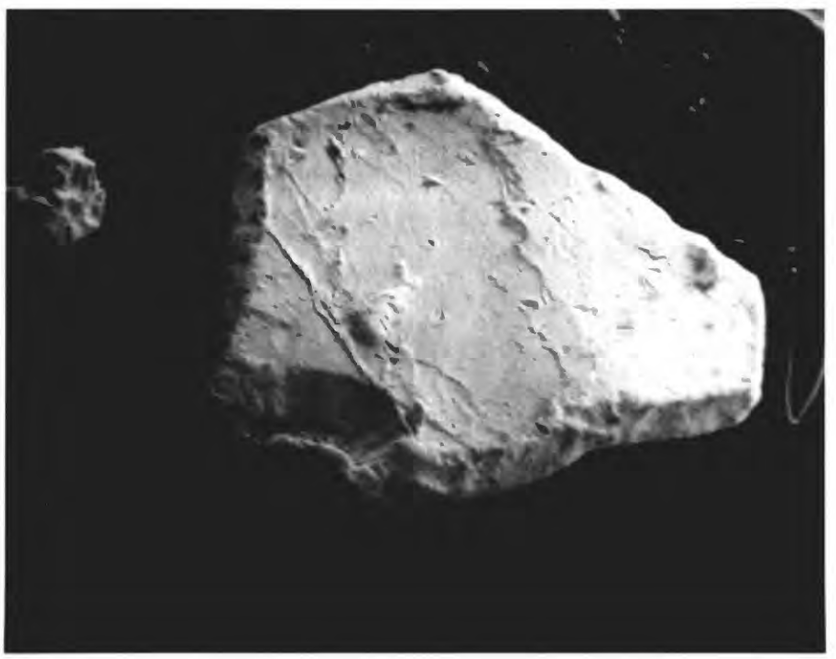
Observation of placer gold under the SEM revealed a wide variety of shapes and textures. Many of the gold grains are irregular nuggets, but some are remarkably euhedral. The unusually angular nature of the gold from the Lillian Creek placer was noted early in the mining history of the area (Mertie, 1918). Some of the placer crystals are clearly dodecahedra, but other crystals take the form of spikes, and pseudo-hexagonal plates and rods (figs. 2a, 2b, and 2c). Based on single-crystal precession photographs, the spikes were found to be actahedra elongatedon the octahedral ([111]) axis and the plates to be octahedra modified by cubes and flattened on the [111] axis (E.E. Foord, U.S. Geological Survey, written commun., 1989). The rod which is hexagonal in cross section is presumed to have the same crystallography as the plates, except elongated along the [111] axis.

The textures of the placer gold are of three basic types: smooth, porous, and striated. Gold which has a smooth texture may have irregular surface features, but these features are generally rounded and have low relief. Most of the euhedral crystals and some of the nuggets exhibit this texture (fig. 3a). The porous gold has very high relief and often appears spongy (fig. 3b). The surface of the striated gold has a "stair-step" appearance (fig. 3c).

The overall shape of the vein gold was difficult to determine because the vein material was jaw-crushed in order to liberate the gold from the quartz. However, the crystals which did survive the crushing are all of the octahedral spike form described above. The surface texture of the vein gold is unlike that of any of the placer gold. The vein gold has numerous ridges running approximately perpendicular to the axis of elongation ([111]), giving the crystal a rough appearance (fig. 4). As gold is highly malleable, these regular ridges are not likely to be the result of crushing.

Analysis of gold from the Lillian Creek placer deposit and vein material by electron microprobe showed that the major element composition of the placer gold ranges from 92.5-97.3

a



b

c

Figure 2.--Crystalline gold from the Lillian Creek placer deposit: **a**. spike; **b**. pseudohexagonal plate; and, **c**. pseudohexagonal rod. Scale bar equal 10 μm.

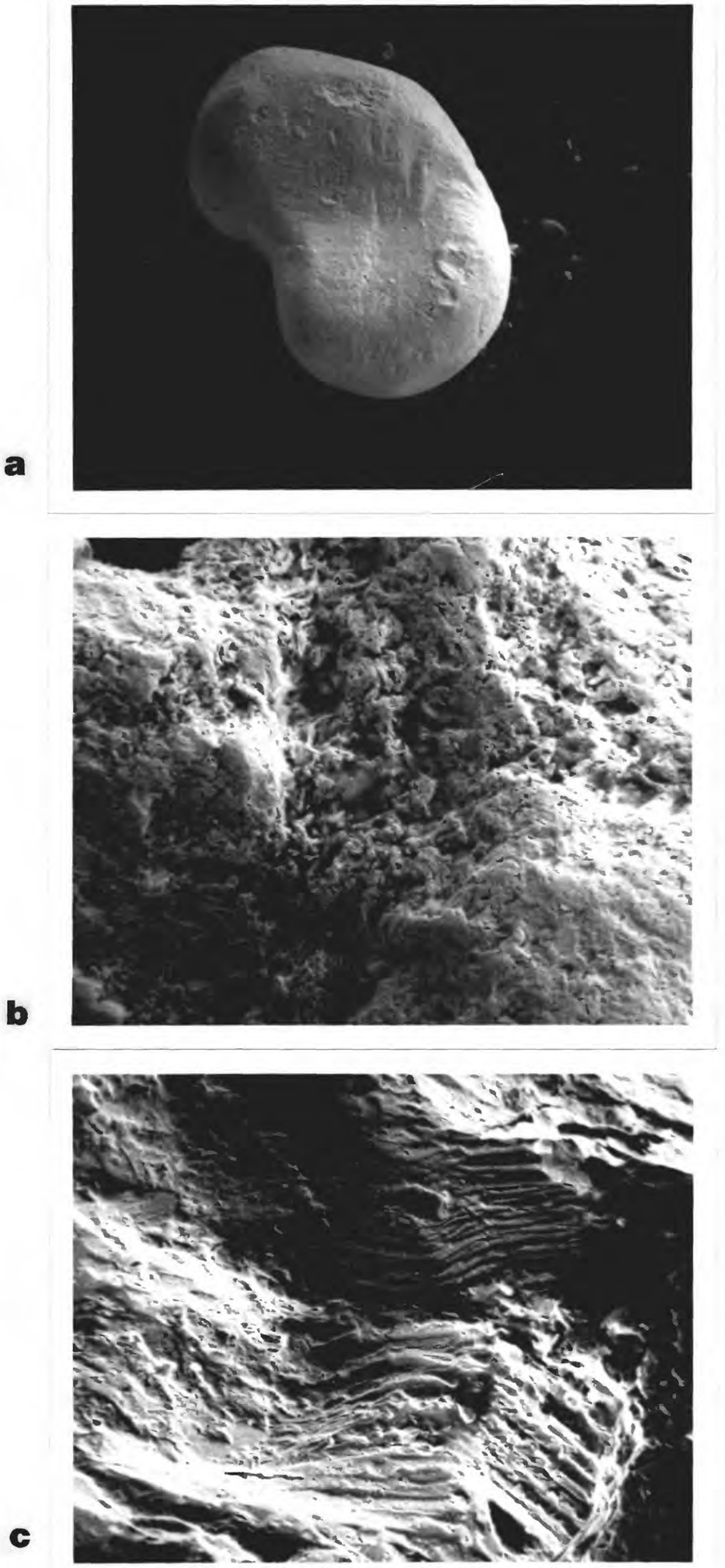


Figure 3.--Surface textures of gold from the Lillian Creek placer deposit; **a**. smooth; **b**. porous; and, **c**. striated. Scale bar equals 10 µm.

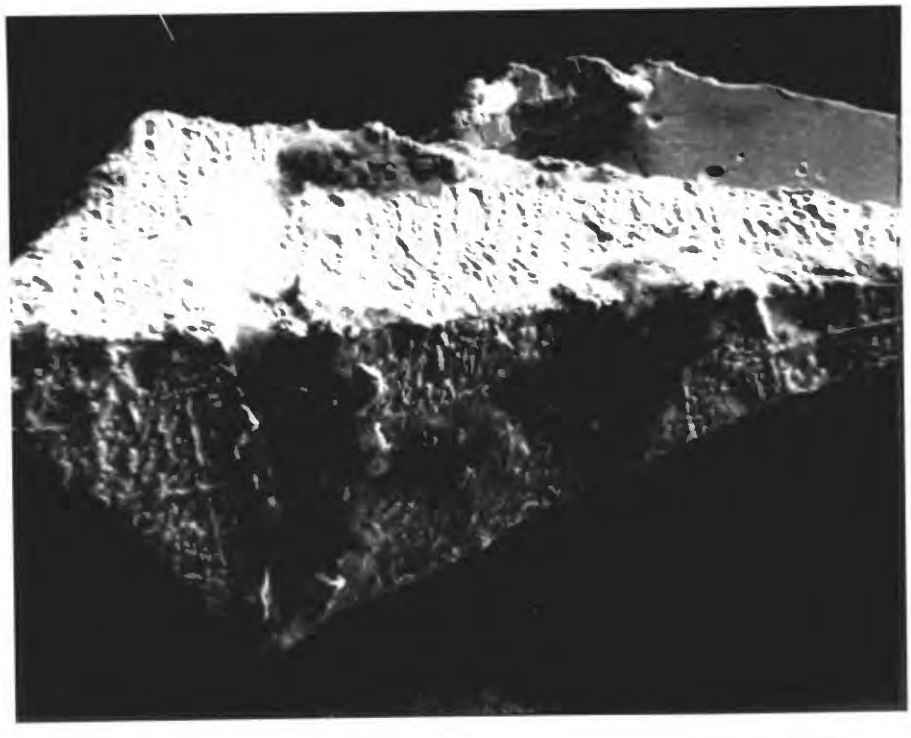


Figure 4.--Photograph showing the texture of the vein gold. Scale bar equals 100 μm.

percent gold, 2.6-7.0 percent silver, and trace amounts of quartz (table 8). The vein gold is 94.5-95.4 percent gold, and 4.6-5.5 percent silver, with no detectable quartz (table 8). Three of the placer gold samples analyzed were euhedral crystals and were found to have very consistent compositions: 95.6-95.7 percent gold and 4.3-4.7 percent silver. Copper and iron were not detected. The analytical totals of the placer gold averaged 99.9 percent, whereas the analytical totals for the vein gold were lower, averaging 98.7 percent.

Plant Chemistry

The plants were thoroughly washed and their ash content calculated for use as a qualitative indicator of contamination by airborne mineral matter. The ash content of the plant samples was not found to be anomalously high (table 9). Airborne contamination does not therefore have a significant effect on the plant chemistry in this study. It is important to note that raw plant samples were analyzed by INAA for metal content. Many of the chemical data reported in the literature represent the metal content of plant ash. The values for raw plant material in this study can be expected to be approximately 2-5 percent that of the ash.

All of the plant samples contain gold, and values range from 0.2 ppb to 5.7 ppb, with one anomalous sample containing 3,700 ppb gold (table 9). The ashed split was reanalyzed by flame-AAS to confirm the extremely anomalous gold concentration that occurred in the labrador tea sample from site 3. The sample contained 4,900 ppb gold by this method (whole plant value recalculated from gold content of ash). Plant samples taken in the upper part of the drainage (sites 1-4) contained significantly more gold (median = 2.7 ppb) than those collected farther downstream (median = 0.3 ppb). Labrador tea samples almost always contain more gold (median = 2.3 ppb) than the alder samples (median = 0.5 ppb), in agreement with the findings of Severson and others (1986).

The arsenic content of the plants ranges from 0.18 ppm to 6.6 ppm. The plants show a steady decrease in arsenic content with distance downstream. Labrador tea consistently contains higher levels of arsenic than alders collected at the same site.

Labrador tea contains more antimony, chromium, barium, and iron than the alders at any one site (table 9). The highest levels of antimony are found in plants collected from sites 1, 2, and 4, and the highest levels of chromium are found in plants collected from sites 1, 2, 4, and 8. Most of the plant samples were found to have a high barium content. Only one plant sample, the labrador tea collected at site 4, contains an elevated level of iron. Molybdenum and zinc were the only metals that were found in higher concentrations in alders than labrador tea (table 9). Elevated levels of molybdenum are present in alder samples from sites 2, 4, 5, and 8. No nickel nor silver was detected in any of the plant samples. The determination limits for nickel and silver are 5 ppm and 0.3 ppm, respectively. The standard INAA analytical package included several elements that are not relevant to this study (Cohen and others, 1987). The results of these analyses are also given in table 9.

Table 8. Major element composition by electron microprobe of vein gold and placer gold collected from Lillian Creek, Alaska

[Detection limits: gold=0.55%, silver=1.5%, and silica (as quartz)=0.02%; --- = not detected. Data are reported to ±0.1%]

Sample no.	Au %	Ag %	Silica %	Analytical total %
placer crystals:				
LCX1	95.6	4.4	---	100.4
LCX2	95.6	4.3	0.1	99.9
LCX3	95.7	4.3	---	100.7
placer nuggets:				
LCN1	97.3	2.6	---	99.7
LCN2	92.9	6.9	0.2	99.3
LCN3	93.7	6.3	---	99.8
LCN5	93.1	6.7	0.7	100.5
LCN4	92.5	6.8	---	98.5
LCN6	95.5	4.5	---	99.7
LCN7	92.9	7.0	0.1	99.7
LCN8	95.6	4.4	---	100.2
LCN9	97.2	2.8	---	100.8
LCN10	94.7	5.3	---	99.1
vein gold:				
LCV1	95.4	4.6	---	98.3
LCV2	94.5	5.5	---	98.6
LCV3	94.9	5.1	---	98.7
LCV4	94.5	5.5	---	98.7
LCV5	94.8	5.2	---	99.3
LCV6	95.0	5.0	---	98.5

Table 9. Plant chemistry by INAA for plant samples collected near Lillian Creek, Alaska

[ND = not detected]

	Sample no.	Ba ppm	Ca %	Cs ppm	Hf ppm	K %	Na ppm	Rb ppm	Sc ppm
Alder	1A	14	0.46	0.39	ND	0.486	41.0	13	0.02
	2A	68	0.58	3.8	ND	0.800	52.7	17	0.02
	3A	5	0.84	0.12	ND	0.529	33.0	7	0.02
	4A	95	0.73	1.2	ND	0.535	790	5	0.05
	5A	34	1.10	0.1	ND	0.443	46.2	5	0.03
	6A	6	0.51	0.17	ND	0.363	37.4	10	0.02
	7A	68	0.93	0.8	ND	0.556	40.0	18	0.02
	8A	27	1.00	ND	ND	0.863	42.2	6	0.03
Labrador Tea	1LT	55	0.37	ND	0.05	0.441	87.6	7	0.08
	2LT	95	0.37	ND	ND	0.382	62.1	2	0.07
	3LT	76	0.44	ND	ND	0.452	62.4	4	0.04
	4LT	130	0.42	0.22	0.06	0.346	117	4	0.23
	6LT	88	0.56	ND	ND	0.376	43.8	6	0.03
	8LT	78	0.50	ND	ND	0.552	58.7	1	0.07

	Sample no.	Sr ppm	U ppm	La ppm	Ce ppm	Sm ppm	Yb ppm	Lu ppm
Alder	1A	ND	ND	0.09	0.1	0.010	ND	ND
	2A	52	ND	0.14	0.2	0.016	0.007	ND
	3A	27	ND	0.05	ND	0.007	ND	ND
	4A	80	ND	0.17	0.2	0.029	ND	ND
	5A	67	ND	0.10	0.1	0.013	0.008	0.002
	6A	ND	ND	0.06	0.2	0.008	ND	ND
	7A	41	ND	0.11	0.1	0.012	ND	ND
	8A	ND	ND	0.08	0.1	0.012	ND	ND
Labrador Tea	1LT	ND	0.03	0.31	0.4	0.045	0.024	0.003
	2LT	ND	0.04	0.25	0.3	0.034	0.016	0.002
	3LT	ND	ND	0.03	ND	0.004	ND	ND
	4LT	ND	ND	0.58	0.9	0.088	0.047	0.002
	6LT	ND	ND	0.09	0.2	0.013	ND	ND
	8LT	ND	ND	0.18	0.3	0.029	0.018	0.003

	Sample no.	Au ppm	As ppm	Br ppm	Co ppm	Cr ppm	Fe ppm	Mo ppm	Sb ppm	Zn ppm	% ash
Alder	1A	0.6	1.3	0.85	ND	0.5	0.011	1.00	0.098	40	3.7
	2A	0.5	1.3	1.0	0.3	ND	0.010	1.00	0.190	33	4.4
	3A	3.1	0.74	0.54	ND	0.4	0.006	ND	0.044	13	3.8
	4A	5.7	0.49	1.1	0.4	0.8	0.018	1.60	0.180	49	4.3
	5A	0.5	0.46	0.94	0.1	0.4	0.012	1.30	0.034	34	4.8
	6A	0.2	0.18	0.79	ND	ND	0.008	0.50	0.017	2	2.8
	7A	0.3	0.24	5.6	0.5	0.4	0.012	0.21	0.060	37	4.9
	8A	0.4	0.31	0.61	ND	0.6	0.013	2.80	0.019	27	5.0
Labrador Tea	1LT	2.1	6.6	0.57	0.1	1.3	0.025	ND	0.270	23	3.2
	2LT	2.6	5.8	0.52	0.2	1	0.023	0.13	0.580	26	2.8
	3LT	3,700	1.8	0.82	ND	ND	0.010	ND	0.142	4	2.7
	4LT	2.8	2.5	0.76	0.4	4.4	0.079	0.33	0.370	32	3.7
	6LT	0.3	0.28	0.68	ND	0.4	0.009	0.07	0.027	21	2.7
	8LT	0.3	0.37	0.71	0.1	1.1	0.019	0.11	0.037	25	3.2

EXPERIMENTAL STUDY

Methods

Fulvic acid was extracted from an organic-rich soil from Golden Gate Canyon Park, near Golden, Colorado. The soil was leached with 0.1 N sodium hydroxide to extract the humic and fulvic acid (Schnitzer, 1978). The solution was then acidified with hydrochloric acid causing the humic fraction to precipitate. The acidified solution was purified by passing it through molecular exchange resin (Amberlite XAD-4). This treatment allows the hydrophilic nonhumic substances, such as simple carbohydrates, to remain in solution while the fulvic acid, which is nonionic at low pH, is adsorbed onto the resin (Aiken, 1985). The fulvic acid is eluted from the resin with sodium hydroxide and the sodium is replaced by hydrogen by passing the FA through cation exchange resin (Bio-Rad AGG 50W-X8). The fulvic acid solution was then concentrated in a rotary evaporator, and brought to dryness at room temperature. The humic acid fraction was discarded.

A solution containing naturally-produced plant root exudates was made by allowing horsetail (*Equisetum hyemale* L.) to grow in a beaker of distilled water over the course of the 60-day experiment. The horsetail used in this experiment were collected on the University of Texas at Austin campus. Horsetail has been reported to be accumulators of gold (Nemec and others, 1936), although such reports have not been substantiated recently (Brooks, 1983). Cannon and others (1968) analyzed horsetail from several locations in the United States and did not find them to be gold accumulators. After careful removal of the horsetail from the soil, the roots were thoroughly rinsed in distilled water. The plants were then placed in a flask of distilled water, where they remained for the duration of the experiment. Distilled water was added to the flask as necessary during the experiment.

In a preliminary experiment, solutions of fulvic acid (500 ppm), potassium chloride (1 mM), horsetail root exudates, and distilled water were tested for their ability to dissolve gold at room temperature. A large flake of reagent grade gold was added to each solution. No attempt was made to buffer the pH of the solutions, or inhibit microbial growth. The beakers, except for the one containing the horsetail, were covered with paraffin film and left standing exposed to room light for 60 days. The beakers were gently swirled several times a week.

At the end of 60 days, the gold flakes were removed, the solutions were taken to dryness, and the residue was digested with a hydrobromic acid-bromine solution. The samples were then diluted, the gold was extracted into MIBK, and the MIBK was analyzed by GF-AAS (after McHugh, 1984). The horsetail samples were divided into three parts: roots, live stems, and dead stems. These were allowed to dry in a forced air oven at room temperature. They were then ground and pelleted, and analyzed for gold by neutron activation. The gold flakes which were removed from the solutions were air-dried and observed under the SEM to determine if any changes in the surface texture of the gold had occurred in the course of the experiment.

A different set of solutions were tested in a second experiment. Sodium oxalate (1 mM), which can be produced by plant roots, was used in place of the naturally produced root exudates. Instead of testing a chloride solution, which would require lower pH and a strong oxidizing

agent to dissolve gold, a 1 mM solution of sodium thiosulfate was used. Fulvic acid was retested at lower concentrations (25 and 250 ppm) which represent more realistic levels of organic acids in a natural environment.

Differences in pH of the unbuffered solutions in the first experiment made interpretation of the results difficult, and the effect of microbial activity in the solutions was impossible to quantify. In the second experiment, each of the solutions tested was buffered to pH 3.0 and 6.0 using a potassium phosphate buffer adjusted with sodium hydroxide or hydrochloric acid. Two drops of chloroform were added to each solution to inhibit microbial activity. A blank for each test solution was analyzed for gold. New, acid-washed Nalgene bottles were used.

The small surface area of the gold flakes used in the first experiment could be expected to have a considerable kinetic effect on the amount of gold dissolved. In the second experiment, approximately 0.2 g of fine gold (-80 mesh) from the Lillian Creek placer deposit (Au=93-97%, Ag=3-7%) was added to each of the test solutions.

The solutions were kept in a drawer throughout the experiment to avoid exposure to artificial light and sunlight. The solutions were gently agitated every day. Aliquots of the solutions were taken at 15 and 60 days and filtered to 5 μm to remove any of the original gold particles, but allow any colloidal gold resulting from the experiment to remain suspended. The aliquots were taken to dryness and the resultant residue was digested with hydrochloric acid and extracted into MIBK (after the method of Gregoire, 1985).

Results

The results of the first experiment showed that the fulvic acid solution contained five times as much gold (9.0 ppb) as the other solutions (table 10). The background value of gold in the fulvic acid was found to be 0.2 ppb. Little gold was detected in the potassium chloride solution, and only 0.5 ppb gold was detected in the distilled water. Although little gold was detected in the root exudate solution, neutron activation analysis of the various parts of the plant revealed that a significant amount of gold had entered the horsetail (fig. 5). The horsetail, which were collected on the University of Texas at Austin campus, were found to contain gold in amounts comparable to the other types of plants collected in the auriferous field area. Background level of gold in the plant, 0.6 ppb, was determined by analyzing the stems of horsetail which were also grown on the University of Texas campus, but were left in the soil for the duration of the experiment.

The flakes of gold from the first experiment were observed under the scanning electron microscope after being removed from the solutions. The surface of the gold particles from the fulvic acid and root exudate solutions were found to be covered with fibers which appeared to be of microbial origin. Small, spheroidal bodies which may be bacteria were also noted.

The results of the second dissolution experiment (table 10) show that, even with the great increase in surface area of the gold, the fulvic acid failed to dissolve a significant amount of gold, as did the sodium oxalate. The sodium thiosulfate dissolved a considerable amount of gold at both pH 3 and 6 after 15 days, but gold in solution decreased after 60 days. The levels of gold were higher in the pH 6 sodium thiosulfate solution than in the pH 3 sodium thiosulfate solution.

Table 10. Results of dissolution experiments

[ND = not detected; --- = no sample]

Results of first dissolution experiment

Solution	pH	Au in solution mg/L
Fulvic acid (500 ppm)	3.3	9.0
KCl (1mM)	5.3	1.8
Distilled water	5.1	0.5
Plant root exudates	?	1.0

Results of second dissolution experiment

Solution	pH	Au in solution (mg/L) 15 days	60 days
K phosphate buffer	6	---	0.14
	3	---	ND
Fulvic acid (250 ppm)	6	2	1
	3	ND	ND
Fulvic acid (25 ppm)	6	0.8	---
Na thiosulfate (1 mM)	6	2,360	290
	3	1,640	240
Na oxalate (1 mM)	6	ND	ND
	3	ND	0.3

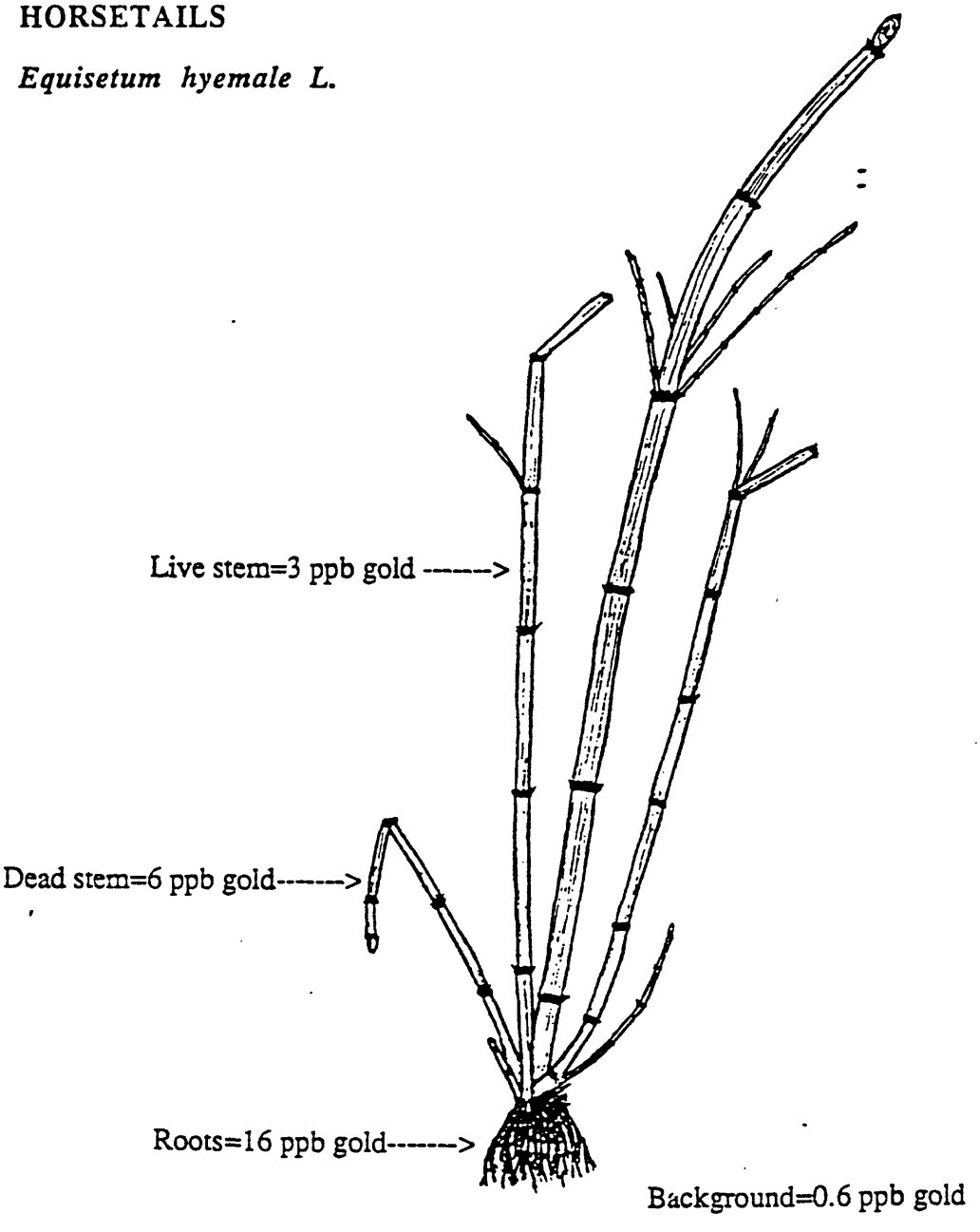


Figure 5.--Gold content of horsetail stems and roots after 60 days in contact with metallic gold in distilled water.

DISCUSSION

Geochemical and Biogeochemical Anomalies

The analytical results for soil total element concentration are given in tables 5 and 6. The distribution of gold, arsenic, and antimony in the soils supports the presence of bedrock mineralization in the upper portion of the drainage (Mertie, 1918; Foster, 1969; Eakins, 1974). Most of the high values for these elements occur upstream of sample site 4, with the exception of sample 7-20+, which contains high concentrations of all three of these elements. The arsenopyrite-quartz vein which was found to contain 90 ppm gold runs roughly perpendicular to the drainage near sample site 3 (fig. 1) and may account for some of the high Au and As values found in soils there. The highest antimony values are centered around sampling sites 2a and 2b.

The distribution of base metals, particularly chromium, nickle, zinc, copper, and iron, in the soil also support the presence of mineralization in the Tertiary intrusions in the upper reaches of the drainage (sites 1-4), particularly in the vicinity of sites 2a and 2b.

The pattern of gold, arsenic, and antimony concentrations in plants from the Lillian Creek drainage, like the soil anomalies for these same elements, support the presence of bedrock mineralization in the upper part of the drainage. Only one plant sample was found to be a "gold accumulator," that is, the plant is capable of absorbing gold in amounts greater than those present in the substrate (Berry, 1986). The labrador tea collected at site 3 contained greater than an order of magnitude more gold than any of the soil samples collected at that site (3,700 ppb vs 100 ppb). One possible explanation for the extremely high amount of gold found in this plant sample is the presence of the arsenopyrite-stibnite-quartz vein in the vicinity of site 3. Another factor which may have caused the absorption of elevated levels of gold by this plant may be the apparently slow growth rate of the plants at this north-facing sample site (Berry, 1986) or from the unusually high metal content of the soil. This sample site is unlike all of the others in that it is more "tundra-like" in its characteristics. There are few trees, and the vegetation is dominated by low-growing species, such as mosses, lichens, and blueberries. The alders and labrador tea present at this site appear stunted, and it took many individual plants to make up an adequate sample. A slow growth rate may contribute to elevated metal content in plants because a plant may continue to absorb metals over the same period of time, even though it is growing slowly and has a smaller mass (Berry, 1986). Increased ice activity on the north-facing side of the valley results in poor drainage which may also be a factor in determining the metal content of plants. Poorly drained soils contribute to higher levels of metals in plants (Thornton, 1986). Watterson (1985) speculated that mobilization of gold may be increased by the concentration of soil components such as gases, organic acids, and mircoorganisms into the bound water during freezing. Theoretically, this effect may also contribute to the elevated levels of gold in plants, such as that observed in the labrador tea collected at site 3.

The alder collected at this site also contained a relatively high level of gold (3.1 ppb), but was not found to be a gold accumulator. Differences in gold contents between labrador tea and alder are probably accountable for by differences in uptake physiology.

Although the metal contents of plants and soil at a given site are not directly related, data from both types of samples indicate the presence of mineralization. Soil anomalies should be

displaced downslope from the site of mineralization through slumping and solifluction, and plant anomalies may be even further displaced through fluid flow. This may explain the extension of the plant gold anomaly from site 1 down to and including site 4, even though the soil gold anomaly is concentrated on sites 1, 2, and 3.

The Role of Inorganic Ligands

The low concentration of chloride in the surficial material suggests that it does not play a large role in the gold cycle in the Lillian Creek drainage. In addition, the pH of the soil is generally too high for the formation of significant amounts of gold chloride complexes. There is little correlation between chloride content of the soils and concentrations of water-extractable gold or gold in plants. Keeping in mind that water-extractable gold and plant gold are indicators of gold mobility, this relationship suggests that chloride is not closely linked to gold mobilization in the study area. These findings effectively eliminate chloride as an important part of the gold cycle in the study area.

Sulfur may be present in the soil in many forms, but generally will be oxidized to sulfate in the vadose zone. For this study, only the total sulfur content of the surficial material was determined, as the original sulfur compounds were most likely altered by sample preparation. The low total sulfur values suggest that thiosulfate is not likely to be an agent of gold mobilization in this area. In addition, the pH of the soil, which was generally below seven, indicates that thiosulfate would not be an intermediate product of sulfide oxidation (Goldhaber, 1983). A graph of total sulfur versus organic carbon shows a strong association with the organic fraction in the soil (fig. 6). This correlation implies that the sulfur in the soil is present mostly as organic compounds, as is expected in a noncalcareous soil (Biederbeck, 1978), and not as inorganic species such as thiosulfate. The chemical evidence does not support thiosulfate as a probable gold complexing agent under the conditions present in the Lillian Creek drainage.

Neither labrador tea nor alder is cyanogenic (cyanide-producing), and none of the other species of plants native to the study area are known to be cyanogenic (Severson and others, 1986). Cyanide was not detected in the soil samples by either of the methods used. Therefore, it is unlikely that cyanide plays a role in the mobilization of gold in the Lillian Creek drainage.

Distribution of Gold in the Soil

Water-extractable gold was more often detected in soil samples from the C-horizon than in those from the 0-horizon. This may be due to the leaching of relatively mobile forms of gold from the upper soil horizons into the lower soil horizons. Alternatively, it could be due to the presence of a greater abundance of gold-mobilizing agents in the C-horizon, or the adsorption of gold onto insoluble organic material in the 0-horizon.

The low quantity of water-extractable gold in the soils suggests that gold is not highly mobile under the current conditions present in the Lillian Creek drainage. However, the high levels of gold in some of the plants show that it is available. This discrepancy may be due to the uptake of gold by plants in some form that is not readily water-extractable. As the study by King and others (1984) and the experimental portion of this study demonstrates, even elemental

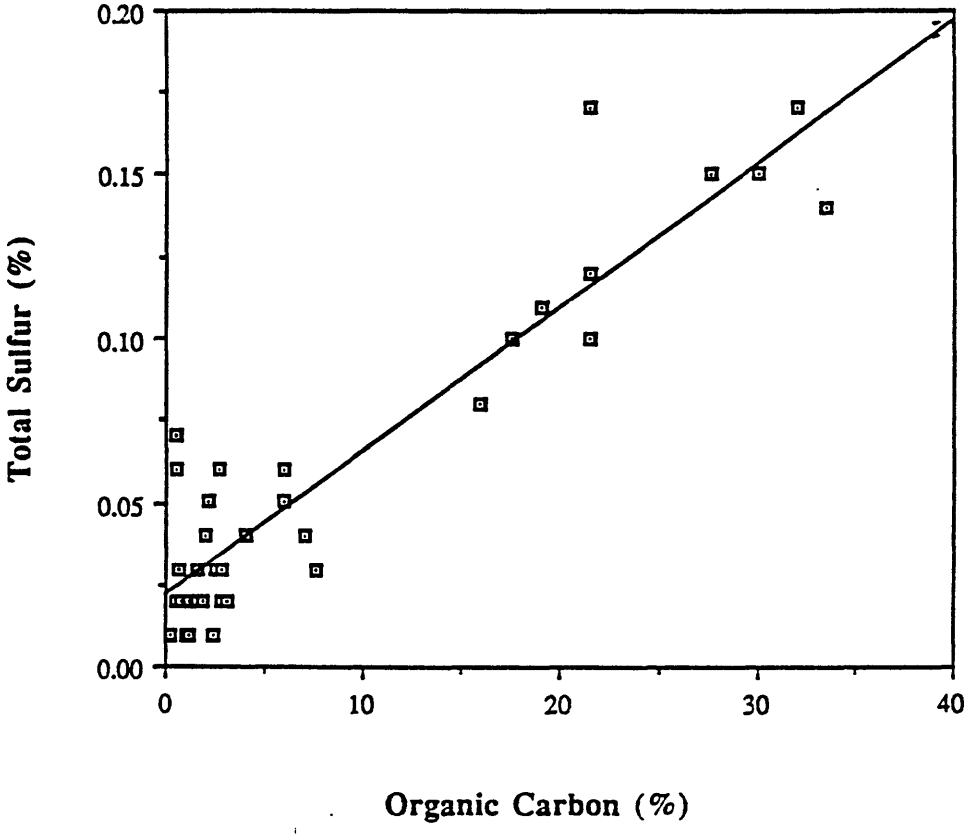


Figure 6.--Diagram showing the relationship between total sulfur and organic carbon in soil samples collected from Lillian Creek, Alaska.

gold can be made available to plants after a relatively brief exposure to moderately oxidizing conditions. Plants may absorb nutrients through a cation exchange process whereby they produce hydrogen to exchange with nutrients bound to particles in the soils (Malyuga, 1964; Brooks, 1983). These nutrients may not otherwise be available in the soil solution. Another reason for this discrepancy may be the incomplete recovery of water-extractable gold due to the readsorption of gold released during the extraction onto mineral and organic surfaces.

The gold which was measured in the water extracts may have been present in the soil in a variety of forms. These include colloids less than 0.45 μm, weakly adsorbed cations, or soluble complexes. The results of this study suggest that any soluble gold complexes are more likely to be organic than inorganic, due to a lack of inorganic ligands in the soil. The levels of loosely bound gold in the samples tested were approximately in the same range as water-extractable gold (0-10 ppb), and the two extractions may be identifying the same form or forms of gold. The water extraction was allowed to proceed overnight, however, while the ammonium acetate extraction was accomplished in two hours. Slight differences between the two data sets may have been caused by a lack of equilibration of the samples with the ammonium acetate.

A significant amount of gold is apparently associated with the organic fraction of the soil, present either as organic complexes or as cations adsorbed onto organic surfaces. The ratio of organic-associated gold to total gold decreases as total gold increases (fig. 7). There is little correlation between organic-bound gold and organic carbon in the soil. These observations suggest that the organic-bound gold is not in equilibrium with either elemental gold or organic material in the soil, and that the adsorption or complexation of gold by organics is controlled by nonequilibrium processes. Given the chemical stability of gold and the relative abundance of organic ligands in the soil, it is reasonable to assume that the oxidation of gold is the rate-controlling factor, and that organic ligands are always present in excess. It could be postulated that, given an infinite amount of time, equilibrium will be reached and the relationship between organic gold and total gold will be linear.

There is little correlation between organic-bound gold and water-extractable gold. This observation implies that, although a significant amount of organic-associated gold exists in the soil (up to 150 ppb), it is not highly mobile. It may be hypothesized that gold in this form is associated primarily with an insoluble organic fraction of the soil, such as the humin. If the organic-bound gold is sparingly soluble, it is possible that it may account for some of the gold measured in the water extracts.

The water-extractable organic carbon content of the soil parallels total organic carbon, and shows little correlation to water-extractable gold (table 6). These relationships neither support nor disprove the existence of soluble organic-gold species in the surficial material of the study area, and can be explained by either a lack of soluble organic-gold compounds in the soil or a disequilibrium relationship between dissolved organic carbon and gold, as was suggested for total carbon and gold.

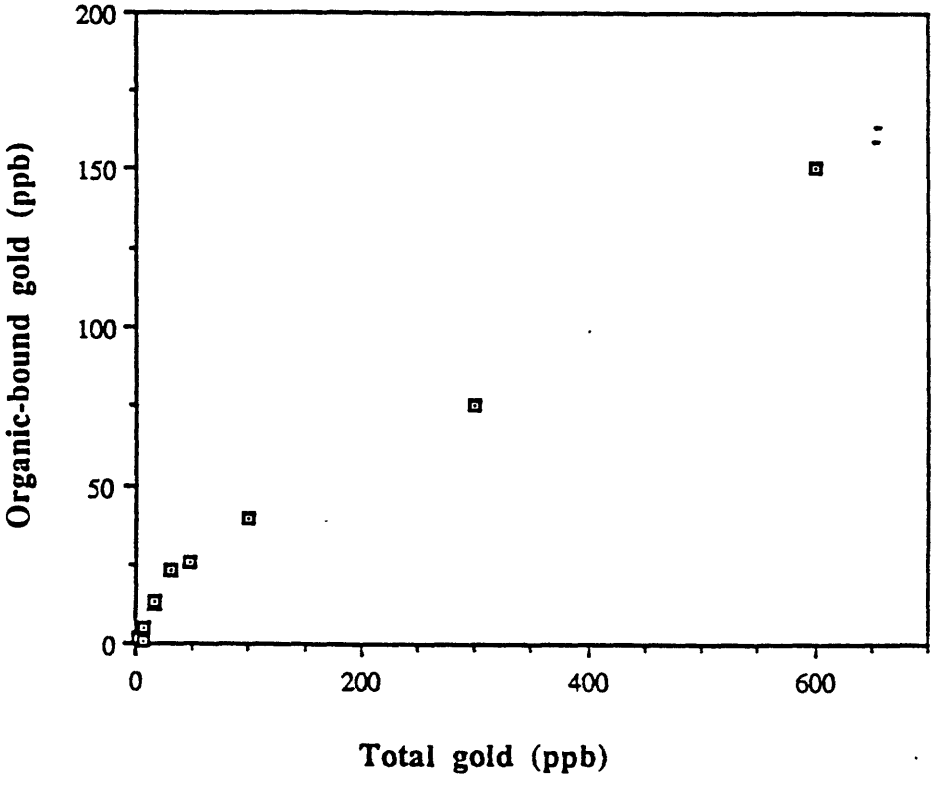


Figure 7.--Diagram showing the relationship between organic-bound gold and total gold in soils collected from Lillian Creek, Alaska.

Elemental Gold

The presence of crystalline gold in placer deposits has been used as evidence of the precipitation of gold from soil solutions at low temperatures (Warren, 1982; Severson and others, 1986). Many of the crystals from the Lillian Creek placer deposit observed in this study are very delicate and euhedral, and it is difficult to envision their deposition through physical displacement downstream without obvious damage. However, the crystals themselves cannot definitively indicate a chemical origin of some of the gold in the placer: the gold may escape deformation by weathering out of the rock very near to the place of its deposition, or through deposition by the slow process of solifluction (Severson and others, 1986).

Wilson (1984) documented the presence of euhedral "pseudo-trigonal" crystals in Western Australia which he stated were precipitated by groundwater in weathered mafic schists. These pseudo-trigonal crystals are crystallographically the same as the flattened octahedra which are found in the Lillian Creek placer deposits (fig. 3b). Trigonal and hexagonal crystals of supergene gold were noted in the weathering zone of the Fazenda Brasileiro deposit in Bahia, Brazil (Vasconcelos, 1987), as well as the Hannan South gold mine in Western Australia (Lawrence, 1988). Such crystals have also been formed experimentally by the reduction of dilute auric chloride solution at relatively low temperatures (99.5 °C) (Suito and Uyeda, 1953). Perhaps this morphology is typical of gold precipitated from low temperature aqueous solutions.

The striated and porous surface textures of some gold particles from the placer may be indicators of gold dissolution under conditions present in the surficial material of the placer. Severson and others (1986) found gold crystals from the Lillian Creek drainage with surface textures similar to the striated gold in figure 4c, and suggested that chemical etching may be the cause of this texture. The formation of the porous texture may also be the result of preferential leaching of silver from the nuggets as they weather, leaving a pitted surface (Mann, 1984).

The placer gold is of high fineness, containing less than 7.5 percent silver and quartz combined. Two of the samples contained greater than 97 percent gold. The nuggets from the placer exhibit the broadest range of chemical compositions, and may indicate that they are in various stages of weathering and, consequently, silver depletion (fig. 8) or from different sources. The compositions of the crystalline placer gold and the vein gold are similar and may suggest a common origin for both types of gold, but only two placer crystals were analyzed. The lower analytical totals of the vein gold may indicate the presence of an undetected element.

Factors Influencing Gold Uptake by Plants

Using the Spearman's rank correlation coefficient, several statistically significant correlations were found between plant and soil data. Due to the diverse nature of the surficial material in the placer, and the uncertainty of its origin, only correlations with the locally formed 0-horizon will be discussed.

Gold in labrador tea has a good positive correlation with the amount of organic carbon in the 0-horizon (fig. 9), as well as a negative correlation with pH. This relationship may be due to the formation of a gold complex, organic or inorganic, which is available to labrador tea under

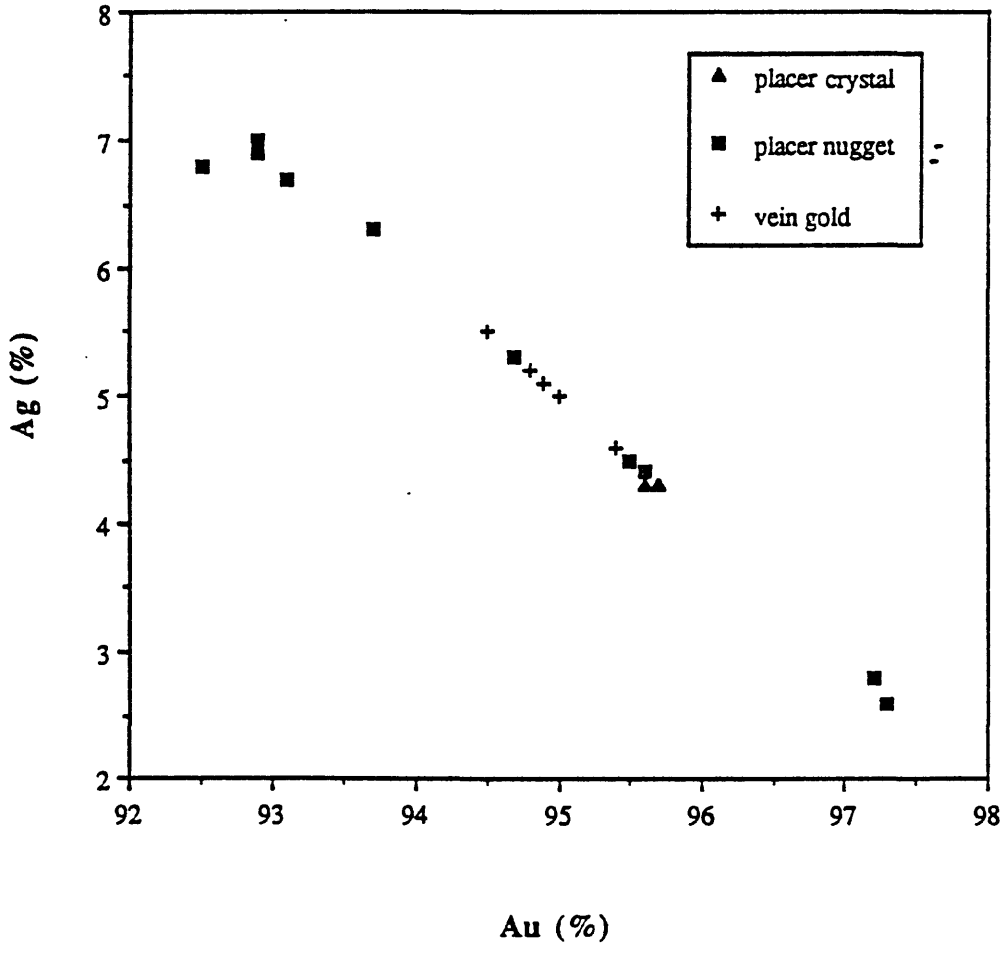


Figure 8.--Diagram showing the relationship between silver and gold for crystalline placer gold, placer nuggets, and vein gold from the Lillian Creek area, Alaska.

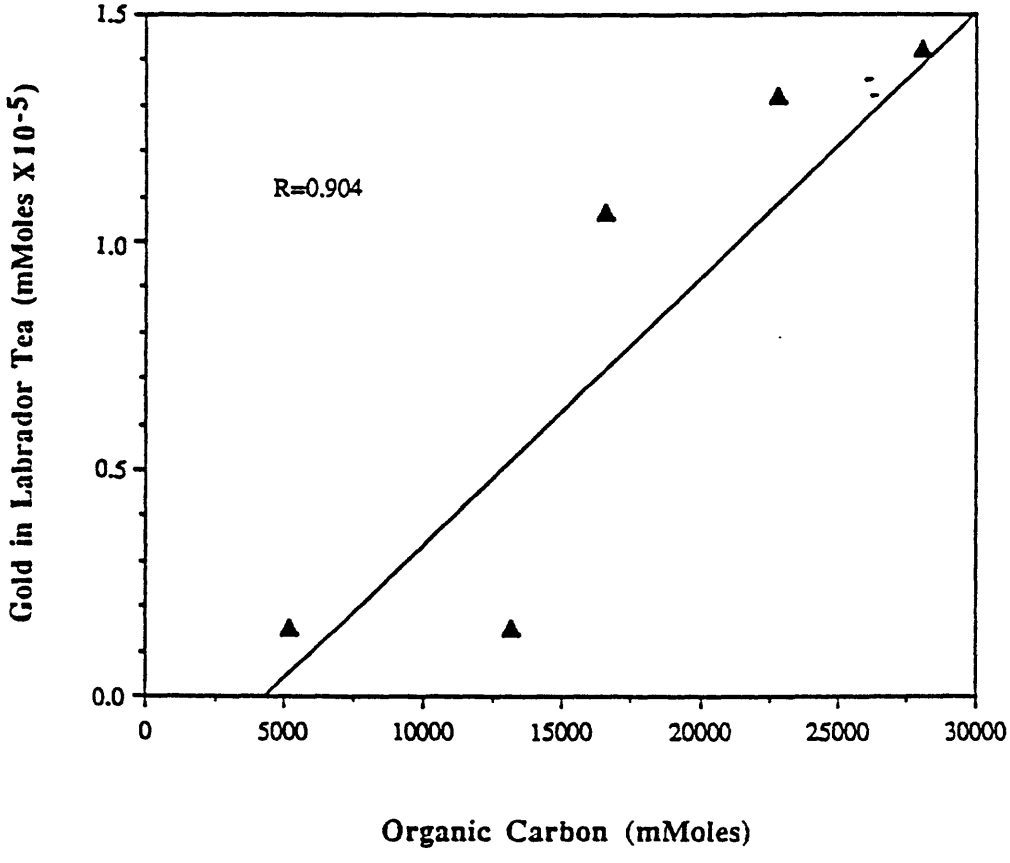


Figure 9.--Diagram showing the relationship between gold in labrador tea and organic carbon in the soil 0-horizon from Lillian Creek, Alaska.

the acidic conditions brought about by the presence of organic material. Because little correlation was found to exist between organic carbon and organic-bound gold in the soil, the relationship between plant gold and organic carbon probably is not due to the uptake of an organic-gold compound by labrador tea. There is no direct indication that the labrador tea is absorbing organic or inorganic gold species.

Most of the sampling sites which yielded the only two alder samples with high levels of gold, sites 3 and 4, but not 5, also yield 0-horizon soil samples (3-0-4, 4-0-4, 5b-0-2) which contain water-extractable gold (fig. 10). This relationship suggests that gold must be in a relatively more mobile form to be absorbed by alders than by labrador tea. This hypothesis is supported by the lower gold content of the alders as compared to the labrador tea, as the levels of water-extractable gold in the soil is generally low.

Significance of Experimental Results

The first experiment indicates that gold can be mobilized, albeit in small amounts, by fulvic acid in the absence of a strong oxidizing agent. It is not clear, however, whether gold is present as a true organometallic complex or as a protected colloid, as suggested by Ong and Swanson (1969), or in some other form. However, the oxidation of the gold must be achieved in any case, and as previously stated, the strength of the oxidizing agent necessary to accomplish this is dependent upon the stability of the gold compound formed (Lakin and others, 1974). The lack of strong oxidizing agent in the fulvic acid solution suggests that a relatively stable gold compound is being formed.

The chloride solution failed to dissolve a significant amount of gold in the first experiment; however, the pH of this solution was two pH units higher than that of the fulvic acid solution which would have a marked effect on the stability of gold chloride.

Although only 1 ppb gold was detected in the plant root exudate solution, the relatively high amount of gold in the various parts of the horsetail indicates that the solution was able to mobilize gold in some form. Cannon and others (1968) reported generally low values of gold in the ash of horsetail growing in mineralized areas, but they analyzed only the above-ground part of the plants. This study shows that the major concentration of gold in horsetail is located in the roots. Due to the difficulty of removing soil contamination from the roots, however, most biogeochemical surveys do not utilize plant roots.

The results of this experiment may be significant to the understanding of the uptake of gold by plants because it shows that gold may be dissolved and assimilated by plants in an oxidizing, organic system in a short period of time. This is in agreement with the findings of King and others (1984).

The results of the first experiment were believed to represent minimum values for gold dissolution in the natural environment because the single flakes of gold had limited surface area. In addition, the solubility of pure gold is generally lower than that of the gold-silver alloy which is usually found in nature. However, the gold content in the fulvic acid solution from the second experiment was even lower than in the first. Although the decrease in concentration of the fulvic acid solutions in the second experiment could account for some decrease in the amount of gold

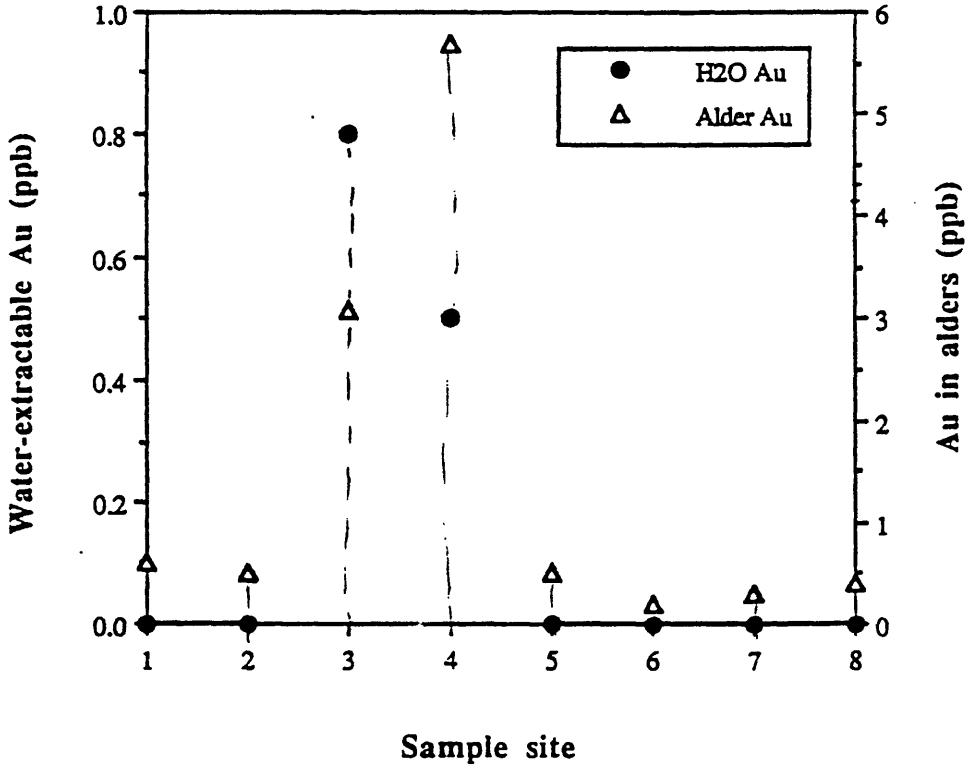


Figure 10.--Diagram showing the relationship between gold in alders and water-extractable gold in the soil 0-horizon at each sample site from Lillian Creek, Alaska.

mobilized, the increased surface area of the metallic gold would be expected to cause a much greater increase in gold dissolution.

One explanation for the greater amount of gold in the fulvic acid solution in the first experiment as compared to the second experiment is the presence of microbial activity in the solutions of the first experiment. It is possible that microbial activity in some way catalyzes the dissolution reaction, or oxidizes the gold, an essential step in the dissolution of gold. Both microbes and their products are capable of oxidizing metals in a variety of forms and by many mechanisms (Ehrlich, 1986), and it is reasonable that these processes may affect gold similarly. Once the gold is oxidized, however, a suitable "sink" must be available for the gold cations as gold is very unstable in ionic form. If the ionic gold forms complex with fulvic acid or microbial metabolites, or is adsorbed onto the surface of organic colloids or microorganisms (Watterson and others, 1985), it may be measured in solution.

The dissolution and uptake of gold by the horsetail may also have been significantly aided by the presence of microorganisms. The products of the plant roots and microorganisms were the only substances available to dissolve gold in the distilled water in which the horsetail were growing. This implies that microorganisms and root exudates are sufficient to initiate the uptake of gold by plants where metallic gold comes into contact with the plant-root microenvironment. Although it is not possible to determine the form of the gold in the fulvic acid or root exudate solutions, there is a limited number of components in each system. It appears from these experiments as if microbial products and (or) processes play a role in gold dissolution in the low temperature organic environment.

The second experiment shows that thiosulphate is able to dissolve significant amounts of gold in the absence of strong oxidizing agents and microbial activity. The decrease of gold in solution over time is probably due to the oxidation of the thiosulfate. The greater amount of gold in the pH 6 thiosulphate solution as compared to the pH 3 solution illustrates the greater stability of gold thiosulfate complexes at higher pH values (Goldhaber, 1983). However, the presence of gold in solution is great enough in either case to make thiosulphate a viable gold-mobilizing agent in any soil environment where it is available, even in small amounts. More investigations into the availability of thiosulphate in the study area must be conducted.

CONCLUSIONS

The geochemical and biogeochemical data identify an area of high gold concentration in the upper part of the Lillian Creek drainage. Other elements, particularly arsenic and some of the base metals, follow this distribution. These data support the hypothesis that the mineralization which is the source of the placer gold is localized at the head of the drainage.

The results of this study show that gold in the soil is not present entirely as the metal. An organic-bound form of gold accounts for more than half of the total gold in some soil samples. Although its exact nature is unknown, the organic-associated gold may be complexed with organic compounds or strongly adsorbed onto organic surfaces. This form of gold is not readily water-extractable, which implies that it is not highly mobile. It may be associated with humin, the insoluble organic fraction of the soil.

Small concentrations of water-extractable gold were found in the soil samples, suggesting that gold is being mobilized in the weathering zone. The form of this mobile gold is unknown, but this study has eliminated a few of the potential gold complexing agents. The data indicate that chloride and cyanide are not important in the cycling of gold in this environment. Although thiosulfate was shown by the experimental study to be an effective gold dissolving agent, it is not likely to be present in appreciable quantities in the slightly acidic soil of the placer deposit. Possible forms of the water-extractable gold include small colloids, weakly adsorbed ions, and soluble organic complexes.

Many of the plant samples taken from the Lillian Creek drainage were found to contain elevated levels of gold, even though very little water-extractable gold is present in the soils. This suggests that gold does not have to be highly mobile in order to be available to plants. The two species sampled, labrador tea and alder, were found to assimilate gold in different quantities, as might be expected due to differences in uptake physiology between the species. Correlations with the soil chemistry suggest that each species may assimilate a different form of gold. In this study, labrador tea consistently takes up more gold and arsenic than the alders, making it a more favorable target for biogeochemical gold prospecting.

Dissolution experiments suggest that microbial activity may be important in the mobilization of gold in the weathering zone. These experiments also showed that, given a short amount of time, plants may assimilate gold from a metallic source in the absence of any complexing agents other than those produced by the plant and (or) microorganisms. The precise role that is played by microorganisms or their products in either case is yet unknown, but may involve catalyzing the dissolution reaction, or aiding in the oxidation of the gold. The microorganisms or their products may be able to bind the gold, thus keeping it in solution.

Although more work must be done to identify exact processes affecting the geochemistry of gold in the soil environment, the field and experimental studies suggest that organic material and biological processes are important in the gold cycle.

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REFERENCES CITED

Aiken, G.R., 1985, Isolation and concentration techniques for aquatic humic substances, *in* Aiken, G.R. and others, eds., Humic substances in soil sediment, and water: New York, John Wiley and Sons, 692 p.

Albanese M.D., 1983a, Geochemical reconnaissance of the Livengood B-3, B-4, C-3, and C-4 quadrangles, Alaska--Summary of data on stream sediment, pan-concentrate, and rock samples: Alaska Division of Geological and Geophysical Surveys Report of Investigations 83-1, 55 p.

Andrade, W.O., Machesky, M.L., and Rose, A.W., 1988, Interactions of gold with humic substances [abs.]: Geological Society of America Abstracts with Programs, p. A240.

Baker, W.E., 1978, The role of humic acid in the transport of gold: Geochim. et Cosmochim., v. 42, p. 645-649.

Berry, W.L., 1986, Plant factors influencing the use of plant analysis as a tool for biogeochemical prospecting, *in* Carlisle, D. and others, eds., Mineral exploration: Biological systems and organic matter, Rubey Volume V: Englewood Cliffs, Prentice-Hall, p. 13-32.

Biederbeck, V.O., 1978, Soil organic sulfur and fertility, *in*Schnitzer, M., and Khan, S.U., eds., Developments in soil science 8: Soil organic matter: Amsterdam, Elsevier Scientific Publishing Company, p. 273-310.

Boyle, R.W., 1979, The geochemistry of gold and its deposits: Geological Survey of Canada Bulletin 280, 584 p.

Brooks, A.H., 1916, Preliminary report on the Tolovana district, Alaska: U.S. Geological Survey Bulletin 642, p. 201-209.

Brooks, R.R., 1983, Biological methods of prospecting for minerals: New York, John Wiley & Sons, 322 p.

Cannon, H.L., Shacklette, H.T., and Bastron, H., 1968, Metal absorption by Equisetum (horsetail): U.S. Geological Survey Bulletin 1278-A, 21 p.

Chao, T.T., 1984, Use of partial dissolution techniques in geochemical exploration: Journal of Geochemical Exploration 20, p. 101-135.

Cohen, D.R., Hoffman, E.L., and Nichol, I., 1987, Biogeochemistry: A geochemical method for gold exploration in the Canadian shield: Journal Geochemical Exploration, v. 29, p. 49-73.

Crock, J.G., and Lichte, F.E., 1982, An improved method for the determination of trace-level arsenic and antimony in geological materials by automated hydride generation-atomic absorption spectroscopy: Analytica Chemica Acta, v. 144, p. 223-233.

Crock, J.G., Lichte, F.E., and Briggs, P.H., 1983, Determination of elements in National Bureau of Standards Geological reference materials SRM 278 Obsidian and SRM 688 Basalt by inductively coupled argon plasma-atomic emission spectrometry: Geostandards Newsletter, v. 7, p. 335-340.

Crock, J.G., and Severson, R.C., 1980, Four reference soil and rock samples for measuring element availability in the western energy regions: U.S. Geological Survey Circular 841, 16 p.

Curtin, G.C., Lakin, H.W., and Hubert, A.E., 1970, The mobility of gold in mull (forest humus layer): U.S. Geological Survey Professional Paper 700-C, p. 127-129.

Dexter-Dyer Grosovsky, B., 1983, Microbial role in Witwatersrand gold deposition, *in* Westbroek, P., and deJong, E.W., eds., Biomineralization and biological metal accumulation, p. 495-498.

Eakins, G.R., 1974, Preliminary investigations, Livengood mining district, Alaska: Alaska Div. Geol. Geophys. Surveys Open-File Report 40, 16 p.

Ehrlich, H.L., 1986, Interactions of heavy metals and microorganisms, *in* Carlisle, D. and others, eds., Mineral exploration: Biological systems and organic matter, Rubey Volume V: Englewood Cliffs, Prentice-Hall, p. 221-237.

Fedoseyeva, V.I., Fedoseyev, N.F., and Zvonareva, G.V., 1985, Interaction of some gold complexes with humic and fulvic acids: Geokhimiya, no. 9, p. 1386-1390.

Fetzer, W.G., 1934, Transportation of gold by organic solutions: Economic Geology, v. 29, p. 599-604.

Foster, R.L., 1966, The petrology and structure of the Amy Dome area, Tolovana mining district, east-central Alaska: unpublished Ph.D. thesis, University of Missouri, 227 p.

Foster, R.L., 1968, Descriptions of the Ruth Creek, Lillian Creek, Griffin, Old Smoky, Sunshine No. 2, and Olive Creek lode prospects, Livengood district, Alaska: U.S. Geological Survey Open-File Report ____, 21 p.

Foster, R.L., 1969, Potential for lode deposits in the Livengood gold placer district, east-central Alaska: U.S. Geological Survey Circular 590, 18 p.

Freise, F.W., 1931, The transport of gold by organic underground solutions: Economic Geology, v. 26, no. 4, p. 421-431.

Goldhaber, M.B., 1983, Experimental study of metastable sulfur oxyanion formation during pyrite oxidation at pH 6-9 and 30 °C: American Journal of Science, v. 283, p. 193-217.

Gosling, A.W., Jenne, E.A., and Chao, T.T., 1971, Gold content of natural waters in Colorado: Economic Geology, v. 66, p. 309-313.

Gregoire, D.C., 1985, Selective extraction of organically bound gold in soils, lake and stream sediments: J. Geochem. Explor., v. 23, p. 299-313.

Hare, F.K., and Hay, J.E., 1974, The climate of Canada and Alaska, *in* Landsberg, H.E., ed., World Survey of Climatology, v. 11: Amsterdam, Elsevier Scientific Publishing Company, p. 49-192.

Helgeson, H.C., and Garrels, R.M., 1968, Hydrothermal transport and deposition of gold: Economic Geology, v. 63, no. 2, p. 622-635.

Henley, R.W., 1973, Solubility of gold in hydrothermal chloride solutions: Chemical Geology, v. 11, p. 73-87.

Huheey, J.E., 1983, Inorganic chemistry: Principles of structure and reactivity [3d ed.]: New York, Harper & Row, 936 p.

Jackson, L.L., Brown, F.W., and Neil, S.T., 1987, Major and minor elements requiring individual determination, classical whole rock analysis, and rapid rock analysis, *in* Baedecker, P.A., ed., Methods for geochemical analysis: U.S. Geological Survey Bulletin 1770, p. G1-G23.

Johnson, B.F.G., and Davis, R., 1973, Gold, *in* Bailor, J.C. and others, eds., Comprehensive inorganic chemistry: Oxford, Pergamon Press, Inc., p. 129-186.

Jones, K.C., and Peterson, P.J., 1989, Gold uptake by perennial ryegrass--the influence of humates on the cycling of gold in soils: Biogeochemistry, v. 7, p. 3-10.

Krauskopf, K.B., 1951, The solubility of gold: Economic Geology, v. 46, p. 858-870.

King, H.D., Curtin, G.C., and Shacklette, H.T., 1984, Metal uptake by young conifer trees: U.S. Geological Survey Bulletin 1617, 23 p.

Lakin, H.N., Curtin, G.C., and Hubert, A.E., 1974, Geochemistry of gold in the weathering cycle: U.S. Geological Bulletin 1330, 50 p.

Lawrence, L.M., 1988, The morphology and geochemistry of supergene gold at Hannan South gold mine, Western Australia, *in* Bicentennial gold '88 extended abstracts and posters programme: Geological Society of Australia, Inc., Abstracts no. 23, v. 1, p. 360-364.

Levitskiy, V.V., Razvozzhayeva, E.A., Demin, B.G., Khrenov, P.M., Baburin, L.M., and Odintsova, I.V., 1983, Asfal'teny neftey i zolotykh rudkontsentratory metalloorganicheskikh soyedineniy: Doklady Akademii Nauk SSSR, v. 270, no. 1, p. 196-199.

Malyuga, D.P., 1964, Biogeochemical methods of prospecting: Consultants Bureau, New York, 205 p.

Mann, A., 1984, Mobility of gold and silver in lateritic weathering profiles--Some observations from Western Australia: Economic Geology, v. 79, p. 38-49.

McHugh, J.B., 1984, Gold in natural waters--A method of determination by solvent extraction and electrothermal atomization: J. Geochem. Explor., v. 20, p. 303-310.

Mertie, J.B., Jr., 1918, The gold placer of the Tolovana district, Alaska: U.S. Geological Survey Bulletin 662-D, p. 221-277.

Mertie, J.B., Jr., 1937, The Yukon-Tanana region, Alaska: U.S. Geological Survey Bulletin 872, 276 p.

Mineyev, G.G., 1976, Organisms in the gold migration-accumulation cycle: Geokhimiya, no. 4, p. 577-582.

Munsell Soil Color Charts, 1975 ed., Macbeth Division of Kollmorgen Corporation, Baltimore, Maryland.

Nelson, D.W., and Sommers, L.E., 1982, Total carbon, organic carbon, and organic matter, *in* Page, A.L., ed., Methods of soil analysis, Part 2: Chemical and microbiological properties, [2d ed.]: Madison, Wisconsin, ASA-SSSA, p. 539-579.

Nemec, B., Babicka, J., and Oborsky, A., 1936, Uber das vorkommen von gold in den schachtelhalmen [On the accumulation of gold in horsetails]: International Academy of Science Boheme Bulletin, nos. 1-7, 13 p.

Ong, H.L., and Swanson, V.E., 1969, Natural organic acids in the transportation, deposition, and concentration of gold: Quarterly of the Colorado School of Mines, v. 64, p. 395-425.

Overbeck, R.M., 1920, Placer mining in the Tolovana district, Alaska: U.S. Geological Survey Bulletin 712, p. 177-184.

Pearson, R.G., 1973, Hard and soft acids and bases: Stroudsburg, Pennsylvania, Dowden, Hutchinson & Ross, 302 p.

Péwé, T.L., 1952a, Geomorphology of the Fairbanks area: Ph.D. thesis, Stanford University, 220 p.

Péwé, T.L., 1975, Quaternary geology of Alaska: U.S. Geological Survey Professional Paper 835, 145 p.

Rashid, M.A., and Leonard, J.D., 1973, Modifications in the solubility and precipitation behavior of various metals as a result of their interaction with sedimentary humic acid: Chemical Geology, v. 11, p. 89-87.

Renders, P.J., and Seward, T.M., 1989, The stability of hydrosulphido- and sulphido- complexes of Au(I) and Ag (I) at 25 °C: Geochim. et Cosmochim. Acta, v. 53, p. 245-253.

Robinson, M.S., 1983, Bedrock geologic map of the Livengood C-4 quadrangle, Alaska: Alaska Division of Geological and Geophysical Surveys Report of Investigations 83-4, 1 sheet, scale 1:40,000.

Saunders, R.H., 1958, Notes on the mineral resources of Livengood Creek, Hess Creek, and their tributaries: Territory of Alaska Department of Mines, MR 49-3, 3 p.

Schnitzer, M., 1978, Humic substances--Chemistry and reactions, *in* Schnitzer, M., and Khan, S.U., eds., Developments in soil science 8: Soil organic matter: Amsterdam, Elsevier Scientific Publishing Co., p. 1-64.

Severson, R.C., Crock, J.G., and McConnell, B.M., 1986, Processes in the formation of crystalline gold in placers, *in* Dean, W.E., ed., Proceedings of the Denver region Exploration Geologists Society symposium: Organics and ore deposits, p. 69-80.

Seward, T.M., 1973, Thio complexes of gold and the transport of gold in hydrothermal solutions: Geochim. Cosmochim. Acta, v. 37, p. 379-399.

Seward, T.M., 1982, The transport and deposition of gold in hydrothermal systems, *in* Foster, R.P., ed., Gold '82--The geology, geochemistry, and genesis of gold deposits: Rotterdam, A.A. Balkema, p. 165-181.

Shacklette, H.T., Lakin, H.W., Hubert, A.E., and Curtin, G.L., 1970, Absorption of gold by plants: U.S. Geological Survey Bulletin 1314-B, 23 p.

Sigafoos, R.S., 1958, Vegetation of northwestern North America as an aid in the interpretation of geologic data: U.S. Geological Survey Bulletin 1061-E, p. 165-185.

Smith, P.S., 1933, Past placer gold production from Alaska: U.S. Geological Survey Bulletin 857-B, p. 92-98.

Smith, T.E., 1983, Bedrock geologic map of the Livengood C-3 quadrangle, Alaska: Alaska Division of Geological and Geophysical Surveys Report of Investigations 83-5, 1 sheet, scale 1:40,000.

Stevenson, F.J., 1982, Humus chemistry--Genesis, composition, reactions: New York, John Wiley & Sons, 443 p.

Suito, E., and Uyeda, N., 1953, Study of single micro-crystals of gold by a three-stage electron microscope: Proc. Japan Academy, v. 29, no. 7, p. 324-330.

Thompson, C.E., Nakagawa, H.W., and VanSickle, G.H., 1968, Rapid analysis for gold in geological materials: U.S. Geological Survey Professional Paper 600-B, p. 130-132.

Thornton, I., 1986, Soil and plant factors that influence element availability and uptake--Implications for geochemical prospecting, *in* Carlisle, D. and others, eds., Mineral exploration--Biological systems and organic matter, Rubey Volume V: Englewood Cliffs, Prentice-Hall, p. 47-59.

United States Environmental Protection Agency, 1986, Test methods for evaluating solid waste--Physical and chemical methods, v. 1C, [3d ed.]: NTIS SW846, Springfield, Virginia, 218 p.

Van Dijk, H., 1971, Cation binding of humic acids: Geoderma, v. 5, p. 53-67.

Vasconcelos, P.M., 1987, Gold geochemistry in a semiarid weathering environment--A case study of the Fazenda Brasileiro deposit, Bahia, Brazil: unpublished M.A. thesis, Austin, University of Texas, 254 p.

Vinogradov, A.P., 1959, The geochemistry of rare and dispersed chemical elements in soils [2d ed., revised]: New York, Consultants Bureau, Inc., 209 p.

Warren, H.V., 1982, The significance of a discovery of gold crystals on overburden, *in* Levinson, A.A., ed., Precious metals in the Northern Cordillera: The Association of Exploration Geochemists, p. 45-51.

Watterson, J.R., Nishi, J.M., and Botinelly, T., 1985, Evidence that gold can nucleate on bacterial spores, *in* Bartsch-Winkler, S., and Reed, K.M., eds., The United States Geological Survey in Alaska: Accomplishments during 1983: U.S. Geological Survey Open-File Report 82-1004, p. 25-26.

Watterson, J.R., 1985, Crystalline gold in the soil and the problem of supergene nugget formation--Freezing and exclusion as genetic mechanisms: Precambrian Res., v. 30, p. 321-335.

Weber, F.R., Smith, T.E., Hall, M.H., and Forbes, R.B., 1985, Geologic guide to the Fairbanks-Livengood area, east-central Alaska: Anchorage, Alaska Geological Society, 44 p.

Webster, J.G., 1986, The solubility of gold and silver in the system Au-Ag-S-02-H_20 at 25 °C and 1 atm: Geochim. et Cosmochim. Acta, v. 50, p. 1837-1845.

Wilson, A.F., 1984, Origin of quartz free nuggets and supergene gold found in laterites and soils--A review and some new observations: Australian Journal of Earth Sciences, v. 31, p. 303-316.