

Microbial Processes in Gold Migration and Deposition: Modern Analogues to Ancient Deposits

David Mossman, Thomas Reimer and Hans Durstling

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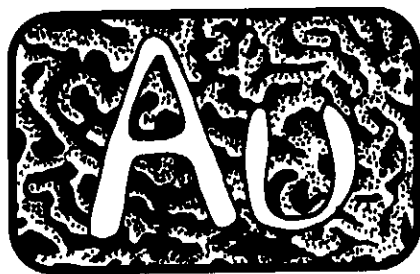
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Article abstract

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Microbial Processes in Gold Migration and Deposition: Modern Analogues to Ancient Deposits

David J. Mossman
 Department of Physics, Engineering
 and Geoscience
 Mount Allison University
 67 York Street
 Sackville, New Brunswick E4L 1E6
 dmossman@mta.ca

Thomas Reimer
 43 Bernhard-May Strasse
 D- 65203 Wiesbaden
 Germany

Hans Durstling
 62 High Street
 Moncton, New Brunswick E1C6B3

SUMMARY

Results of selected experimental work on the biomineralization of gold are reviewed against the background of historical accounts. The intrinsic ability of certain plants, and of micro-organisms in particular, to bind metals, functions in diverse ways to dissolve, immobilize, transport, or precipitate gold under a wide range of geological conditions. In exceptional cases, ore deposits may be formed, examples of which may be the phenomenal concentrations of gold in the Witwatersrand paleoplacers of South Africa. These deposits originated on early Earth under atmospheric conditions which may have promoted microbial activity in a continental setting more efficiently and on a larger scale than at present. A complication is that bacterioform gold in mineral deposits may be imitated in every detail by inorganic processes. However, there is now compelling evidence that micro-organisms play key roles in influencing

the geochemical behaviour of gold, and effecting its precipitation. This is provided by the results of laboratory experiments designed to simulate natural occurrences of gold, and to examine the metal absorption, gold-binding affinities and properties of specific microbes.

RÉSUMÉ

Le présent article passe en revue les résultats de certaines expériences dans le domaine de la bio-minéralisation aurifère et considère leur applicabilité aux vues des données historiques de gisements connus. La capacité de certaines plantes et de certains microorganismes en particulier, de mobiliser des ions métalliques peut expliquer la dissolution, l'immobilisation, le transport ou la précipitation de l'or sous une grande diversité de paramètres géologiques. Et, dans certaines conditions particulières, des gisements minéraux peuvent ainsi se constituer; l'extraordinaire concentration d'or du gisement de Witwatersrand en Afrique du Sud pourrait bien en être un exemple. Ces gisements se sont constitués au début de l'histoire de la Terre, dans des conditions atmosphériques qui pourraient avoir favorisé une activité microbienne continentale plus efficace et sur une plus grande échelle que dans les conditions actuelles. Cependant, les formes bactériogéniques aurifères peuvent être imitées dans leurs caractères les plus fins par sa contrepartie inorganique ce qui en complique d'autant l'identification. Il demeure cependant qu'on a maintenant des indications convaincantes de l'importance clé du rôle des microorganismes sur la précipitation et le comportement géochimique de l'or. Ces indications nous viennent de résultats d'expérience en laboratoires visant à simuler les formes naturelles des minéralisations aurifères et à étudier les phénomènes de l'absorption des métaux, les affinités de l'or et les caractéristiques de microbes particuliers.

INTRODUCTION

Microbes pervade the natural environment and play a major role in geochemical recycling of chemical elements. The ability of microbes to bind metals is an integral characteristic of their metabolism, and with their enormous surface area to volume ratio, they exhibit highly efficient sorption properties (Ferris, 1995; Ehrlich, 1996; 1998). Beveridge *et al.* (1992) may even have understated

the case when they wrote that "The bacterial cell surface can be visualized as a bristling forest of molecules that protrude into the environment and provides a large surface area for interaction with the metal ions in which the cell is constantly being bathed." Remarkable agents of biomineralization, these micro-organisms work either passively to bring about nucleation and growth of crystals upon individual cells, or actively precipitate minerals as a result of metabolic activity. These are the two main processes of biomineralization that are recognized (Lowenstam and Weiner, 1989; Ferris, 1995).

The first (passive) biomineralization process is mediated by the matrix or external organic framework of an organism, an example being the calcium carbonate secreted by corals. The second (active) process, biologically induced mineralization, is exemplified by the results of metabolic activity through which a metal becomes concentrated within the tissue of an organism. More subtly, biomineralization effects a similar result on the minute scale of algal and micro-bacterial growth (Ehrlich, 1990; 1996). Altogether, these biomineralization processes exert a profound impact on the mineral world by catalyzing or controlling key stages in mineral dissolution or precipitation up to, and including, ore deposit scale (Savvichev *et al.*, 1986; Mann *et al.*, 1986; Dyer *et al.*, 1994; Ferris, 1995; Neelson, 1997).

In addition to calcium carbonate and silica, the most notable constituents thus affected are phosphorus, iron, manganese, and to a lesser extent copper (Korobushkina *et al.*, 1976; Beveridge *et al.*, 1983; Savvichev *et al.*, 1986; Lowenstam and Weiner, 1989). Gold too, is affected, but because of its rarity in most geological environments, it is quantitatively far less significant in biochemistry, and does not always feature in high-profile reviews of geomicrobiology (*e.g.*, Banfield and Neelson, 1997).

In the case of gold, the role of micro-organisms appears to go far beyond active biomineralization *sensu stricto*. In a qualitative sense there is a great deal of evidence suggesting that microbial activity influences the geochemical behaviour of gold. On an experimental scale there is compelling evidence of biomineralization of gold (Brooks *et al.*, 1995; Fortin *et al.*, 1997). Here, following a brief historical perspective, we

examine mechanisms of biomineralization and review the possible impact of microbial activity on mobilization and concentration of gold.

BACKGROUND

Early Accounts

Traditionally, experts otherwise well-versed in experimentation, maintained that gold was so noble as to be virtually insoluble. Stories of attempts to turn other substances into gold probably originated from misunderstandings of smelting processes. Alchemists appreciated the noble nature of gold (Yardley, 1991). Popular wisdom has long held otherwise, however. Thus, ancient Arabic manuscripts describe gold as "growing like a plant" (Ibn QI-Fakih, 903; Al'Oumari, 1342). Unfortunately, old stories and translations of early sources, themselves heavily influenced by hearsay and old beliefs, with few exceptions are suspect. Gold in roots, "vegetable gold" (Boyle, 1987), sprigs and dendrites of gold, gold as fruit, gold-forming plants, all are phrases that could stem from translations dealing with alluvial gold. Nevertheless, as Boyle (1987) pointed out, enrichment of gold in the A soil horizon beneath trees, as observed by medievalists, has been confirmed by modern analysis. For a comprehensive account of the earliest literature on gold, the reader is referred to Boyle (1979, 1987).

Gold in Plants

Plants too, such as those of the carrot family (*Umbelliferae*), which contain appreciable amounts of thiocyanates, are well known for their ability to complex gold (Edwards *et al.*, 1995). Also, although the notion of gold growing like a plant might be suggested by the occurrence of dendritic gold, Arabic records are quite clear as to the type of plant (*nadjil*), the season of growth and even the particular parts of the plant with which gold was thought to be associated. According to Al'Oumari (1349), harvesting of gold-bearing plants took place in the spring after the rains came to the Egyptian desert. The Saharan plant *Typha elephantina* is almost certainly the "*nadjil*" or "*Aghrastus*" referred to by Al'Oumari (1349). *Typha* is a monocotyledon, certain portions of the roots of which are traditionally an important source of food for North African nomads (Foucauld, 1951). There is also apparently a second species which oc-

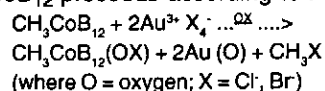
curs in humid areas, as along the edge of the bed of the Nile, where according to Al'Oumari (1349) "...là, on creuse des trous et on recueille des racines d'or ressemblant à des pierres ou à du gravier" (...there, one digs holes and collects roots covered with gold).

Provided that the appropriate concentrations of gold are available, *Typha* might very well concentrate the metal in its roots (Boyle, 1979). J.P. Franc (unpublished) speculated that the young roots of *Typha* secrete a sugary, viscous substance and that this possibly causes fine-grained particles of gold to agglutinate on the roots and/or otherwise result in the dissolution and incorporation of gold into the roots themselves. According to Dunn (1995), natural Au concentrations of more than 100 to 200 ng/gm dry weight in plants are rare, although surprisingly, even assays applied to plant tissues are subject to the nugget effect. However, Anderson *et al.* (1998) described experiments in which various plants, grown on soils treated with ammonium thiocyanate as a chelating agent, absorb gold in economically attractive amounts.

Mobility of Gold

In recent years the scientific community has been increasingly persuaded to view as plausible, the concept that gold and noble metals in general, are far more mobile at Earth's surface than hitherto appreciated. A host of geochemical conditions and reactions are now recognized as capable of dissolving/transporting/precipitating gold in natural waters at Earth's surface under present geological conditions. Recent reviews of these phenomena are included in Mossman and Dyer (1985) and Greffié *et al.* (1996). An intermediary process between strictly geochemical fixation of gold, and biomineralization, deserves special mention for its efficacy. This concerns the ability of certain heavy metals such as mercury and palladium to form organometallic complexes *via* methylation (Rapsomanikis and Weber, 1986), a process mediated in all cases by methyl cobalamin, a methylated derivative of B₁₂ which itself contains Co (Alloway, 1995). This is a microbiology-related process of potential significance in the transport of gold. Methylation takes place by either aerobic or anaerobic species of bacteria (or fungi), although it occurs more readily in anaerobic sediments of aquat-

ic environments. The rate at which the reaction proceeds depends on the ambient conditions including pH, temperature, and Eh. Abiologic methylation can also occur (Fergusson, 1990). A redox mechanism also exists for gold. According to Rapsomanikis and Weber (1986) the reaction of Au³⁺ with CH₃CoB₁₂ proceeds according to :



Organometallic complexes thus formed, readily undergo transport at the low temperatures and pressures encountered at Earth's surface. Methanogenic complexation thus may be said to only indirectly involve the role of living organisms to supply, *via* respiration, the required methane. Nevertheless, methanogenic complexation illustrates one of the many processes available in nature, abiological and biological, that impact on gold solubility and generally effect the concentration of certain metals, including the noble metals in aqueous solution.

Indirectly, micro-organisms can also work in favour of enhanced gold recovery. On an applied basis, bioleaching, an important new commercial gold-ore pretreatment, relies on the "low technology" of bacteria such as *Thiobacillus*, *Leptospirillum* and *Sulfolobus* to promote the dissolution of the sulfides in order to liberate gold and make it available for recovery. *Thiobacillus ferrooxidans*, for example, works by catalyzing oxidation of ferrous iron, below pH of about 3, up to a million times faster than in its absence (Ehrlich, 1996).

BIOMINERALIZATION OF GOLD

Biochemical Evidence

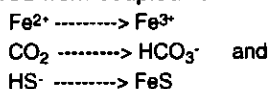
Although the simplest of all living things, bacteria are the most adaptable and environmentally versatile. In addition to photosynthesis and other methods used by multicellular organisms (eukaryotes) to obtain energy, bacteria also use methods unique to themselves (see Table 1), depending on their carbon source, energy source and electron acceptor needs.

If one accepts that various micro-organisms manage to concentrate gold, the question is not only how but why they should do so. The first part of this question can be answered somewhat more objectively than the second. Certainly it does not follow that satisfaction of particular trace element require-

ments explains why some micro-organisms concentrate gold. As shown in Table 2 numerous organic processes may be involved in gold transportation and deposition.

Micro-organisms on early Earth may not have been so highly evolved as those living today. Among prokaryotic (single-celled) communities, enzymatic functions may have since changed with little if any accompanying change in the morphology of the organism. Microbes, particularly bacteria, control mineral formation and dissolution in order to gain energy for respiration under re-

stricted oxygenation. Thus in anaerobic respiration any one of Fe^{3+} , Mn^{2+} , nitrate, sulphate or CO_2 may serve as an electron acceptor in lieu of the O_2 required by more complex organisms. The energy sources for most microbes (Ehrlich, 1996; Skinner, 1997) are derived from coupled reactions such as:



The energy obtained from these reactions facilitates construction of the biomolecules needed for all organelles and cell walls. As such, microbes are

opportunists that exploit situations where competing microbes are at a disadvantage (Ehrlich, 1996).

Bacteria might be expected to reflect the mineral content of their environment in terms of nutrient requirements and their resistance to toxic metals. Sorption is attributed to carboxyl-phosphoryl groups in the bacteria's surface fabric (Beveridge *et al.*, 1992). Hence the composition of the resulting fine-grained minerals which nucleate upon the cells will depend on the anions and cations supplied in the solution. A good example is the accumulation to over 10% dry weight of cell-bound uranium on brewer's yeast recorded by Strandberg *et al.* (1981). Beginning as amorphous precipitates, these grow and gradually crystallize.

Certain minerals may be precipitated through enzyme-catalyzed microbial redox reactions (Beveridge *et al.*, 1983; Ferris *et al.*, 1986; *cf.* Silver, 1997; Beveridge *et al.*, 1997). Enzymes are proteins which catalyze chemical reactions and promote cellular metabolism. Gold could possibly play an essential role in an enzyme, much like the Co in the vitamin B_{12} co-enzyme. No such enzyme has yet been observed, however, and even if it did exist, it might not suffice to account for the extreme concentrations found on, or in, micro-organisms. Alternatively, Au may be co-precipitated with a second element like Ag, which the micro-organism eliminates as a cell poison by precipitating it upon the cell membrane or elsewhere in the cell. This type of reaction is well known, for example, where Fe^{3+} -reducing bacteria generate Fe^{2+} enzymatically, which in turn reduces Cr^{6+} to Cr^{3+} non-enzymatically (Ehrlich, 1996). Perhaps iron, as an essential ingredient of bacterial metabolism (Lewin, 1984), plays the role of the "big brother" element here, in competition with gold. Alternatively gold, although usually not encountered in potentially harmful concentrations in modern geochemical environments, could have been such a cell poison for earlier forms of microbes which the organism needed to eliminate.

Additional Experimental Evidence

Experiments conducted by Dyer *et al.* (1994) revealed that the marine cyanobacterium *Plectonema terebrans* absorbs gold from an experimental medium ["artificial ocean" of Carolina Biological Supply Company], supplement-

Table 1 Summary description of bacteriochemical processes mentioned in the text.

Chemolithotrophs (chemosynthetic autotrophs): *e.g.*, *Thiobacillus ferrooxidans*
 • use oxidizable inorganic compounds such as H_2 , H_2S , as source of energy and reducing power, while inorganic carbon (*e.g.*, CO_2 , CO_3^{2-} , HCO_3^-) is converted to organic compounds. Some (facultative) chemolithotrophs may use organic carbon as their sole source of energy.

Photolithotrophs (photosynthetic autotrophs) *e.g.*, sulfur bacteria (*B. Subtilis*) and some cyanobacteria

• using hydrogen atoms as electron donors, these bacteria incorporate CO_2 into organic compounds and convert visible light into chemical energy using chlorophyll and other pigments. The process is always anaerobic; photolithotrophs are obligatory photosynthesizers.

Mixotrophs: these bacteria obtain their carbon from organic compounds and part or all of their energy from oxidizing inorganic compounds. Most are aerobic although *Desulfovibrio desulfuricans* is anaerobic.

Anaerobically respiring heterotrophs: use organic compounds as carbon and energy source, but instead of oxygen they use inorganic compounds as electron acceptors. Most are facultative organisms; only those reducing CO_2 and SO_4^{2-} are obligatory anaerobes.

Table 2 Selected organic processes involved in gold concentration.

1. Absorption of gold by various plants
2. Methylation mediated by methyl cobalamin
3. "Low tech" bacteria (*T. ferrooxidans*) promote liberation of gold through sulphide dissolution
4. Precipitation of gold by enzyme-catalyzed microbial redox reactions
5. Absorption and binding of gold by living cyanobacteria (*e.g.*, *P. terebrans*; *C. vulgaris*)
6. Sequestering of gold (*e.g.*, *S. natans*) by enzymes and proteins to bind and/or form complexes.
7. Immobilizing gold as intracellular colloids (*B. subtilis*) and subsequent diagenetic transformation into octahedral gold.
8. Transport of gold as fine-grained colloids by humic, fulvic and amino acids.
9. Role of organic matter in the biochemical cycling of gold.
10. Complexing of gold by chlorides, thiocyanates, thiosulfides and organic acids.
11. Anaerobic weathering of auriferous source rock in presence of sulfur-cycling microbial communities.
12. Precipitation and flocculation of gold by microbial mat communities.

ed with $\text{AuCl}_3 \cdot \text{H}_2\text{O}$ to yield a concentration of $2 \text{ mg} \cdot \text{L}^{-1}$. In this instance, ionic species in solution will have included AuCl_4^- , AuCl_2^- and AuO_2^- , the most stable forms of gold in seawater (Korobushkina *et al.*, 1983). Among microorganisms, *P. terebrans* thus increases the list of known gold absorbers, namely eukaryotic algae (*Chlorella*), fungi and heterotrophic bacteria (Darnall *et al.*, 1986; Karamushka *et al.*, 1989).

In the above experiments (see Fig. 1) gold uptake occurred in the glycolyces (sheaths) of the organism, and possibly within the cells themselves. It is important to note, however, that according to Hosea *et al.* (1986) at least three different classes of sites are available for binding of gold on the algal (*Chlorella vulgaris*) cell. Elsewhere, documented fossil indicators such as gold-replaced setae, gold-plated pedomicrobia and glycolyces of cyanobacteria (Watkins *et al.*, 1987; Dyer *et al.*, 1988) point to bacterioform gold as a reality. The efficacy of the process of biomineralization is such that percentage amounts of gold have been known to be absorbed by living cyanobacteria (Mossman and Dyer, 1985; Watkins *et al.*, 1987). Absorption of gold by various non-living biomass types, such as *Chlorella* (Hosea *et al.*, 1986; Watkins *et al.*, 1987) is likewise reported to be very efficient. Another example is *Sargassum natans* (Kuyucak and Volesky, 1989a) in which sequestering of elemental gold is accomplished by interaction of enzymes and proteins with Au^+ , reducing it to Au^0 or at least effectively binding it, and/or forming complexes. In this process molecular groups containing P and S will promote ligand exchange and substitution reactions. Evidently the cell walls of the biosorbant in this instance were the major focus for gold concentration, with the carbonyl groups ($\text{C}=\text{O}$) functional in binding the metal (Kuyucak and Volesky, 1989b).

Octahedral Gold and Nugget Formation

Bacterial processes have long been suspected of promoting nugget development in placer processes (*cf.* Waterson, 1992). Laboratory simulation of these processes using *Bacillus subtilis* under acid conditions efficiently immobilized ionic gold (Au^{3+}) as fine-grained intracellular colloids. The exact mechanism whereby the gold was precipitated in cytoplasm inside the bacterial cell

envelope is not known (Southam and Beveridge, 1994). However, the result is exactly like the transport of Au as fine-grained colloids by humic acids, fulvic acids and amino acids in the natural environment reported, respectively, by Bergeron and Harrison (1989), Bowell *et al.* (1993) and Mineyev (1976). Following up on the experimental results of their "acid prediagenesis reaction system," Southam and Beveridge (1994) observed, over several months at atmospheric pressure and 60°C , the transformation of elemental colloidal gold into octahedral gold. During this experimental low-temperature diagenesis, the formation of gold coincided with bacterial autolysis (autolytic breakdown of bacterial macromolecules under acid conditions), indicating that bacteria play an essential role in transforming the colloidal gold into crystalline gold. The procedure is viewed as analogous to the occurrence of (secondary) octahedral gold particles as widely reported in various gold deposits that have undergone relatively low grade metamorphism (Southam and Beveridge, 1994).

In a subsequent study Southam and Beveridge (1996) discovered that S and P play important roles in octahedral gold formation. Specifically, S-containing organics are involved in solubilization and

precipitation of the gold, whereas P is contributed to the organics by *Bacillus subtilis*, with PO_4^{3-} furnishing highly reactive oxygen atoms to complex with Au in the diagenetic model. Another very important development is the discovery by Southam (1998) of S and P within the octahedral gold grains on the periphery of nuggets of Yukon placer gold. This strongly suggests a significant role for organic matter in the biochemical cycling of gold. As possible natural analogues of this process one can look to occurrences of octahedral gold in, for example, weathered Precambrian meta-sediments in western Australia (Wilson, 1984); the Witwatersrand paleoplacers (Frimmel *et al.*, 1993), and the alluvial and sapropelic deposits of Serra Pelada, Brazil (New York Times, 1996; Meiveles and da Silva, 1988). A prime candidate as a geologically recent analogue is the discovery of submicroscopic dendritic gold associated with living microbacteria (personal communication, Dr. Moshe Shirav, Geological Survey of Israel; see Fig. 2) in a shallow auriferous deposit in southern Israel (Bogoch *et al.*, 1994).

Biosorbents

Certain micro-organisms can act as biosorbents to concentrate metal without cellular metabolism. Examples in-

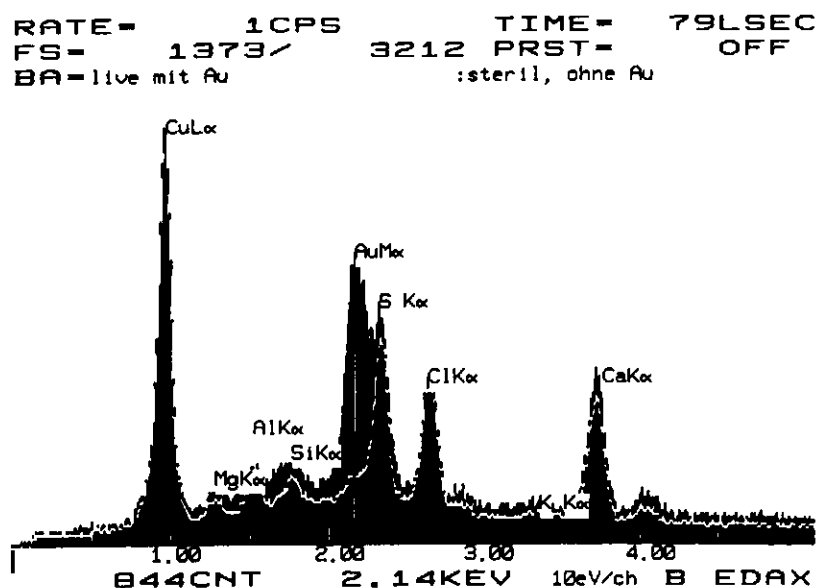


Figure 1 Energy dispersive X-ray microanalysis, at 2.14 KEV, of elements in the glycolyx of a filament of *Plectorema terebrans*. The solid curve filled in black shows results of analysis of live cultures incubated in gold solution; notice the peak for gold. The superimposed white curve shows results from heat-killed cultures in gold solution. The two curves are similar except for the absence of gold in the heat-killed microorganisms. The analysis was made at a rate of 1 count per second for 79 seconds. (From Dyer *et al.*, 1994, with permission)

clude *Saccharomyces cerevisiae* and *Pseudomonas aeruginosa* in which, under experimental conditions, concentration of uranium occurs to the extent of more than 10% of the original dry weight in a matter of minutes, extracellularly and intracellularly (Strandberg *et al.*, 1981). Biosorption probably occurs in *S. cerevisiae* by complexation of cations with negatively charged reactive sites on the surface of the cells or in extracellular polymers; however the mechanism whereby uranium is taken up so rapidly by *P. aeruginosa* is not

well understood. Together these examples suggest that a range of biosorption mechanisms by micro-organisms exists for uranium (Strandberg *et al.*, 1981). For gold, however, no such biosorbent mechanism is known.

Morphology of the Gold

In the past one of the most convincing arguments for biomineralization of gold has been the shape assumed by the metal. In the case of microbially produced gold, the shape might well be expected to be bacterioform; indeed,

much of the Witwatersrand gold appears to be bacterioform (Hallbauer and van Warmelo, 1974), an interpretation that has not gone unchallenged (*e.g.*, Schidlowski, 1981). Could the shape/form be an artifact of nature? This whole problem of correctly identifying the morphology of "organic" material as organic or inorganic has been focussed recently by the controversy over the origin of microbial-like remains in a Martian meteorite (McKay *et al.*, 1996). In the case of microbial-like gold morphologies the problem is illustrated elegantly by Watterson's (1992, 1994) studies of the lace-like networks of micrometer-sized filamentous gold present in Alaskan gold placers. At first interpreted as the result of Pedomicrobium-like budding bacteria (Watterson, 1992), it turned out that these forms can be imitated by inorganic processes. One such process (Watterson, 1994) involves exposure of fine-grained gold to mercury with the concomitant production of micrometer scale lace-like gold amalgam (see Fig. 3). In Watterson's words "...morphology alone can no longer be considered adequate evidence of microbial involvement..." (Watterson, 1994). This is an important conclusion because it indicates the most rewarding direction for future research: to establish experimentally the conditions favourable for biomineralization, thus facilitating identification of natural analogues.



Figure 2 Workers from the Israeli Geological Survey examine MAZ gold prospect in southern Israel on the occasion of the 18th International Geochemical Exploration Symposium, May, 1997. Large diameter drill hole is capped with a wooden plug (just right of center of photograph), the base of which holds SEM mounts upon which bacteria, living downhole, have accumulated. (Photograph by D. Mossman)

The Witwatersrand:

A Case for Biomineralization?

One of the economically most important issues concerning biomineralization

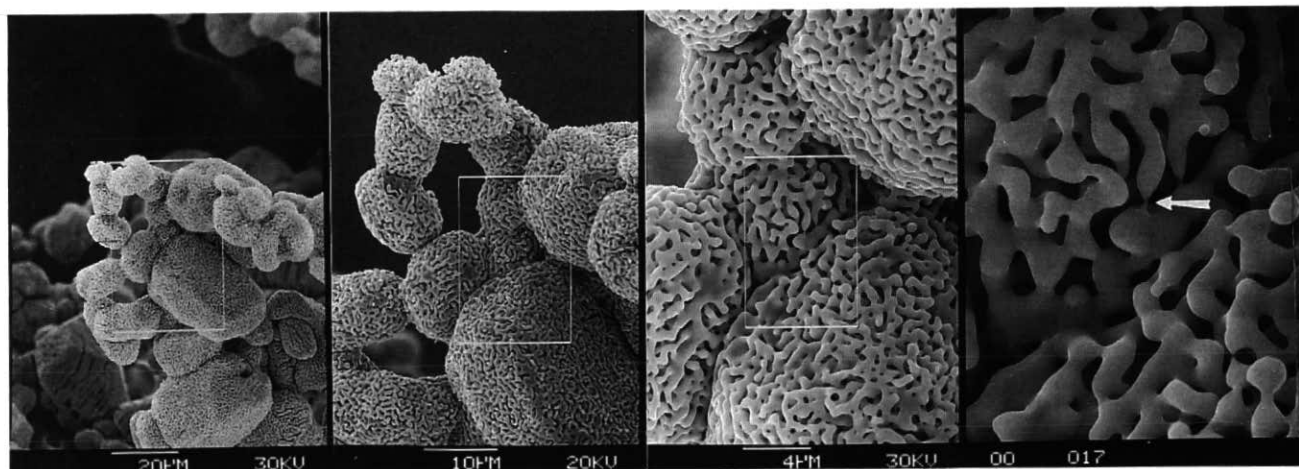


Figure 3 (a, b, c, and d, at increasing levels of magnification) Structure produced in strip of rough manufactured gold foil following amalgamation with mercury and treatment with 16N HNO₃ at 200°C for 2 hours. Scale bars indicate magnifications. Filiform structure is indistinguishable from structures previously thought to be based on budding bacteria. Hypha-like connection shown by white arrow. (Courtesy of Dr. J.R. Watterson)

of gold is its potential involvement in the genesis of ore deposits. An important case is the origin of the gigantic late Archean Witwatersrand goldfields of South Africa. According to The Gold Institute (written communication, August, 1998) 133,000 metric tonnes of gold have been produced from all sources since the dawn of civilization. Of this total, some 45,400 mt (ca. 34%) have been extracted from Witwatersrand conglomerates. The origin of gold in these quartz-pebble-conglomerates continues to be controversial (Reimer and Mossman, 1990; Frimmel *et al.*, 1993; Phillips and Law, 1994; Robb and Meyer, 1995; Reimold, 1995). As in most ore deposits, probably no single process is exclusively responsible for the present appearance of the gold in the conglomerates (Hallbauer, 1986; Robb *et al.*, 1997). Certainly, placer deposition of particulate gold (for example, see Fig. 4) upon ancient erosional surfaces will have played a prominent role (Frimmel, 1997). Late enrichment and redistribution processes too, resulting from hydrothermal and/or metamorphic fluids (Robb *et al.*, 1997; Drennan *et al.*, 1997) will have modified the conglomerates to varying degrees. The question of where this huge amount of gold came from has so far received little attention.

The Grain Size Problem

Reimer (1984) compiled data on grain fineness, shape, and size in the region of the Witwatersrand deposits. These data suggest that the gold deposits of the Archean schist belts of the Kaapvaal Craton are unlikely to have been the source of the particulate gold in the Witwatersrand deposits. In particular the specific gold yield of the Witwatersrand Basin to date, at a rate of about 1.16 mt·km⁻² is about two orders of magnitude greater (Reimer, 1984) than that of the "richest" Archean granite/greenstone craton, *viz.*, that of Zimbabwe in the eastern part of Africa. It is therefore not warranted to assume that the particulate Witwatersrand gold, with a median grain size of 40-120µm, was derived directly from the erosion of gold deposits in greenstone belts, or in granite/greenstone terranes where the median diameter of constituent gold grains is usually < 20µm (Reimer, (1984). Indeed, it has been commonly observed that gold in old placers is far larger than that of potential source rocks (*e.g.*,

Freise, 1931; Leube, 1968; Wilson, 1984; Watterson, 1992). The same argument holds concerning the proposal for gold sourced from low-grade concentrations in granitoids flanking the Witwatersrand basin. Weathering and subsequent mechanical transport therefore appear to be of only very minor importance. Consequently we must look for a process which would be able to yield, from weathering areas, sufficient gold particles large enough to be affected by normal placer processes.

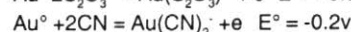
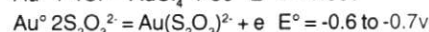
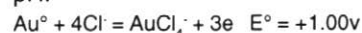
Processes of Transport and Deposition

Some of the processes that set the stage for the formation of certain prolifically rich gold deposits are outlined below (see also Fig. 5). They illustrate several of the complex processes of biomineralization in nature, but which in the primitive atmospheric conditions on early Earth might have been promoted more efficiently and/or on a larger scale than at present.

By late Archean time a wide range of prokaryotes living in diverse, complex communities were affecting conditions in localized areas such as microbial mats and stromatolites on Earth's surface, and to some extent also in the lower atmosphere (Cloud, 1983). Un-

like modern Earth, where very few environments are prokaryote-dominated, during the depositional interval in the Witwatersrand Basin between about 3074Ma and 2714Ma (Poujol *et al.*, 1998), the hydrosphere and Earth's surface were probably exclusively populated by prokaryotes. These communities in turn will have exercised important controls on the dissolution and precipitation of minerals.

Many abiological geochemical processes too are available for effecting dissolution and redeposition of gold, among them complexing with chloride, thiosulphide and cyanide ions (Cloke and Kelly, 1964). According to the following equations, these form complexes with gold that are stable under geological conditions of relatively high Eh and pH.



Of the above three processes of dissolution, the first two are perhaps the most geochemically feasible under reducing conditions (Ling Ong and Swanson, 1969; Boyle, 1979; Mossman and Harron, 1983). For example, with chloride complexing, enhanced build-up of Au in the aqueous phase may result. This result is favoured if the above com-

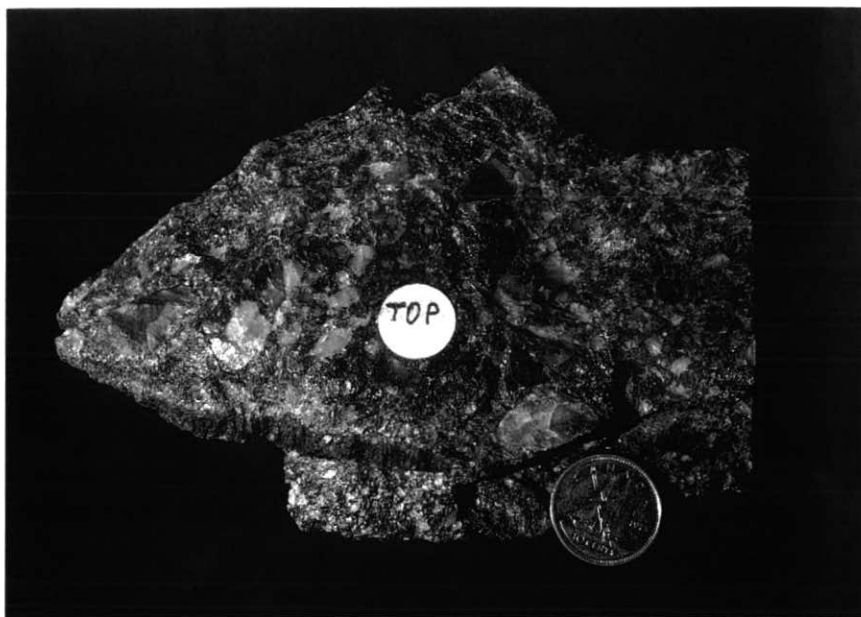


Figure 4 Photograph shows hand specimen of gold ore in quartz-pebble conglomerate from the Blyvooruitzicht mine, Carletonville, Transvaal, South Africa. "Top" indicates stratigraphic top. Gold is concentrated in percentage amounts near the base of the specimen in the dark thin carbonaceous band, which is believed to be the remnants of algal matter. Microfossil-like filamentous structures extracted from such carbonaceous material are indistinguishable from that shown in Figure 6. (Photograph by D. Mossman)

plexes are bound by organic acids (Ling Ong and Swanson, 1969). Cyanides and thiocyanates are prime movers in the above process. They readily complex gold under anaerobic conditions, allowing transport of gold to relatively oxygenated environments favourable to precipitation and/or regrowth of gold. Cyanides are produced by the hydrolysis of cyanogenic glycosides, which abound in plant residues and soils. Today more than 1000 species of plants are known to produce cyanides, as do some arthropods and fungi (Edwards *et al.*, 1995). Organic acids reduce the auriferous solution to stable negatively charged colloids of metallic gold by coating the colloidal particles with hydrophilic organic molecules, yielding "armoured colloids."

Transportation and deposition of gold is here not so much dependent upon high Eh. Thus all that would be required to trigger precipitation of the armoured colloids is a change in chemical environment, say from alkaline to relatively acidic conditions (*cf.* Reimer, 1984). The situation is somewhat reminiscent of the *ouro preto* (black gold) of Brazil, as mentioned earlier (*cf.* Friese, 1931). Note too, that this is a good example of the type of mechanism whereby the size increase from Archean schist belt gold

to the notably larger detrital Witwatersrand gold could have been achieved (Reimer, 1984). Grain size increase of gold evidently does not require millions of years, judging from examples like *ouro preto*. Leube (1968) has confirmed that placer heaps in the tropics have been repeatedly reworked after 15- to 25-year intervals. Northern hemisphere examples include central Germany where Kulick *et al.* (1997) reported the reworking in earlier times of mine dumps in the Rhenish Slate Belt every 4-7 years.

Origin of the Witwatersrand Deposits: A Model

Mossman and Dyer (1985) favoured biological mechanisms over abiological processes to effect the dissolution, transportation and precipitation of gold during Witwatersrand times. Details of their model are summarized as follows: weathering of Archean source rock proceeded under anaerobic conditions in the presence of sulphur-cycling microbial communities. These micro-organisms helped to establish unique geochemical conditions. Anaerobic photosynthesizers would have used H₂S as a proton donor in CO₂ fixation, releasing sulphate as an end-product. Anaerobic Desulphovibrio-type bacteria con-

verted the sulphates back to H₂S. In this manner prokaryotes were able, by means of the sulphur-cycle intermediates (such as thiosulphate or elemental sulphur), to dissolve large quantities of gold from source rocks. Transport of gold occurred in river water in solution and/or as colloids stabilized by humic acids, or by sulphur-cycle intermediates. Subsequent deposition took place in a paralic setting as a result of oxygen produced in localized environments within microbial communities. Grain size increase of gold thereby could have been actively promoted by microbial activity. As shown by Southam and Beveridge (1996), under experimentally designed "diagenetic conditions," microbes readily transform colloidal gold into pseudocrystalline gold particles and subsequently into crystalline octahedral gold. In consequence, particle size is increased by roughly three orders of magnitude (Southam and Beveridge, 1996).

The results of Southam and Beveridge's (1994, 1996) experiments clearly indicate the very important role of prokaryotes in the genesis of placer gold deposits. With respect to biomineralization, this is a case of precipitation of gold being biologically induced. The example is directly analogous to modern microbial mat communities, which can precipitate and flocculate gold (*cf.* Grosovsky, 1983). Micro-organisms may thus account for a substantial portion of the syngenetic gold in Earth's greatest repository of gold, the Witwatersrand.

Carbonaceous substances (including solidified bitumen) occur in the Witwatersrand (Willingham *et al.*, 1985; Mossman, 1987; Parnell, 1996), and are intimately associated with much of the gold. A wealth of features, reviewed by Dyer *et al.* (1988), indicate the syngenetic nature of a substantial portion of the Witwatersrand carbonaceous substances, constituting indirect evidence of the activities of ancient microbial communities. Direct evidence is in the form of microfossil-like structures, hollow cylindrical sheaths, filamentous structures and spheroidal unicellular forms (Dyer *et al.*, 1988). The last-mentioned structures range from 1-3µm and show unimodal size grouping compatible with features documented elsewhere as characteristic of cyanobacteria (Dyer *et al.*, 1988). Dyer *et al.*'s (1994) illustrations (see Fig. 1) show that gold can be precipitated as a direct result of the activity of modern cyanobacteria; in

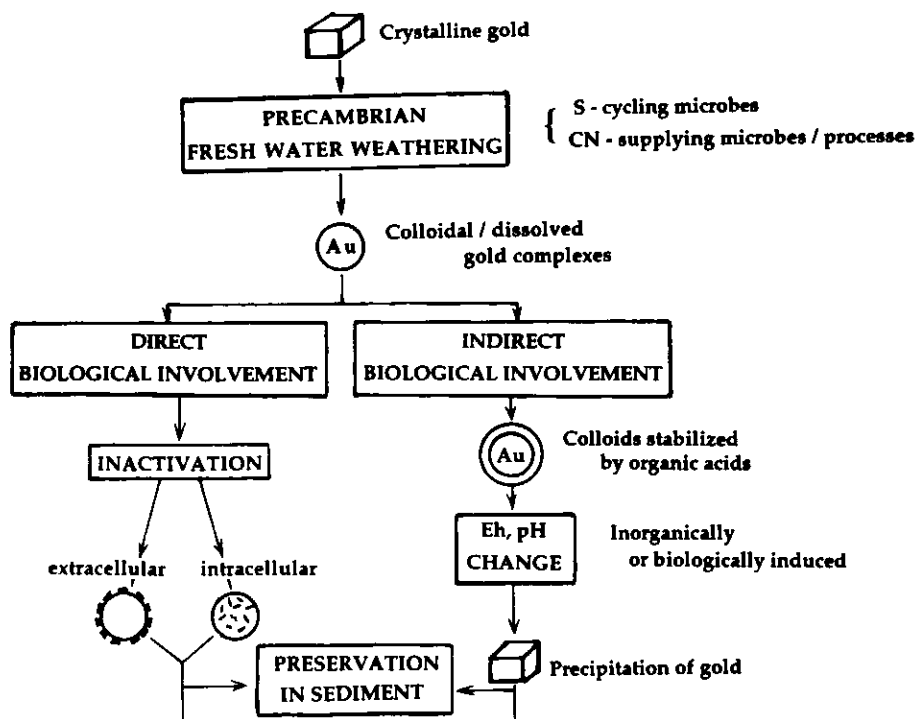


Figure 5 Generalized flow chart showing processes involved in transportation and precipitation of gold that operated on early Earth and which continue to do so at present.

this instance the end-product may be considered as analogous to that shown in Figure 6.

Witwatersrand: Why So Much Gold?

On a speculative note we now pose two related questions: 1) Why should such an enormous percentage of gold that has been mined on Earth be concentrated by what appear to be biological processes in the quartz-pebble conglomerates of the Witwatersrand? 2) Where are the modern analogues to microbial gold?

First, how can we account for the extreme enrichment of gold in the Witwatersrand paleoplacers? Could it be that the evolution of micro-organisms was a critically important process? Is it possible that by Witwatersrand time (ca. 3000 Ma) living organisms had gained access to subaerial weathering regimes (cf. Mossman and Harron, 1983) and presumably to potential source areas for gold? Is there a parallel in the metallogeny of gold to genesis of Precambrian banded iron formations? For iron, the appearance of obligatory photosynthesizing organisms first supplied the required oxygen levels for the sudden precipitation of vast amounts of sedimentary iron (Cloud, 1983). In the case of gold, precipitation might have been triggered by prokaryotic organisms moving inland across the daunting transition from saline environments to fresh water-dominated continental settings. Could isolated continents have become populated by micro-organisms at different times? Progressing inland during Witwatersrand time, micro-organisms may have encountered what for them were lethal amounts of gold. According



Figure 6 Characteristic microfossil-like filamentous structure of gold extracted from oxidized carbonaceous matter (kerogen) from the Carbon Reef Leader, Witwatersrand. Scale bar (lower right) = 2µm. (Photograph courtesy of Dr. D.K. Hallbauer, University of Pretoria)

to this scenario, neutralization of the gold as a microbial cell poison may well have triggered the initial burst of stratabound gold deposition.

Modern Analogues of Microbial Gold?

Realistically, modern environments in which aurophilic microbes can be anticipated include: certain hydrothermal, subaerial or submarine hot springs, and the natural weathering environments of auriferous deposits (cf. Bogoch *et al.*, 1994). In this respect, effluents from old mine workings, tailings dumps (eg., Schaefer, 1933), *etc.*, should also provide fertile fields for research. As a practical aid to geochemical exploration, *Bacillus cereus* shows promise as a pathfinder for gold in the subtropical soils of Argentina and Mexico (Dejonghe, 1997).

CONCLUSIONS

Living organisms are recognized increasingly as playing major roles in a host of important geological processes, among them those which determine the distribution of most elements in the lithosphere. The ability to bind metals is an integral characteristic of most micro-organisms. Thriving under diverse geochemical conditions and a tremendous variety of habitats, they are found wherever there is water, and at temperatures from -7°C to about 120°C (Ferris, 1995; Ehrlich, 1996). Indeed, there are strong indications that some micro-organisms thrive at even higher temperatures, and under otherwise extraordinarily hostile conditions.

Micro-organisms are remarkably efficient agents of biomineralization. There are few natural environments on earth where microbes do not exist. They promote mineral genesis in two ways: passive growth, and growth linked to metabolic activity. During metabolism and reproduction they generate and interact with minerals to an extent that, owing to their versatility and wide-ranging occurrence, appears to have resulted in the formation of various ore deposits, including gold, throughout geologic time. Under various experimental conditions widely encountered in nature, micro-organisms (especially bacteria) are able to: dissolve gold; stabilize it in colloidal condition for transport; and catalyze the formation of crystalline gold.

The phenomenal concentration of

gold in Witwatersrand paleoplacers may in large measure owe its origin to the advent of microbes into a continental environment where, on a large scale, in order to survive, they needed to first neutralize gold as a cell poison.

Evidence of microbial activity influencing the geochemical behaviour of gold has long been inferred for certain gold deposits (Friese, 1931; Petrovskaya, 1973; Boyle, 1987). However, in unequivocal placer deposits such as Klondike gold (as in the case of an unequivocal Martian meteorite) only suggestive evidence for the role of microbes seems likely to be forthcoming. This is due to the fact that the morphology of "bacterioform" gold can be imitated in every detail by inorganic processes. Nevertheless, the widespread occurrence in nature of specific gold-loving microbes attests to the reality of microbial gold deposition.

The results of experimental studies now provide compelling evidence for the active role of microbes in processes of gold migration and concentration, effectively gold biomineralization. Interaction between gold and microbes is either enzymatic, involving for example the direct role of bacteria, or non-enzymatic, in which a more passive binding or nucleation occurs on cell surfaces. Gold dissolution/precipitation may also occur through organic complexing using ligands. Evidence for these processes stems chiefly from geomicrobiological studies such as laboratory simulations of natural occurrences of gold, documentation of gold binding properties *etc.*, stressing detailed examination of individual activities/ reactions and the microbes responsible for them.

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