> Es thut kein Gang so gut
> Er hat einen eisernen Hut.
>
> There is no lode like that,
> Which has an iron hat.
> –Old German mining proverb

Chapter IV. Oxidation and secondary enrichment of gold deposits

General principles

Gold deposits, subjected to oxidation, may become enriched near the surface both as a result of chemical processes involving the migration of gold and by the removal of soluble gangue and sulphides. Where silver and lead occur in quantity in auriferous deposits in argentite, tetrahedrite, galena or other sulphides, there is also a parallel enrichment of these elements as a result of oxidation processes. In contrast to copper and silver, however, gold exhibits less tendency to be enriched in secondary sulphide zones in veins and other deposits.

The mobility, migration, concentration or dispersion of gold during the oxidation of gold deposits are strongly influenced by the following factors:

1. The type of deposit and its mineral composition. The nature of the gangue, types of sulphides and primary gold-bearing minerals are the main considerations. The first two control to a large degree the nature and presence of solubilizing and precipitating constituents in the oxidizing waters. They also control to a varying degree the various reactions between the solid components of the veins and the oxidizing waters.
2. Types of enclosing rocks, specifically their mineral and chemical composition. These have some control on the nature and presence of solubilizing and precipitating constituents in the oxidizing waters. They also control to a varying degree the various reactions between the oxidizing waters and the solid components in the wall rocks.
3. Degree of fracturing, crushing or shearing of the deposit and its enclosing rocks.
4. Climatic factors.
5. Position of the water table.
6. Organic agencies. Gold is soluble as certain organic compounds, or it may be complexed and rendered soluble by the products of these agencies, e.g., H_2S produced by bacteria that gives rise to $[AuS]^-$.

All these factors interact to produce a variety of complex chemical systems that are impossible to follow in detail here. The discussion will be restricted to some of the general features of oxidized gold deposits and to a relatively simple view of the chemical processes involved. Data on the oxidation of gold minerals and deposits may be found in the publications by Skey (1871), Weed (1901, 1902), Emmons, S.F. (1901), Rickard (1902), Lenher (1904, 1912, 1918), Stokes (1906), Brokaw (1910, 1913), Soper (1911), Palmer and Bastin (1913), Grout (1913), Emmons, W.H. (1917), Schneiderhöhn (1924), Freise (1931), Lindgren (1933), Fetzer (1934), MacKay (1944), Chukhrov (1947), Smirnov (1951), Al'bov (1952, 1960), Morris and Lovering (1952), Shcherbina (1956*b*), Kreiter *et al.* (1959), Sato (1960), Machairas (1967, 1970*a*), Radtke *et al.* (1972*a*), Perel'man (1972), Roslyakov *et al.* (1971*a*, 1972), Rusakova and Povarennyk (1973), Bezverkhnii and Baumshtein (1973), Nesterov *et al.* (1974*a,b*), Nikolaeva and Badalova (1974), Borodaevskaya and Rozhkov (1974), Petrovskaya (1974), Kolotov *et al.* (1975*b*), Pitul'ko (1976), Roslyakov (1976) and Nestorenko *et al.* (1976). Other references to the migration of gold in natural waters and soils and its presence in biological materials will be found in Chapter II. The present chapter should be read in conjunction with Chapter IV in the writer's monograph on silver (Boyle, 1968*b*).

In this chapter we shall deal mainly with the course of gold during oxidation processes. The fate of various elements associated with gold in its deposits during oxidation processes is given in the section on elemental associates of gold in Chapter III.

The principal hypogene gold-bearing minerals are native gold, aurostibite, fischesserite and the various tellurides, e.g., sylvanite. Auriferous pyrite, pyrrhotite and arsenopyrite should also be included because although they are not gold minerals *per se* they provide a large proportion of the gold in a number of districts.

There is only one supergene mineral of gold namely the native metal. In some auriferous lodes there is a suggestion that aurostibite and some of the tellurides may be of supergene origin, but the evidence is equivocal. Supergene native gold occurs in a great variety of forms ranging from irregular slugs, nuggets, platelets, dendrites, wires, sprigs, tufts, hairs, filaments, filligrees, spongy masses, mossy aggregates and foils to very finely divided metal commonly called paint or mustard gold. Much of the gold in the oxidized zones of auriferous deposits occurs in relatively discrete particles and aggregates perched on, attached to or coating the various products of oxidation or in some cases intimately intergrown with minerals such as secondary calcite, gypsum, sulphur, kaolinite and opal. In addition there is commonly much microscopic and submicroscopic gold in mineral aggregates such as limonite and wad. Some of this exists in discrete microcrystals and masses; the remainder is in an adsorbed or chemically combined form.

Native gold is relatively inert and in many of its deposits, especially those with a paucity of sulphides and sulphosalts, the mineral passes into the oxidized zones in essentially the same condition as it is present in the primary ore. Under other conditions it is dissolved or migrates in a variety of forms discussed in some detail subsequently.

The fate of gold during oxidation processes is greatly affected by the nature and size of the gold particles in the primary deposits. As noted in Chapter II and elsewhere in the text, the solubility of gold is much greater when the element is released in an ionic form from the lattices of pyrite, arsenopyrite, etc. or when the gold is released in a submicroscopic (colloidal) form from these host minerals. Much of this gold evidently migrates either in solution, as a colloid or in suspension. When the gold is present in particles greater than about 100 μ in diameter, its solubility is greatly restricted. Most of this gold migrates in a physical form as platelets, spangles or small nuggets. Gold in this form also tends to restrict the migration of ionic gold, since it forms readily available nuclei for precipitation of the dissolved gold. Al'bov (1952) has claimed that the size of the gold basically determines its behaviour in the zone of oxidation.

Oxidation of gold tellurides may yield soluble gold and silver or finely divided native gold (containing some silver) and tellurite or a variety of tellurites and tellurates. Native tellurium may also be of supergene origin in the oxidized zones of some auriferous telluride deposits, although it is often difficult to prove that this is in fact the case. In the zones of reduction of certain auriferous telluride deposits, however, there is little doubt that at least some of the native tellurium is supergene in origin. In some deposits tellurite and/or paratellurite is a product of the oxidation of sylvanite, calaverite, etc.

$$AuTe_2 + 2O_2 \rightarrow Au + 2TeO_2$$

In others, insoluble iron tellurites such as emmonsite, mackayite and blakeite are precipitated mainly by reaction of Fe^{3+} with the tellurous acid formed during the oxidation of the tellurides.

$$AuTe_2 + 2O_2 + 2H_2O \rightarrow Au + 2H_2TeO_3$$

In still other places, tellurates may be precipitated by reactions involving telluric acid formed by the oxidation of the tellurides under very high oxidation potentials.

$$AuTe_2 + 3O_2 + 6H_2O \rightarrow Au + 2H_6TeO_6$$

Relatively little is known about the oxidation of aurostibite, $AuSb_2$. My observations indicate that the common products of oxidation are spongy masses of gold and antimony ochres, probably the oxides cervantite, senarmontite and valentinite although they give no X-ray patterns. The oxidation reaction can be written empirically as:

$$2AuSb_2 + 3O_2 \rightarrow 2Au + 2Sb_2O_3$$

Presumably under certain conditions the gold may be liberated in a soluble form. Similarly the Sb (III) and Sb (V) oxides may be dissolved under alkaline conditions and may precipitate various antimonites and antimonates. The oxidation of gold-bearing tetrahedrite is somewhat similar to that for aurostibite.

The oxidation of the silver-gold selenide, fischesserite, probably yields native gold enriched in silver and various selenites and/or selenates depending on the magnitude of the oxidation potential.

The oxidation of auriferous pyrite, pyrrhotite and arsenopyrite yields various soluble iron and arsenic compounds and gold. The latter may be released in a soluble form or as finely divided, spongy or mustard gold.

The fate of primary gold and finely divided native gold released by the oxidation of auriferous pyrite, pyrrhotite, arsenopyrite, chalcopyrite, stibnite, various other sulphides and sulphosalts, tellurides, aurostibite and fischesserite is varied and depends on many factors operating in the oxidized zone. My observations show that much of the primary gold and finely divided gold released from sulphides is incorporated into the cementing minerals of the gossans where it is inextricably intermixed with limonite, wad and other mineral aggregates. Some of this gold also finds its way into the eluvium and ultimately into alluvial placers. The very finely divided gold (flour gold), however, may retain considerable mobility in the water and be moved downstream in the drainage system for great distances. Where the oxidation zones are highly porous and loose, much of the fine gold moves physically downward simply by gravity or in downward percolating waters. Finally, the gold may migrate in a variety of chemical forms under certain conditions. We do not know the actual chemical forms of gold in the oxidizing waters of gold deposits for no one has measured these directly. However, we can infer certain possible forms from the known chemistry of the element and from the chemistry of groundwaters and mine waters. Some of the mechanisms of chemical migration follow. The details of these mechanisms are discussed more fully in the section on natural waters in Chapter II.

During oxidation processes in gold-bearing deposits gold may migrate in the oxidizing waters:

1. As the metal Au° apparently in solution or in a dispersed state as a colloid protected by a variety of other colloids including silica, hydrous iron oxides, hydrous manganese oxides, etc. Extremely finely divided gold and lattice gold released as a result of the oxidation of auriferous pyrite, pyrrhotite, arsenopyrite, chalcopyrite, stibnite, tetrahedrite, the various gold tellurides and aurostibite would seem to be especially susceptible to migration in these forms.

2. As hydroxocomplexes of the type $[Au(OH)]$, $[Au(OH)_2]^-$, $[Au(OH)_4]^-$ and $[Au(HS)(OH)]^-$. Roslyakov *et al.* (1972) claim that some of these complexes are relatively stable in oxidized zones.

3. As various dissolved sulphur (thio) species. During the oxidation of sulphides and sulphosalts the sulphur component may yield a variety of species, including sulphide ion, thiosulphate, sulphite, polythionate and sulphate depending upon the Eh and pH.

$$\frac{\text{MS}}{\text{Metal sulphide}} \rightarrow S^{2-} \rightarrow (S_2O_3)^{2-} \rightarrow (SO_3)^{2-} \rightarrow (S_nO_6)^{2-} \rightarrow (SO_4)^{2-} \quad (n = 2\text{–}6)$$

A number of other complexes may also be formed such as HS^-, HSO_3^- and probably many other H-S-O species, making the oxidation of a sulphide a most intricate process. A number of these complexes render gold (and silver) soluble, in the neutral and alkaline pH range including particularly HS^-, $(S_2O_3)^{2-}$ and $(SO_3)^{2-}$. The complexes formed are of the types $[AuS]^-$, $[Au(HS)_2]^-$, $[Au(S_2O_3)_2]^{3-}$ and $[Au(SO_3)_2]^{3-}$. Where arsenic and antimony are abundant in gold-bearing sulphide deposits gold arsenothio and gold antimonothio complexes of the type $[Au(AsS_3)]^{2-}$ and $[Au(Sb_2S_4)]^-$ may be responsible for the migration of gold. That such complexes are probable is suggested by analogy with silver, the presence of secondary (supergene) pyrargyrite and proustite being relatively common in some silver deposits.

Gold (III) salts of oxy-anions are not very stable, but complex auric sulphates of the type $[Au(SO_4)_2]^-$ are known. Such complexes may be present where the oxidation potential is high in oxidizing sulphide zones and where H_2SO_4 and an oxidant such as MnO_2 are present. This mechanism may partly account for the relatively high migration capacity of gold in some oxidizing sulphide bodies. (*See also* the section on gold in natural waters in Chapter II.) Roslyakov *et al.* (1972) consider that the solubility of gold as sulphate complexes is improbable from thermodynamic considerations, the standard electrode potential for the formation of the $[Au(SO_4)_2]^-$ complex being unfavourable, even under strongly oxidizing conditions.

It seems probable that much of the migration of gold in sulphide deposits is the result of solution of gold by sulphur, arsenic and antimony complexes particularly the thiosulphate, sulphite and sulphide species. Complex auric sulphates may also be a factor in the mobility of gold since we have observed that finely divided gold is slightly soluble in ferric sulphate solutions (Boyle *et al.,* 1975).

Listova *et al.* (1966) carried out a number of experiments involving solutions formed during the oxidation of various natural Pb, Zn and Fe sulphides. They found that gold was dissolved in these solutions, especially when $CaCO_3$ was present and concluded that the metal was complexed under weakly alkaline conditions by thiosulphates and polythionates formed during reaction of carbonates with the products of the oxidizing sulphides.

4. As various dissolved halide species, mainly chloride complexes. Gold has long been known to be soluble as chloro complexes:

$$2Au^\circ + 2H^+ + 4Cl^- \rightarrow 2[AuCl_2]^- + H_2$$

Provided an oxidant such as Fe^{3+} is present, gold may have a relatively high mobility in oxidized zones where chloride occurs in the waters. It has been considered for many years that the generation of the reactive chlorine that solubilizes the gold is due to the following reaction.

$$MnO_2 + 2Cl^- + 4H^+ = Mn^{2+} + 2H_2O + Cl_2$$

Since all of these reactants may be present in some oxidation zones it seems probable that some gold migrates as the soluble chloride complexes. There have, however, been critics of the MnO_2 mechanism mainly because of the lack of this compound or because of unfavourable pH conditions. Eddingfield (1913*a*) for instance notes that the influence of manganese applies mainly to noncalcareous deposits. In the Philippines where abundant manganiferous calcite occurs in the veins the oxidizing waters are neutral or alkaline, and this prevents the formation of any free chlorine. He attributes the near-surface enrichment in the gold deposits of the Philippines mainly to the removal of gangue elements. Other critics have doubted that all of the necessary reactants are brought together at the most propitious time to effect solution of gold. Another possibility obtains, however, in oxidized zones, and this would seem to be the most important. Ferric salts such as the sulphate solubilize gold in the presence of dissolved chlorides under acid conditions. The ferric ion maintains the gold in an oxidized state that is then capable of binding with chloride to form soluble complexes. The simplified ionic reactions probably run as follows in an acidic and complexing environment:

$$Fe^{3+} + Au^\circ \rightarrow Fe^{2+} + Au^+$$
$$Au^+ + 2Cl^- \rightarrow [AuCl_2]^-$$

Since ferric sulphate is one of the most common compounds in oxidizing zones containing sulphides and dissolved salts such as NaCl, KCl, etc. are present in some oxidizing waters, it follows that gold may be solubilized as suggested.

Lakin (1969*b*) observed that when NaCl was added to synthetic leach solutions approximating the composition of solutions resulting from the commercial leaching of dumps of porphyry copper deposits gold was dissovled in the presence of manganese dioxide. The test solution of ferric sulphate and cupric sulphate (pH 1.5) contained 0.5 wt. per cent NaCl. Leaf gold was added to two 200 ml portions of solution, and 0.5 g MnO_2 was added to one of these portions. Air was bubbled through both solutions for 3 days, and the solutions were then filtered. The filtrate of the portion that had been in contact with MnO_2 contained 400 μg (micrograms) of gold, the other portion only 4 μg.

Supergene gold is frequently found in association with the silver halides, chlorargyrite, bromargyrite and iodargyrite in a manner suggesting that the two precious metals were carried as the chloride, bromide or iodide in the supergene waters.

5. As various organic complexes. Gold is readily soluble as cyanide and thiocyanate complexes of the type $[Au(CN)_2]^-$, $[Au(CN)_4]^-$ and $[Au(CNS)_4]^-$. Such complexes may be present in oxidized zones where large amounts of organic matter are present in the overlying soils and eluvium as suggested in Chapter II. Humic substances may also solubilize or carry gold in an adsorbed form under similar conditions. Actually we have few data on the efficiency of these particular types of organic compounds to carry gold in oxidizing zones. Cyanide complexes if present would seem to be only transitory because of the relatively low pH in zones where sulphides are undergoing oxidation. Similarly, the stability of humic complexes would not seem to be particularly high under acidic conditions.

6. Adsorbed to various organic and inorganic colloids. The possibility of this mode of transport by humic colloids has been alluded to above and is discussed at length in Chapter II. It may be important where highly humic conditions prevail. Transport as an adsorbed constituent on inorganic colloids such as hydrous iron and manganese oxides and silica is highly probable in the oxidized zones of most types of gold-bearing deposits. In these substances (colloids and gels) we have repeatedly found enriched amounts of gold (and silver) in gold-silver deposits.

The pH and Eh of the oxidizing solutions and environment affect the mobility and precipitation of gold in a number of ways. Many of the soluble complexes of gold including the various sulphide species such as $[Au(HS)]^-$, $[Au_2(HS)_2S]^{2-}$, the thiosulphate, sulphite, cyanide and the thioarsenic and thioantimony species are stable only in neutral or alkaline solutions. Acidification of such solutions breaks up the complexes and native gold is precipitated. On the other hand the chloro complexes are stable only in acid and near neutral media. Increase in pH precipitates native gold. The pH and Eh also affect the mobility of gold in other ways, the principal ones being the effect on the ferrous-ferric and manganous-manganese dioxide couples which in turn markedly influence the solubility and precipitation of gold as we shall see.

The pH of oxidizing solutions in gold deposits is controlled mainly by the presence of various acids, especially H_2SO_4, which derives directly from the oxidation of pyrite and other sulphides or the hydrolysis of certain sulphates, mainly ferric sulphate, and by the neutralizing effect of carbonate rocks or gangue. Thus, where the gangue is mainly quartz, pyrite and other sulphides and the wall rocks unreactive such as slate, greywacke, quartzite, gneiss or schist the conditions are commonly acid, and the waters are only very slowly neutralized. If chlorides are present in the environment, gold may show considerable migration as the chloro complexes. In addition there is less tendency for absorption of gold on hydrous iron oxides (limonite) and hydrous manganese oxides (wad). In fact, the latter may not be precipitated at all because of the acidic conditions. On the other hand where the gangue or wall rocks are carbonate bearing the solutions are quickly neutralized, and the alkaline complexes of gold are stable thus imparting a relatively high mobility to the element. However, abundant hydrous iron and manganese oxides are formed under slightly acid, neutral and alkaline conditions, and these tend to adsorb gold strongly in this pH range (5–8). The mobility of gold is, therefore, a rather complicated phenomenon, particularly so when one encounters various mixtures of gangue minerals and a variety of host rocks. Gold deposits tend to be individual, and the factors that have led to the supergene mobility and precipitation of gold have to be worked out for each deposit. To generalize one can say that gold is particularly mobile in an acidic or strongly alkaline environment, and hence the most favourable conditions for secondary enrichment are weakly acid, neutral and weakly alkaline conditions. This is also the general view of Roslyakov (1976).

With respect to silver and the base metals, gold generally has a relatively low mobility during oxidation processes. In the absence of humic complexing, studies carried out by the writer indicate that the generalized sequence of mobility is $Zn>Cd=Hg>Ag>Cu\geq Mo>Co\geq Ni>Au>Pb>Sn\geq W\geq Bi$. Morris and Lovering (1952) found a somewhat similar sequence in their study of the dispersion of heavy metals in the Tintic district, Utah. As with all generalized sequences there are commonly local modifying influences. When humic matter is present in the system the order of the mobility of the various elements may be greatly modified, depending on the type of humic complexes present and other factors. Gold appears to have a relatively high mobility in humic waters as noted in Chapter II; its mobility is probably about the same as that of Ag, Cu, Hg and Mo.

A number of mechanisms for the precipitation of gold from downward migrating supergene solutions are possible. Some of these are:

1. Increase or decrease in the pH of the solutions due to oxidation of pyrite with the consequent production of H_2SO_4, hydrolysis of ferric sulphate which produces H_2SO_4 and reactions with gangue minerals and wall rocks, which tend to neutralize or make the solutions alkaline. Increase in pH destroys the chloro complexes of gold and precipitates the native metal. Decrease in pH has a similar effect on the alkaline complexes such as $[AuS]^-$, $[Au(HS)_2]$, thiosulphate, sulphite, etc., and native gold is precipitated.

2. Precipitation of native gold from solution by ferrous ion. Where gold-bearing solutions encounter ferrous ion as in zones where a low oxidation prevails native gold is precipitated.

$$Fe^{2+} + Au^+ \rightleftharpoons Au^\circ + Fe^{3+}$$

Commonly this reaction is characteristic of the deeper zones of oxidizing deposits, but in some veins and lodes the phenomenon is marked in the near-surface zones. This mechanism of precipitation seems to be one of the most important in deposits containing abundant pyrite, pyrrhotite, arsenopyrite, siderite and other readily oxidized iron minerals. It is probably the main mechanism of precipitation of gold in many gossans; also in the zone of reduction (zone of supergene sulphides).

Experimentally, Machairas (1967) has shown that auriferous pyrite and arsenopyrite yield secondary gold as a result of reduction by $FeSO_4$. He recognized three stages in the process: (1) oxidation of pyrite and arsenopyrite to yield H_2SO_4 + $Fe_2(SO_4)_3$, which solubilizes the primary gold; (2) reduction of the dissolved gold by $FeSO_4$ to give secondary gold; and (3) hydrolysis reactions, which precipitate the iron oxides (limonite). These results agree with those carried out in our laboratories and reported elsewhere (Boyle *et al.*, 1975).

3. Precipitation of gold from solution by manganous ion in feebly acid, neutral or alkaline solutions:

$$2Au^+ + Mn^{2+} + 4OH^- \rightarrow 2Au^\circ + MnO_2 + 2H_2O$$

This commonly takes place in the deeper parts of gossans and oxidized gold deposits. The native gold is commonly adsorbed or absorbed by the hydrous manganese oxide in a very finely divided form and is rarely visible (*see* 4 below).

4. Adsorption and/or coprecipitation of negatively-charged gold complexes and colloids by positively charged gels such as hydrous ferric oxides (limonite). This mechanism appears to be particularly effective since most gelatinous iron oxides in or near gold-bearing deposits are generally enriched in gold (Table 22). Gelatinous manganese oxides, likewise, adsorb and/or coprecipitate gold, but the mechanism is not entirely clear. Since the gold complexes and colloids are negatively charged they should be repelled by the negative hydrous manganese oxides. However, these gels invariably contain considerable iron and other elements that may reverse the overall charge giving the complex a positive charge which is effective in precipitating the negative gold complexes and colloids. Alternatively, anionic gold complexes may be adsorbed on the positively charged hydrous manganese (II) oxides. (*See also* the section on gold in wad in Chapter II.)

The writer's observations on natural gold- and silver-bearing hydrous iron and manganese oxide gels suggest that initially the reaction is essentially an adsorption phenomenon, that is, the gels exist as a random arrangement of micelles of the oxides with adsorbed gold and silver ions. No gold or silver can be observed in these dried gels even under the highest powers available with the optical microscope. With aging of the gel some of the gold and silver may be desorbed and split out of the complex yielding small spangles and filaments of native gold in the vicinity of the oxides (limonite and wad). In other cases much of the gold and silver is retained by the oxides as an adsorbed phase or in an extremely finely divided form inextricably mixed with the oxides.

Clay minerals and gelatinous silicate complexes also tend to markedly concentrate gold. One frequently finds seams, bunches and patches of clay minerals in the oxidized zones of gold deposits greatly enriched in gold. Gouge and puggy clay along fractures and faults, likewise, tends to concentrate gold in the oxidized zones. The reason for this is evidently largely due to adsorption processes as explained in the section on natural waters in Chapter II.

Numerous other natural gellike substances tend to precipitate gold readily. Among these may be mentioned humic gels, humic-limonitic gels, humic-limonite-wad-alumina gels, bismuth ochres, tellurium ochres and amorphous antimony and arsenic ochres. The precipitation mechanism is evidently largely due to adsorption on these substances.

5. Coagulation and/or precipitation of gold colloids by various charged ions, sols and gels. Metallic gold colloids carry a negative charge and hence positively charged clay minerals, hydrous iron oxide and various other positively charged ions, sols and gels should effectively coagulate or precipitate the gold. The importance of this mechanism is unknown since we have no data on the transport of gold as a colloid in the oxidized zones of gold deposits.

6. Precipitation due to the presence of various natural reductants. Various field and laboratory observations show that native gold is readily precipitated from gold-bearing solutions by practically all sulphides, silicates, carbonates, native metals, clay minerals, carbonaceous substances, and a great variety of supergene hydrous oxides, arsenates, antimonates, etc. The gold is only rarely found coating these various substances; more generally the dissolved metal is precipitated on nearby minute nuclei of native gold, and these continue to grow to give relatively coarse platelets, wires, sprigs, flakes, slugs and nuggets in the oxidized zones. In some veins, however, there is a general precipitation of gold in the form of finely divided particles throughout such materials as disintegrated sulphides, limonite, wad, puggy clay and various ochres in the oxidized zones.

7. Coprecipitation and/or adsorption by numerous supergene minerals. Among these may be mentioned bismutite, chlorargyrite, the jarosites, beudantite, bindheimite, malachite, azurite, gypsum, native sulphur, pyromorphite, scorodite, and various other phosphates, vanadates, arsenates and antimonates. The exact nature of gold in some of these materials is unknown. Some gold is evidently in lattice positions in these minerals, but most is probably present in a very finely divided form (dust). In some occurrences in chlorargyrite and the analogous bromide and iodide the gold may be coarse and often well crystallized.

8. Precipitation of gold by H_2S. Hydrogen sulphide precipitates native gold from solution in the absence of solubilizing agents such as the alkali carbonates. Such a mechanism may operate where pockets of H_2S occur in the oxidized zones due to the oxidation of various sulphides at low Eh, due to the action of H_2SO_4 on sphalerite and other sulphides, and possibly due to the bacterial reduction of sulphates. In the zones of reduction (supergene sulphides) the precipitating effect of H_2S may also be partly responsible for the enrichment of gold in chalcocite, covellite and other supergene sulphides.

9. Precipitation of gold by reaction with supergene and hypogene sulphides. Gold is commonly enriched in supergene sulphide zones and also in the upper parts of sulphide orebodies just below the zone of oxidation, even where the latter are lacking in supergene sulphides. As mentioned above part of the precipitation of gold in these zones of reduction may be due to the effect of H_2S. On the other hand electrochemical and replacement effects are probably also involved. Gold is the lowest metal in the electro-chemical series and its sulphide is probably less soluble than the sulphides of copper, zinc and iron (pyrite). Hence gold should replace these elements in their sulphide combinations. Whether this is actually what takes place or not is a question. However, it is a fact that many chalcocite zones in copper sulphide deposits are enriched in gold (and silver). Much of the gold is submicroscopic or extremely finely divided. Only occasionally does one see visible gold in these zones that is obviously of supergene origin.

Examples of gold enrichment in deposits

The supergene enrichment of gold in deposits may take place by a simple mechanical mechanism, by chemical means or by a combination of these. First the enrichment may be primarily the result of the chemical removal of a large part of the gangue minerals, in which case the gold migrates slowly downward by gravity or is left behind as a residual component. Such enrichments require no chemical movement of the gold; the lodes simply weather down and the gold collects mainly by gravity in the accumulated residue. Secondly, the gold is enriched as a result of chemical migration of gold. In most deposits the movement of the gold is usually downward, although some exhibit chemical enrichments that indicate a degree of lateral movement of the solutions. In the oxidized zones of gold deposits both mechanisms have generally operated, and there are rarely sufficient criteria to distinguish which mechanism is the dominant one.

Furthermore, the supergene enrichment of gold in deposits is often highly irregular and not all deposits exhibit the same features. Practically every deposit is a study in itself. There are, however, certain general regularities that deserve mention, and these are best outlined by dealing individually with the types of deposits in which gold occurs. Before proceeding, however, there is one generality with respect to the vertical zoning of oxidized gold deposits that can be mentioned. Many deposits exhibit a surface-oxidized zone or gossan in which there is frequently, but not always, an enrichment of gold often in the free state. This generally passes imperceptibly into the primary gold-quartz or gold-sulphide ores that are leaner in gold. This common near-surface enrichment must be taken into account when examining surface prospects lest grave errors be made in estimating the grade of the primary ores. Where conditions were such as to produce supergene sulphides in the zone of reduction at depth, enrichments of gold may also be encountered in this zone. The ideal zonation in an oxidized gold lode is, therefore, a moderately gold-enriched near-surface gossan or oxidized zone, a highly gold-enriched secondary sulphide zone at or near the present or former water table and a lean gold-bearing primary zone that extends to depth. Considerable divergence from this ideal zoning arrangement is common.

For a summary of the chemistry of the various elements that are enriched or depleted in the various zones noted above see the section on associated elements in Chapter III.

The oxidation effects displayed by gold-bearing pegmatites, coarse-grained granitic rocks and porphyries are essentially the same as those described for gold-quartz veins. In general the degree of enrichment of gold in these deposits depends in large measure on the amount of pyrite and arsenopyrite that they contain.

Skarn-type gold deposits usually contain much auriferous pyrite, pyrrhotite and arsenopyrite and considerable amounts of carbonates. Oxidation of the sulphides yields abundant ferrous sulphate that is rapidly oxidized to ferric sulphate. This undergoes hydrolysis and hydrous iron oxides are precipitated. Some H_2SO_4 may be produced by direct oxidation of sulphides and by the hydrolysis of sulphates, but this is soon neutralized by the carbonates. In general the oxidized zones and gossans on skarn-type gold deposits are deep and extensively developed in unglaciated areas, and most are enriched in gold compared with the primary ores. Furthermore, the gold is in a freer state being much more amenable to amalgamation and cyanidation, having been released from its host minerals, particularly pyrite and arsenopyrite. Where lead and silver are abundant in the ores these two elements may exhibit a parallel enrichment with gold. Copper, zinc, cadmium and tellurium are commonly leached from the gossans and upper parts of the oxidized zones. Some arsenic invariably remains in the gossans adsorbed on limonite or present as scorodite and other arsenates; much arsenic is, however, leached in most places.

A good example of a deeply leached gold-bearing skarn type deposit is provided by the Rosita Mine in Nicaragua described by Bevan (1973). The mine is situated in a tropical forest plain where the annual rainfall is around 110 in. The orebodies are in garnet-epidote skarns developed in Cretaceous calcareous sediments (now marbles) mainly on the southern flank of a small Tertiary dioritic intrusion. The primary ore minerals in the skarn are chiefly massive and disseminated chalcopyrite, pyrite, pyrrhotite and magnetite. The metals won from the ores are copper, silver and gold.

Three zones are present, from the surface downward – an oxidized zone, a zone of secondary sulphides and the primary ore. The oxidized zone contained mainly malachite, with some azurite, chrysocolla, chalcanthite, tenorite, cuprite and native copper. The copper grade was over 5 per cent; the content of gold and silver were respectively 0.019 and 0.890 oz/ton as calculated from the production records. In the secondary sulphide zone, chalcocite was the principal economic mineral with minor amounts of covellite, bornite and 'grey coppers'. The copper grade was 4 per cent, and the content of gold and silver were respectively 0.063 and 0.534 oz/ton. As mentioned above the principal copper mineral in the primary ore is chalcopyrite. The copper grade is 1.65 per cent and the gold and silver grades respectively 0.028 and 0.196 oz/ton. These figures show a general depletion of gold in the oxidized ores and an enrichment in the secondary sulphide zone as compared with the primary ore. Silver on the other hand is markedly enriched in the oxidized zone and slightly enriched in the secondary sulphide zone compared with the primary zones.

The gold-bearing skarn-type deposits in the Bau mining district Sarawak described in Chapter III are deeply weathered to depths of 20 ft or more (Wolfenden 1965; Pimm 1967). The weathered materials are multicoloured auriferous clays and sandy clay with mineralized rubble and blocks of limestone and skarn. They average about 0.2 oz Au/ton and range from 0.05 to 1 oz Au/ton. In some the silver is up to 1 oz/ton. The gold is extremely finely divided in most of the clays. Some of the clays contain abundant black manganese oxides; these are enriched in gold, up to 1.5 oz/ton.

The gold-bearing skarn-type deposits in the glaciated parts of Canada exhibit only shallow oxidation effects. At the Nickel Plate Mine, Hedley Mining District, British Columbia the oxidized zone, developed on the skarn containing auriferous arsenopyrite, pyrite, pyrrhotite and sphalerite, was only a few feet thick and consisted of a deep red limonitic and hematitic earth in which resided a rubble of sulphide-skarn material with occasional wisps of erythrite. The gold in the red earth is visible as small ragged particles, which may have been exsolved from the sulphides or which may have been accreted from the finely divided and lattice distributed metal in the auriferous arsenopyrite. The latter seems more probable since free gold was rarely if ever seen in the Nickel Plate ores. According to Camsell (1910) there was a slight surface enrichment of gold, but this was not of any great importance economically.

There are innumerable examples of the oxidation of gold-quartz veins, gold-bearing polymetallic lodes and auriferous massive sulphide deposits throughout the gold districts of the world. Most of the good examples occur in unglaciated terrains, but a few in glaciated areas exhibit features that are of interest. The literature on oxidation of these types of deposits is so voluminous that no attempt will be made to discuss any of the investigations in any detail. The interested reader will find the general reviews and summaries by Maclaren (1908), Lindgren (1933), Emmons (1917) and Smirnov (1951) invaluable if he wishes to pursue the subject in depth. Most of the oxidized and enriched zones described in these works were long mined out before the summaries appeared in print. Likewise, today there are few good examples of oxidized gold deposits available for study.

Gold-quartz veins and gold-bearing polymetallic deposits exhibit oxidation characteristics that can be summarized as follows:

1. Some of these deposits exhibit the three zones commonly found in oxidized deposits – a deep zone of oxidation marked by the presence of oxides, carbonates, sulphates, arsenates, etc. grading into a thin zone of secondary (supergene) sulphides at or near the present or former water table, followed downward by the primary gold-quartz or sulphide ores. Other deposits exhibit no zone of supergene sulphides; the oxidized zone merely passes imperceptibly into the primary zone. Still others show no marked development of an oxidized zone, the primary gold-quartz and sulphide ores being capped only by a few inches or feet of limonitic quartz-sulphide rubble.

2. Many of these deposits show no marked enrichment or depletion of gold as a result of oxidation. The gold is, however, in a freer state, generally coarser, often finer and more amenable to cyanidation and amalgamation in the oxidized zones. There are innumerable references to these particular features in the literature. The reasons for little change in the gold tenor during oxidation in some deposits is not clear. Evidently when a particle of gold is released from its gangue under such conditions it simply remains in situ and accretes any nearby soluble gold, thus growing coarser. Lack of oxidants such as MnO_2 and complexing agents such as chloride and thiosulphate are said by some to be the reasons for the immobility of gold during oxidation processes. The

writer, however, has observed that the state of subdivision of the released gold is a major factor, the finer the subdivision the greater the mobility of the metal in the oxidized zones.

3. In some gold-quartz veins and gold-bearing polymetallic lodes the gossans and oxidized rubble near the surface are extensively leached of gold, the metal being precipitated farther down in the oxidized zones, in the zones where the oxidation zones and primary zones interfinger or in the zones of supergene sulphides if such are present. In the oxidized zones rich pockets of supergene gold are frequently encountered as are gold-rich patches of clay and disintegrated gouge. The zones of secondary sulphides usually have patchy rich streaks or pockets, although in some of these zones the gold values are relatively uniformly distributed.

4. In certain gold-quartz veins and auriferous polymetallic lodes the gossans and near surface oxidized rubble are enriched in gold whereas the lower parts of the oxidized zones and secondary sulphide zones have a normal tenor of gold. In many of these gossans the gold is extremely finely divided and inextricably mixed with the limonite, wad and other products of oxidation.

In Canada there are few examples of deep oxidation of gold-quartz veins and gold-bearing polymetallic deposits mainly because glaciation has removed the oxidized zones. In the Keno Hill–Dublin Gulch area, Yukon the gold-bearing quartz-pyrite-arsenopyrite veins are deeply oxidized, in places down to depths of 600 ft (Boyle, 1965*a*). Unfortunately, from the point of view of research these veins commonly occupy the same fissures and faults as later pyrite-siderite-galena-sphalerite-freibergite lodes, making it difficult if not impossible to separate the effects resulting from oxidation of each of these two types of veins. Nevertheless, some general tendencies can be discerned with respect to the gold veins. As the auriferous pyrite and arsenopyrite are oxidized their gold is released and collects in small slugs, rough wires and dust in the limonite-scorodite-quartz rubble. This gold is much coarser than that which is seen only rarely in the veins. In some veins in the Keno Hill–Dublin Gulch area there is some leaching of gold (and silver) as shown in Table 77, but overall there is no marked migration of gold in most of the veins.

Table 77. Gold and silver contents of gold-quartz veins and lodes and their oxidized zones, Keno Hill–Dublin Gulch area, Yukon

Description of sample	Au	Ag	Powder density
	(oz/ton)		
No. 6 vein Keno Hill			
Composite sample of highly oxidized part of quartz-pyrite-arsenopyrite vein	0.015	0.71	2.89
Composite sample of fresh quartz-pyrite-arsenopyrite vein	0.215	3.36	3.28
Dublin Gulch area			
Composite sample of limonite-scorodite material in ozidized zone of veins	0.30	1.0	2.90
Composite sample of quartz-pyrite-arsenopyrite-jamesonite veins	0.57	1.0	3.25

The Tertiary Mount Nansen gold-silver deposits in the Dawson Range, Yukon are systems of narrow steeply dipping veins in metasediments and volcanics of Precambrian to Paleozoic age, andesitic volcanics and granitic rocks of Mesozoic age and Cretaceous to early Tertiary dacite porphyries (Saager and Bianconi, 1971). The hypogene mineralization is essentially pyrite, arsenopyrite, stibnite, sphalerite, chalcopyrite, galena, freibergite, jamesonite, boulangerite, bournonite and gold. In the intensely oxidized zones and partly oxidized zones that extend to depths of 200 ft or more the common supergene minerals are limonite, scorodite, arsenobismite, arsenolite, covellite, anglesite, bindheimite, beudantite and native silver. Very little migration of silver and gold has taken place, and there are no supergene enrichment zones.

In the Yellowknife district the gold-quartz-pyrite-arsenopyrite-sulphosalt veins and lodes in greenstones are only superficially oxidized down to depths of 1 ft or so in most places. The oxidized materials are a rubble of quartz and disintegrated sericite schist in pulverulent iron oxides, mainly limonite. Some of these oxidized zones are greatly enriched in gold as shown in Table 78. On the other hand gossanous material, composed mainly of disintegrated sericite schist cemented by limonite on certain gold-bearing zones, is only slightly enriched in gold.

Table 78. Gold and silver contents of gold-quartz veins and lodes and their oxidized zones, Yellowknife, Northwest Territories

Description of sample	Au	Ag
	(oz/ton)	
Crestaurum shear zones		
Composite sample of iron oxide rich material in oxidized part of shear zones.	1.16	0.20
Composite sample of quartz-pyrite-arsenopyrite-sulphosalt ore	0.5	0.10
Lynx schist zone		
Composite sample of gossan material	0.005	0.03
Composite sample of silicified and pyritized shear zone	0.001	0.03

The gold-antimony ores of West Gore, Hants County, Nova Scotia occur in Meguma slates and greywackes of Ordovician age. The mineralization is mainly quartz and some calcite in zones of crushed slate. In this gangue there is much pyrite, arsenopyrite, stibnite and some native antimony, all with associated native gold. Near the surface the ores are oxidized to shallow depths probably not exceeding 10 ft in most places. In this zone there is a rubble of unoxidized ore particles and lumps highly stained in places by limonite and antimony ochres. Locally kermesite, Sb_2S_2O, is present, and there is some supergene (?) reddish stibnite, Sb_2S_3, in places in the zone of reduction. The gold in the oxidized parts of the veins is mainly free.

The older literature contains a number of good examples of secondary gold enrichment. At Battle Mountain, Colorado, Guiterman (1890) describes exceptional enrichments of the pyritiferous veins in quartzites down to depths of 250 ft. The pay ore averaged 7 oz Au/ton and 50 oz Ag/ton. Twisted and lumpy nuggets of gold intimately mixed with abundant chlorargyrite are described mainly in oxidized material rich in clay. Guiterman ascribes the enrichment of gold to the solution effect of ferric sulphate derived from the slow oxidation of pyrite.

At Tintic, Utah, Lindgren (1915) described rich shoots of gold ore in the oxidized zones that are undoubtedly due to the migration and enrichment of gold. The primary ores of Tintic are of two types – veins in (Tertiary) monzonite and replacement bodies in (Ophir) limestones and dolomite of Paleozoic age. The former contain essentially quartz, barite, pyrite, enargite, galena and a few other base metal sulphides. The replacement deposits are marked by silicification (jasperoid) and contain quartz, barite, galena, enargite, sphalerite, some pyrite and a little chalcopyrite, tetrahedrite and famatinite. The deposits are oxidized to the unusual depths of 1650 to 2400 ft. The oxidized zones were constituted mainly of limonite with abundant residuals of primary ore, in addition to supergene minerals such as anglesite, cerussite, plumbojarosite, smithsonite, calamine and hydrozincite in the predominantly lead-zinc ores and a variety of copper arsenates, malachite and more rarely cuprite and native copper in the cupriferous deposits. The secondary silver minerals were argentite, cerargyrite and native metal; some rich oxidized ores showed native gold. Most of the oxidized ores were greatly enriched in silver.

Some of the oxidized copper ores contained gold running from 0.5 to 0.75 oz/ton, but in addition certain parts of shoots were very rich, assaying 1 to 5 oz/ton. In these shoots the gold was a deep yellow colour and of high purity. Its secondary nature was apparent from its deposition between quartz grains or as thin flakes on joints. Manganese was always present in the rich shoots of gold, and Lindgren (1915) concluded that sodium chloride, furnished by the winds from the Salt Lake deserts in conjunction with H_2SO_4 and manganese dioxide in the deposits, was responsible for the migration and secondary concentration of the gold.

A secondary sulphide zone is mentioned as being present in one of the mines. It was phenomenally rich in supergene silver (100–3000 oz/ton) contained mainly in pearceite, which accompanies galena, spherulitic sphalerite and marcasite. There is no mention of the gold content of this secondary sulphide zone.

Lovering (Morris and Lovering, 1952) studied the supergene mobility and migration of gold, silver, copper, lead and zinc in the Tintic district. Under the conditions of oxidation that have existed over some 25 years he found that lead had not moved perceptibly, gold had migrated only a few inches, copper had moved a few score feet at most and only in acid solutions, and zinc had travelled hundreds of feet but not as far as silver in some cases. From the data he collected Lovering concluded that gold has a relatively high mobility in acid ferric sulphate solutions with iron just starting to hydrolyze. Silver, he found, may travel far in the oxidized zone, but if it comes into contact with sulphides its migration is quickly halted.

The Creede district in the San Juan Mountain of Colorado is noted for its Tertiary silver-copper-lead-zinc-gold ores that occur mainly in veins and mineralized breccias in faults representing subsidence structures in a large cauldron complex of Tertiary volcanic rocks and associated tuffs (Steven, 1968). The principal primary minerals in the veins and mineralized fault breccias are clay, chlorite, amethystine to white quartz, galena, sphalerite, chalcopyrite, pyrite and minor amounts of argentite, fluorite, barite, rhodochrosite and ankerite. Open-space filling has dominated in the formation of the deposits. Beds of tuff containing fragments of carbonized wood are mineralized with exceptional quantities of silver in places. Apparently none of these are of economic value.

In the older literature on Creede (Emmons and Larsen, 1923; Larsen, 1930), mention is made of the extensive oxidation effects impressed on the veins during which minerals such as limonite, hematite, jarosite, wad, chalcedony, kaolin, gypsum, anglesite, cerussite, oxidized nodules of galena, smithsonite, goslarite, chrysocolla and malachite are developed. Near the surface (150–300 ft) the veins were generally not productive, having been leached of much of their metal content. The most productive (enriched) zone lay at depths of 150 to about 1000 ft. According to Emmons and Larsen (1923) this was the zone of maximum precipitation of both gold and silver. Unoxidized ore carried about 0.1 oz Au/ton whereas the enriched ores carried from 0.5 to 5 oz Au/ton or more. Much of the secondary gold, which was dark yellow and of high fineness, occurred in particles about the size of mustard seed in manganese dioxide (wad). Studies of the annual production showed a noteworthy increase in gold content with depth. Silver on the other hand exhibited enrichment near the surface and a decrease with depth due mainly to the formation of chlorargyrite and native metal in the near-surface parts of the veins.

Some of the Appalachian gold deposits in the southeastern United States were enriched as a result of weathering. Kinkel and Lesure (1968) and Lesure (1971) describe some of these deposits, mainly in Georgia. At the Calhoun Mine, Lumpkin County, the primary ore is auriferous quartz stringers and veins in mica schist. Weathering of the schist and auriferous veins has yielded a saprolite some 20 to 50 ft thick in which there has been much leaching of silica, alumina, total iron and other major constituents; concomitantly there has also been an enrichment of gold, arsenic and a number of other elements including B, Be, Co, La, Nb, Ni, Pb, Zn and Zr. Freshly deposited limonite coating the wall of an adit was found to contain 2.9 ppm Au, indicating that some gold is being transported with iron during weathering.

The gold-quartz and other types of deposits in Brazil, many associated with various facies of iron-formation, are extensively oxidized, and some show marked enrichments near the surface. One unusual type 'jacutinga' occurs as thin (inches to a few feet) lines or bands in itabirite and is a decomposition, or more accurately a surface chemical disintegration, product of the iron-formation. It is composed essentially of powdery ferric oxide (limonite and hematite), manganese oxides, clay minerals and talc in which nuggets, plates and threads of native gold are present. Some of the 'jacutinga' were rich, up to 0.5 oz Au/ton or more, and some extended to depths of 700 ft or more. Oliveira (1931, 1932) thinks that as pyrite is oxidized to form H_2SO_4 it reacted with NaCl, which is found in every mine, to form HCl. The latter attacked the MnO_2 present to give nascent Cl that dissolved the gold. The acidic solution of $AuCl_3$ then reached an area where there was no MnO_2, and there it encountered Fe^{2+} in $FeSO_4$ that precipitated the gold. Alternatively the solution may have reacted with organic compounds, H_2S, carbon, sulphides, tellurides or carbonates resulting in the precipitation of the gold.

Many of the gold deposits of Chile are deeply oxidized and some are enriched. Most of these deposits occur in the Coast Range and in the low hills of the Central Valley, commonly in granodiorite intrusions and their nearby sediments and volcanics. According to Benitez (1959) the primary minerals are essentially quartz, pyrite, hematite and small amounts of the base metal sulphides. The pyrite and sulphides are extensively altered to limonite, chrysocolla, malachite, azurite, atacamite, copper oxides and calcanthite. In the oxidized zones there is also much kaolin, clay and chlorite. The gold is mainly in the limonite in a very finely divided form and much of it is 'rusty' making it difficult to float.

A number of the rich gold veins in the Waihi district, Hauraki goldfield, New Zealand were extensively enriched during oxidation processes (Morgan, 1924). The primary minerals in this field were essentially quartz, calcite, valencianite (adularia), pyrite, galena, sphalerite, chalcopyrite, argentite, pyrargyrite and native gold. Oxidation was pronounced and deep, up to 1500 ft in some of the lodes, yielding limonite, wad, azurite, malachite, chrysocolla, cuprite and native silver locally. Some veins were very nearly completely oxidized to a rubble of disintegrated and platy quartz and the other supergene minerals noted above to depths of several hundred feet; others were only partly oxidized. Morgan (1924) asserts that there was only a minor enrichment due to removal of gangue elements. Most of the enrichment he attributes to the solution and redeposition of gold and silver by descending meteoric waters. In some of the Waihi lodes there was some leafy supergene gold on joint surfaces near the surface, but much of the dissolved gold and silver was carried to deeper levels, some into the primary sulphide zones at depth where the metals were precipitated giving material whose assays averaged 1 to 2 oz Au/ton and 30 to 60 oz Ag/ton.

With respect to the Hauraki goldfield in New Zealand Williams (1974) maintains that the effects of secondary sulphide enrichment were not entirely understood, and that this led to a general conflict in the literature on the origin of the lodes. His view is of interest.

> Unfortunately, Morgan failed to set out the mineralogical form of secondary sulphide enrichment in Waihi mine – the only deep mine-workings then accessible – in fact it is clear that he did not fully understand the practical meaning of secondary enrichment, for he described rich ore comprising pyrite, sphalerite, galena and chalcopyrite as secondary material formed by the action of descending waters. He more correctly ascribed the pyrargyrite and proustite in the Waihi and Grand Junction mines to secondary enrichment.
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> Generally then, the Hauraki goldfields were worked for about three-quarters of a century with little awareness of the meaning of secondary enrichment processes. Yet the list of minerals set out by the various writers contains many which are characteristic of secondary enrichment. A clear instance of secondary sulphide enrichment seems to be presented by the exceedingly rich ore in the stopes on 12-level in the Bonanza section of Maria mine–where covellite was reported with a little bornite. While describing Waihi, Maclaren (1908) pointed out that "The uppermost sulphide zone at the base of the zone of oxidation was very rich, averaging from 1 to 2 ounces gold and 30 to 69 ounces silver per ton, while exceedingly rich portions assayed 25 ounces gold and 1,000 ounces silver per ton." As already noted, Fraser and Adams (1907) recorded that "It would appear that proximity to the original surface has been favourable to the deposition of the high-grade silver ores." To the present writer the description of the silver-bearing reefs at Komata and Maratoto seem clearly to indicate secondary enrichment.
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> Although pyrite pervades the mineralization, there is some doubt as to whether it was sufficiently abundant in the lodes to initiate a strong zone of secondary enrichment. For instance in the Tui mine, pyrite is inconspicuous – hence there is no strong gossan and no evidence of a strong secondary enrichment. Moreover, even though sulphides are consistently referred to at Waihi, according to Maclaren (1908) they constitute only 3 per cent of the vein material.

Kraft *et al.* (1974) have carefully examined the effects of oxidation on some gold quartz deposits in the Central Mongolian Peoples Republic. These deposits contain essentially quartz and native gold with about 5 per cent of sulphides and tellurides comprising arsenopyrite, pyrite, enargite, sphalerite, tennantite, tetrahedrite, chalcopyrite, bournonite, galena, hessite, altaite and petzite. The principal oxidation minerals are limonite (goethite, lepidocrocite, hematite), covellite, chalcocite, malachite, azurite, cerussite, scorodite, romeite and smithsonite. In the oxidized zones an increase in the gold content as a whole was noted; the primary native gold in the oxidized ore exhibited a decrease in silver; the silver content of the oxidized ore as a whole was reduced; and the Au/Ag ratio of the oxidized ore increased compared with the primary ore. In addition the gold particles in the oxidized zones exhibited a pronounced coarsening of grain size. Kraft *et al.* (1974) considered that colloidal dissolution and colloidal migration of gold were the dominant factors in the mobility of the gold. Because of the low stability of gold colloids the metal does not travel far in oxidized zones. Local solution and reprecipitation of gold over long periods of time are thought to give rise to the coarsening of grain of the gold particles during oxidation and to lead to important metal (gold, silver) displacements during oxidation processes.

Anhaeusser (1966) describes supergene gold enrichment at the Lily Mine in the Barberton Mountain Land in South Africa. This mine worked quartz veins and a plunging pipelike brecciated shoot filled with quartz, both types of deposits being in the Precambrian Fig Tree series in shear zones comprising shale, banded iron-formation, chert, greywacke and their metamorphic equivalents. The primary ores are composed mainly of quartz, pyrrhotite, arsenopyrite, chalcopyrite, magnetite and gold. The oxidized ores extend to depths of 150 to 200 ft and contain much limonite, goethite, hematite and melnikovite pyrite in a rubble of quartz and partly oxidized sulphides. The oxidized ore averaged between 0.15 and 0.25 oz Au/ton. Bonanzas of rich gold ore were found in the pipelike brecciated body and at intervals along some of the quartz veins. The ore in the oxidized zones was free milling, that in the fresh or sulphide-bearing rock required roasting. Anhaeusser (1966) concluded from this fact, from the fact that the fineness of the gold decreased with depth, from the secondary nature of the gold and from the occurrence of rich pockets of gold in favourable structural traps that much of the gold was of secondary origin, derived from the oxidized protore and concentrated by supergene and residual processes of enrichment in the oxidized and semioxidized sections of the mine.

Some of the auriferous deposits in Ghana were deeply weathered and slightly enriched in gold. Those in the Marlu gold belt are of particular interest (Pickering, 1935; Thomas, 1937). This belt lies about 60 mi north of Takoradi. The deposits occur entirely in Precambrian Birrimian phyllites, ash flows and tuffs. The hypogene ores occur in large argillized, silicified and otherwise altered crush and breccia zones along faults mineralized with fine-grained pyrite, fine needle arsenopyrite, graphitic material and gold. The graphitic material is said to have largely controlled the deposition of the gold. The surface parts of the orebodies down to about 20 ft or so were lateritized and highly oxidized. This ore was deep red ochre in colour and contained large amounts of colloidal size hydrous ferric oxides and aluminum oxides. The gold was present apparently mainly in the finely divided free state in this lateritized material. Below the lateritized zone the phyllites and ore material were highly oxidized but not to the extent of that in the laterites. The gold in this zone was also free. This oxidized zone passed gradually into the primary ore. The average grade of the lateritized ore was 0.26 oz/ton, that of the relatively fresh ore 0.4 oz/ton indicating a general depletion of gold during oxidation, although the metal in the oxidized parts was more amenable to metallurgical treatment.

Deposits like this are particularly difficult to discover because little is left in the oxidized zones but lateritic material and gold. The metal is also often so finely divided that it does not remain in the pan. Such deposits do not generally yield placers, another feature that makes their discovery difficult. Geochemical soil methods using gold, arsenic or antimony as indicators are particularly useful in their discovery and delineation during development.

The supergene geochemistry of tellurium, the element with which gold is so commonly associated, is discussed in Chapter III in the section on associated elements. There it was stated that in general tellurium exhibits a marked mobility under some conditions of oxidation; under others the mobility of the element is restricted and supergene minerals of tellurium such as tellurite, paratellurite, emmonsite (durdenite), etc. are formed. Supergene tellurides, particularly the base metal varieties, such as altaite and tetradymite have been reported from certain oxidized zones, but it is commonly difficult to differentiate these so-called 'supergene tellurides' from those that are paragenetically late in the primary mineral sequence.

Most of the gold-telluride types of deposits appear to exhibit relatively little enrichment of gold during oxidation. At Cripple Creek, Colorado, Lindgren and Ransome (1906) found little enrichment of gold. In a number of the veins the primary minerals of the sheeted zones, essentially quartz, fluorite, pyrite, sphalerite, galena, molybdenite and gold-silver tellurides, were oxidized to depths ranging from 300 to 900 ft to a brownish clayey material composed mainly of limonite and kaolinite in which the original vein structure was lost. The fluorite was dissolved and dispersed while the tellurides were reduced to dark brown powdery gold. Some of the tellurium was carried away in solution, and some remained bound as tellurite and ferric tellurites such as emmonsite (durdenite). There was little or no enrichment of gold in the oxidized zone, but a pronounced leaching of the small amounts of silver originally contained in tellurides and tetrahedrite took place in some veins. It should be noted that Lindgren and Ransome (1906) found that some of the tellurides near the surface, even in the oxidized zones, were relatively unoxidized. This feature is apparently common in some gold districts where the deposits contain tellurides since these minerals are often found in placers.

Stillwell (1953*a*), describing the gold-silver tellurides at Kalgoorlie, Western Australia says that the gold-bearing tellurides are decomposed in the oxidation zone with the liberation of free 'mustard gold'. Iron tellurates have been identified in this field, and it is probable that much of the tellurium remains behind in this form in the oxidized zones. Stillwell further states that occurrences of silver chloride are recorded, but that probably the bulk of the silver migrated downward in solution. Evidence of the downward percolation of silverbearing solutions, he thinks, is disclosed in isolated specimens by the dissociation of the richer gold tellurides into sylvanite, petzite and hessite.

Little definite information exists concerning the oxidation processes in the classical Tertiary gold telluride deposits in Romania (Transylvania). These famous deposits were worked by the Romans, and all of the oxidized portions of the veins have long since been removed. By piecing together bits and pieces of information from a great many old reports and from personal observations in eastern Europe a general summary of the effects of oxidation can be constructed.

The primary minerals in the Romanian (Transylvanian) gold deposits are essentially quartz, calcite, rhodochrosite, pyrite, galena, sphalerite, chalcopyrite, bournonite, alabandite, tetrahedrite, stibnite, realgar, stephanite, pyrargyrite, free gold and various gold tellurides including sylvanite, nagyagite, petzite and krennerite. In general the tenor of these ores ranged from about 0.25 to 0.75 oz Au/ton. The silver contents were highly variable from a few to a few hundred ounces per ton. The veins were oxidized at the surface and down to depths of several hundred feet in places. In these oxidized zones the principal minerals were limonite, wad, rubbly quartz, leached calcite, malachite, anglesite and residuals of oxidized sulphides. Tellurite and native tellurium are mentioned as being present in some of these zones. The gold tenor of these zones and of the zones where they interfinger with the primary zones was much higher than that in the primary zones. Assays of ounces per ton are mentioned for numerous vein systems. The gold apparently occurred relatively free in these zones and was easily won by washing and simple metallurgical practices. It was also of relatively high fineness, 850+ in most veins, whereas the fineness of the gold in the primary ores was usually about 500 to 750 fine. Leafy gold was common in some veins in the oxidized zones and in the upper part of the primary zones. Gold particles of high purity (800–900 fine), perched on pyrite and nests of gold in vugs and open spaces just below the oxidized zones, were common. All these features combined with the observation repeated many times in the literature that the veins decreased in gold tenor with depth suggest extensive enrichment of gold as a result of oxidation processes. Some investigators have attributed this enrichment to extensive removal of the gangue, but some of the facts bearing on the fineness and distribution of gold suggest considerable migration and reprecipitation of the gold. Little detailed information is available in the old reports concerning the oxidation of the tellurides. Some geological papers mention that at Nagyág native gold was rarely seen and when visible is said to have been secondary and to have resulted from the decomposition (oxidation) of the tellurides. In old mineralogical reports there are frequent references to the alteration (oxidation) of sylvanite, nagyagite and other Au-Ag tellurides to mustard gold, tellurite and other tellurites.

The oxidation of the telluride ores of Boulder County, Colorado are discussed in some detail by Kelly and Goddard (1969). There, the primary telluride veins are composed of an interlacing network of pyritic or marcasitic horn quartz seams in which the ore minerals are quite sparse and irregularly distributed. The primary ore and gangue minerals are numerous (about 67), the most important being quartz, roscoelite, ankerite, calcite, fluorite, barite, pyrite, marcasite, galena, sphalerite, sylvanite, petzite, hessite, calaverite, krennerite, various other tellurides, native tellurium and native gold.

The telluride veins have not been deeply weathered and the residual enrichment of gold is correspondingly slight. Partially oxidized ore contains abundant jarosite, limonite and tellurium oxides and in places some supergene native tellurium, mercury, hessite and the copper tellurides. Fine spongy gold in limonite ('rusty gold') is common in the outcrops and is in places associated with native silver and the silver halides. The geochemical behaviour of the principal metals, gold, silver, tellurium and iron is discussed in terms of acidities, oxidation potentials and chloride ion activities in the oxide zone. The mobility of gold has been generally low in the deposits; on the other hand silver has been extensively leached close to the surface, and only minor amounts were reprecipitated at depth. Tellurium was highly mobile in the oxide zone and has been extensively or completely leached from most of the vein outcrops. Eh-pH diagrams for the systems Te-H_2O, Ag-Te-S-H-O-Cl, and for the relations in the near surface telluride ores are given, as is also an equilibrium oxidation potential-chloride ion activity diagram for the system Ag-Te-S-H-O-Cl. Kelly and Goddard (1969) place considerable emphasis on the role of chloride in the various reactions involving the supergene history of gold, silver and tellurium.

Relatively little has been published about the oxidation of auriferous selenide-bearing deposits. Presumably in oxidized zones of these deposits gold appears mainly in the native form and the element selenium, as native selenium, seleniferous sulphur and as various selenites or selenates such as chalcomenite and kerstenite.

The oxidized zones of massive and disseminated base metal sulphide bodies are frequently enriched in gold (and silver) in many parts of the world. Much of this enrichment is due to removal of the gangue components, but some is also the result of chemical migration and redeposition of gold. These deposits commonly exhibit three well-defined zones in ideal cases – a gossan and oxidized zone in which the primary sulphides are leached and altered to minerals such as limonite, wad, jarosite, anglesite, etc.; a secondarily enriched sulphide zone at the base of the oxidized zone at or near the present or former water tables where sulphides such as chalcocite, marcasite, melnikovite pyrite, covellite and more rarely sphalerite, galena, pyrargyrite and proustite are developed; and a primary zone of pyrite, pyrrhotite and various base metal sulphides in massive aggregates or disseminated through intensely fractured, brecciated or faulted rocks of practically all types. Among these deposits we recognize the Ni-Cu orebodies associated with basic igneous rock complexes and the Cu-Zn orebodies commonly found in sedimentary and volcanic terranes. The gold content of the primary ores of these bodies varies widely, but only rarely as in the Kurokô ores of Japan and in a few other deposits are assays greater than 0.1 oz/ton recorded. The silver content varies between wide extremes; some bodies contain only a few tenths of an ounce to 1 oz/ton or so, others average several ounces or tens of ounces per ton. As an example of the variations in gold and silver the great Kidd Creek deposit at Timmins may be mentioned. The main massive sulphide orebodies contain practically no gold (<0.01 oz/ton) whereas the silver content, principally in the form of native silver, ranges up to 5 oz/ton or more. In most massive and disseminated sulphide bodies and in all porphyry copper deposits the Au/Ag ratio is generally much less than 1. The nature and distribution of the gold in the primary ores of these bodies is poorly known despite the importance of the subject. In some, finely divided native gold or electrum is present; in others there is much gold in telluride form and in minerals such as chalcopyrite, bornite, tetrahedrite and other sulphosalts; and in still others pyrite and arsenopyrite are the principal auriferous minerals. In the writer's experience the gold content of these bodies often varies directly with the copper, arsenic and antimony contents, and locally in some deposits with the lead and zinc contents; the silver content generally follows the copper or lead content of the ores. These generalizations are commonly not realized in local samples and even in some orebodies as a whole. In this category also belong the so-called 'porphyry' copper deposits that occur in rocks of many types but commonly in highly fractured granitic rocks such as granodiorite, monzonite and quartz-feldspar porphyries. Their primary gold content is low (~ 0.005 oz/ton) and their Au/Ag ratio is likewise low (~ 0.01). Much of the gold occurs in the native state in these bodies, but some is closely associated with chalcopyrite, bornite, enargite, tetrahedrite-tennantite and pyrite as submicroscopic particles or lattice constituents. Further details on the tenor and distribution of gold (and silver) are given in the following descriptions of oxidized massive sulphide and porphyry copper deposits.

Many of the massive sulphide deposits in Canada were marked by gossans and shallow oxidation zones, but few have been studied. At Sudbury some of the Ni-Cu orebodies had extensive gossans essentially composed of limonite-cemented wall-rock fragments and highly weathered residuals of the massive sulphide ore. Few of these gossans are available for study today, and the remains of those that are present have been considerably disturbed or removed by pitting, mining and road building making any reasonable attempt at adequate sampling virtually impossible. Nevertheless, some bulk grab sampling of some of these gossans has given some interesting results, as shown in Table 79. There is a slight leaching of gold, a marked enrichment of silver, a general enrichment of platinum, a leaching of palladium and general enrichments of selenium and tellurium in most gossans compared with the estimated averages of the primary ores.

All of the massive sulphide orebodies in the Bathurst-Newcastle area of New Brunswick were marked by gossans, some extensive and up to 10 ft or more in thickness. These

Table 79. Precious metal contents of gossans, Sudbury area, Ontario

Description	Au	Ag	Pt	Pd	Se	Te
			(ppm)			
Murray gossan						
Limonite and limonite-cemented weathered sulphides (average of 3 bulk samples)	0.06	6	0.260	0.135	35	2.0
Sudbury primary ores, estimated average	0.08	2.3	0.17	0.27	35	0.1
Vermilion Mine						
Massive limonite and limonite-cemented rubble (average of 2 bulk samples)	0.545	145	67.6	55.0	250	160
Fresh ore, mainly chalcopyrite and pyrite (average of 2 bulk samples)	1.88	100	35.0	108.0	165	115
Worthington Mine area						
Gossan; mainly limonite and rubble of country rock (average of 2 bulk samples)	0.025	3.5	1.25	0.045	76	1.0
Sudbury primary ores; estimated average	0.08	2.3	0.17	0.27	35	0.1

have been studied in some detail by the writer and his colleagues (Boyle and Davies, 1964; Presant, 1971; Davies *et al.*, 1969). Only a brief summary of the features with respect to gold and silver will be attempted here. The primary ores of the massive sulphide orebodies are composed, in decreasing order of abundance, of pyrite, sphalerite, galena, pyrrhotite and chalcopyrite. Less common are arsenopyrite, bornite and tetrahedrite. Small amounts of stannite, boulangerite, cassiterite and domeykite are also present. The distribution and nature of the primary gold in the various deposits is not known. In some deposits finely divided free gold is probably present, but considerable amounts of the metal seem to be either submicroscopic or lattice constituents of minerals such as pyrite, arsenopyrite, chalcopyrite, sphalerite and tetrahedrite. Primary silver tends to be enriched in the zones rich in lead and zinc, particularly where galena is abundant. The gossans are limonite-cemented conglomerates and are composed mainly of limonite with some wad in places both of which cement schist particles, till and stones. Below the limonitic cap there is often an oxidized zone and a residual type of gossan containing limonite, highly leached till, leached quartz, jarosite, scorodite, beudantite, anglesite, cerussite, pyromorphite, barite and highly leached and disintegrated residuals of pyrite and other sulphides. Below this again and along faults in some deposits there is an enriched secondary sulphide zone consisting mainly of pyrite and other sulphides with supergene covellite and chalcocite. The total thickness of all of these various zones only rarely exceeds 20 ft; commonly it is only a few feet. Much of the residual gossan material appears to have formed before Pleistocene time and is preglacial. The remainder is of post-Pleistocene age, for glacial boulders and stones of granitic and other composition are cemented by the limonite and other secondary minerals.

The results in Table 80 show that gold is enriched in most of the gossan zones developed on the massive sulphide bodies. The enrichment appears to be greatest where wad is developed with limonite, or where beudantite and other supergene minerals are present in the gossans. Most of the supergene sulphide zones also exhibit an enrichment in gold. Silver shows a trend similar to gold in the various parts of the gossans.

Table 80. Gold and silver contents of gossans, secondary sulphide zones and primary ores, Bathurst-Newcastle district, New Brunswick

Description	Au	Au	Ag	Ag
	(ppm)	(oz/ton)	(ppm)	(oz/ton)
Brunswick Mining and Smelting No. 6 Deposit				
Gossan, limonite cemented conglomerate (average of 14 bulk samples)	0.18	0.005	30.9	0.90
Gossan, leached zone and residual gossan below above (average of 6 bulk samples)	0.02	0.0006	4.3	0.12
Gossan, beudantite-rich residual material	0.42	0.012	107	3.13
Sulphide zone with some supergene covellite, chalcocite and pyrite (average of 2 bulk samples)	3.1	0.09	262	7.66
Primary sulphide zone (average assay of 3 bulk samples)	0.26	0.007	47.2	1.4
Heath Steele Mine				
Gossan, mainly limonite and wad (average of 4 bulk samples)	1.5	0.043	142.9	4.17
Sulphide zone with supergene covellite and chalcocite (average of 4 bulk samples)	0.5	0.014	95.9	2.80
Sulphide zone (average of primary ore)	0.06	0.002	23.1	0.7
Anaconda				
Gossan, mainly limonite and some wad (average of 2 bulk samples)	20	0.58	171	5.0
Sulphide zone, supergene covellite and chalcocite (average of 2 bulk samples)	2.8	0.08	109	3.2
Sulphide zone (average of primary ore)	0.03	0.001	42.0	1.2
Leger prospect				
Gossan, mainly limonite (average of 2 bulk samples)	1.9	0.05	86.8	2.5
Sulphide zone (average of primary ore)	0.68	0.02	36.5	1.06
Nigadoo veins				
Gossan, mainly limonite (average of 4 bulk samples)	0.181	0.005	220.1	6.4
Gossan, beudantite-rich (1 bulk sample)	0.41	0.01	314.6	9.1
Sulphide zone (average of primary ore)	0.095	0.0027	150.5	4.4

An excellent example of the enrichment of gold in the oxidized zones of a massive and disseminated sulphide deposit is provided by Mount Morgan in Queensland, Australia. This great deposit is a breccia pipe with numerous offshoots primarily mineralized with pyrite, pyrrhotite, magnetite, chalcopyrite, sphalerite, quartz and gold (Staines, 1953; Staff, Mount Morgan Limited, 1965; Cornelius, 1969). The host rocks are tuffs, pyroclastics, rhyolite, andesite and other volcanic rocks intruded by gabbro, diorite, quartz diorite, and rhyolite and quartz latite bodies. Virtually all of the orebodies occur in the intrusive rhyolite and the tuff and lava units.

The grade of the primary ore averages about 0.8 per cent copper and 0.112 oz Au/ton. Some of the gold is native, and some occurs in calaverite. It is also stated that considerable amounts of gold are intimately associated with pyrite, about 30 per cent in solid solution according to I.W. McPheat quoted by Cornelius.

The deposit was deeply weathered during Lower Jurassic time and a deep and extensive gossan (100 acres) and oxidized zone were developed down to a depth of 362 ft. The gossan and oxidized zone were then covered by Lower Jurassic sediments (Cornelius, 1967). Judging from old reports the principal minerals in the gossan and oxidized zone were limonite, hematite, kaolin, wad, cellular quartz, wisps of chalcanthite, chrysocolla, malachite and azurite, disintegrated pyrite, native copper, chalcocite, telluric ochres and gold. The change from oxidized to unoxidized ore was abrupt, and there was no enriched supergene copper sulphide zone, although minor amounts of chalcocite and covellite were noted a few feet below the gossan. Parts of the gossan and nearly all of the deep oxidized zone were greatly enriched in gold. Entire benches in the great open pit ran 5 oz Au/ton, and some large blocks of gossanous ore assayed 800 oz/ton. Silver was notably absent, the fineness of the gold averaging about 997. In the primary ore the gold/silver ratio is about 3:1. Some 2.5 million oz of gold were recovered alone from the gossan and oxidized ore. In some of the old descriptions rich silver-bearing siliceous kaolinitic patches are mentioned, but in general most of the copper and silver were extensively leached.

Cornelius (1969) gives some interesting facts about the migration of gold in the Mount Morgan orebody in the last 75 years. During this time gold has been taken into solution and deposited in stalactites of goethite and melanterite. Assays of these stalactites show them to contain from a trace to 0.161 oz Au/ton. Measurements of pH and Eh values of mine water dripping from the stalactites range from 2.3 to 3.0 and from +0.555 to +0.845 volts respectively.

Mount Morgan was probably near the sea during Lower Jurassic time, and one would expect that considerable amounts of wind-blown chlorine would have been present in the oxygenated meteoric waters leaching the orebodies. This component would complex with gold and silver rendering them mobile. Gold being less mobile than silver in the form of these complexes in the presence of $FeSO_4$ and other reductants would be more easily precipitated whereas silver would be dispersed. This natural refining action has probably led to the fabulous bonanza of gold in the gossan and oxidized zone of the deposit. In this respect it is interesting to note that Dunn (1905) thought that sea water was responsible for the enrichment of gold in the oxidized zone.

Many of the rich copper and gold-copper lodes of the Cobar mining field in New South Wales, Australia were oxidized to varying depths (Rayner, 1969). Most of the deposits are massive and disseminated deposits containing essentially pyrite, magnetite, chalcopyrite, pyrrhotite, sphalerite and galena with smaller amounts of cubanite, vallerite, bornite, tetrahedrite, arsenopyrite, bismuthinite, cassiterite, gold, and a number of other minerals as the primary constituents. The oxidation minerals derived from the above minerals are numerous and include limonite, malachite, azurite, chrysocolla, cuprite, atacamite, covellite, chalcocite, wad, cerargyrite, embolite, iodyrite, cerussite, anglesite, scorodite, erythrite and others. Some of the gossans and siliceous cappings were relatively rich in gold, native silver, cuprite, native bismuth and the bismuth ochres (oxides). Many of the gossans were leached of much of their copper, and some were also leached of their lead and zinc. A number of the deposits were secondarily enriched in supergene copper minerals, mainly chalcocite, at and near the present or past water tables. The oxidation zoning was generally as follows: a near surface siliceous-limonite zone, followed downward by a copper carbonate and oxide zone which gave over to an enriched chalcocite zone at or near the water table, below which the ores were mainly primary. In some deposits this oxidation zonation extended to depths of 500 ft or more. Gold appears to have been present in all of the oxidation zones, enriched in places and depleted in others.

According to a variety of old reports and papers, the great Rio Tinto pyritic copper deposits in Huelva, Spain were capped by extensive hematitic and limonitic gossans up to 100 ft thick. These contained practically no copper and only traces of silver and gold. Immediately below the gossan a clearly demarcated earthy zone was present, and this was greatly enriched in both gold and silver. Below this zone the massive pyrite was leached for 3 ft or more, and this was followed by an enriched chalcocite zone, also somewhat enriched in gold and silver. Below lay the immense pyritic lenses containing a little chalcopyrite, galena and sphalerite in which only traces of gold were present. Most of the mining has been in the pyritic lenses. Recently, however, mining of the 15 million tons of slightly auriferous gossan at Rio Tinto and an underlying enriched copper zone has been in progress (Pryor *et al.*, 1972). Most of these gossans and the underlying leached and enriched zones flank the massive pyritic lenses, now largely mined out, and overlie irregular chimney-shaped pyrite- and chalcopyrite-bearing stockworks. The gossan, composed mainly of hematite, goethite, jarosite and clay is considerably enriched in Au, Ag, Pb, As, Hg and $BaSO_4$. The underlying rich secondary sulphide zone contains abundant chalcocite. The grade of the gossan is 2.5 and 45 ppm gold and silver respectively (0.07 and 1.3 oz/ton). The gold and silver grades of the enriched sulphide zones and primary sulphide stockworks are not given. Much of the gold and silver in the gossan is evidently free since they can be removed by cyanide treatment. Pryor *et al.* (1972) discuss methods of sampling and data processing suitable for estimating grades and tonnages of auriferous gossans and similar oxidized ores that should be useful in dealing with these slightly enriched deposits.

At the Pueblo Viejo Gold Mine in the Dominican

Republic large bodies of gold-bearing oxide and sulphide ore are being prepared for mining.[31] The orebody covers an area of approximately 1200 m by 500 m, the host rocks being Early to Middle Cretaceous acid flows and pyroclastics, cherts and carbonaceous siltstones of the Los Ranchos Formation. These rocks are extensively silicified and pyropylitized in the vicinity of the primary mineralization that consists principally of pyrite, with lesser amounts of sphalerite, enargite, tennantite, covellite and gold-silver minerals in veins and disseminations. The weathered (oxidized) zone is some 30 m thick and is completely leached of sulphides leaving only gold and silver in a lateritic residuum and gossan. There has apparently been relatively little supergene enrichment of gold and silver although the latter metal does show a slight enrichment at the oxide-sulphide interface. The published grades of the ore reserves are as follows:

Weathered zone:	over 20 000 000 tons assaying 0.15 oz Au/ton and 0.76 oz Ag/ton.
Sulphide zone:	over 17 000 000 tons assaying 0.13 oz Au/ton and 1.12 oz Ag/ton; also 2.19 per cent Zn and 0.25 per cent Cu.

The so-called 'porphyry copper' deposits throughout the world provide a large production of gold and silver. Despite this, our knowledge of the details of the distribution and nature of the two precious metals in these deposits is largely unknown. Why this should be so is uncertain since nearly every other aspect of these bodies has been intensively investigated. Since both gold and silver are good indicators in geochemical prospecting for porphyry copper deposits an accurate knowledge of their chemistry, especially in the oxidized zones would be invaluable. The notes that follow are based on the analysis of grab samples from some deposits, a most unsatisfactory procedure, and on bits and pieces of information gleaned from personal communications and the extensive literature on the deposits. For the deposits in the United States and Mexico there is some general information on the distribution of gold and silver in the monograph edited by Titley and Hicks (1966).

The overall content of gold and silver in porphyry copper bodies is low, probably near the values 0.01 oz Au/ton and 0.1 oz Ag/ton. This compares with an average copper content of about 0.5 per cent in most of the bodies as a whole.

Many porphyry copper deposits exhibit three zones from the surface downward – an oxidized zone, a supergene sulphide zone and a primary sulphide zone. Some lack a supergene sulphide zone, whereas others lack both the oxidized zone and supergene sulphide zone, the primary mineralization being capped only by slightly oxidized and leached material a few feet in thickness. The latter type of deposit generally occurs only in glaciated terrains or at high altitudes; in arid, semiarid and humid tropical regions there is generally considerable oxidation, leaching and supergene enrichment of the bodies. In arid and semiarid regions the oxidized zones are often deeply leached leaving an iron-stained porous siliceous mass; in tropical regions a gossanous lateritic cap develops. In both cases, but particularly in the latter, there may be some residual accumulation of gold and silver as noted above for the Pueblo Viejo Mine in the Dominican Republic. Most such zones rarely contain more than 0.1 oz Au/ton and 0.5 oz Ag/ton although there are cases where the grades were evidently higher. Thus, it is said that the oxidized zones at Bingham were considerably enriched in gold and silver, as were also

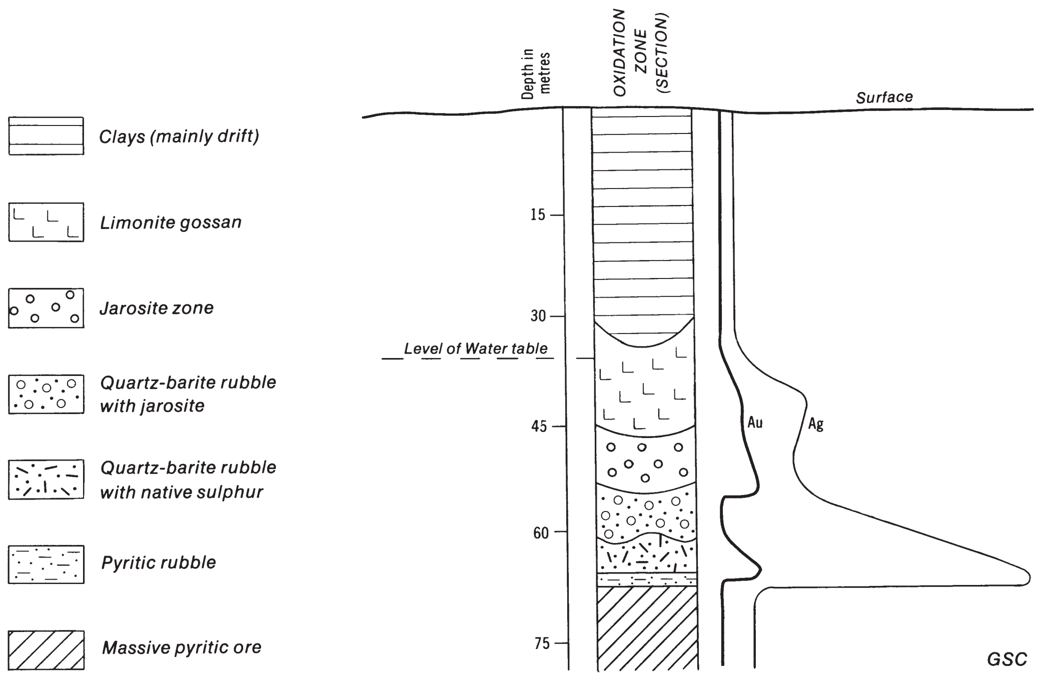

Figure 97. Localization of gold and silver in the oxidized zone of the Maikain 'S' deposit, northern Kazakhstan, U.S.S.R. (after Borodaevskaya and Rozhkov, 1974).

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[31] Information provided by the New York and Honduras Rosario Mining Co. of New York and the J.R. Simplot Company of Boise, Idaho.

those at Butte (Emmons, 1917). In actual fact it would appear from the records that the surface materials (leached outcrops) on the Bingham, Utah and Ely, Nevada porphyry copper deposits, as well as others in the southwestern United States, were worked first for gold. Later at depth these deposits blossomed into enormous copper orebodies of both secondarily enriched and primary types. In the oxidized zones of certain porphyry copper deposits, copper carbonates and silicates may be extensively developed. These generally carry only a little gold and silver (0.01–0.2 ppm Au; 0.34–6.8 ppm Ag). The supergene sulphide zones, marked by the development of chalcocite and covellite, are enriched in gold and silver in most deposits. Few assays of such zones are available, but most appear to carry the two precious metals in amounts around 0.03 oz Au/ton and 0.5 oz Ag/ton (1.02 and 17.1 ppm respectively). This compares with an average of about 2 per cent copper for these zones. Much of the gold and silver appears to be lattice or submicroscopic constituents of chalcocite, but other modes of occurrence are also possible such as the native metal.

In U.S.S.R. it appears that many of the gold deposits are deeply oxidized both in the Urals and in the various gold belts of Siberia. Most of the deposits exhibit features similar to those described above, and hence the details can be omitted. Few of the descriptions in the U.S.S.R. literature give grades and tonnages, and it is most difficult to ascertain the enrichment (or depletion) factors with respect to gold and silver and their accompanying elements. In a paper by Roslyakov *et al.* (1972) describing the general oxidation phenomenon in a large number of oxidized gold deposits in eastern Transbaikal and the Kuznetskii Alatau, the authors state that the ratio of the mean gold content in the oxidized zones to that in the primary ores fluctuates in the range 1.1 to 1.5. It is also stated that the oxidation zones of various metasomatic deposits exhibit less enrichment in gold than other types. Other general discussions of the oxidation phenomena in gold-silver deposits in U.S.S.R. may be found in the publications by Chukhrov (1947), Smirnov (1951), Al'bov (1952,1960), Kreiter *et al.* (1959), Berzon and Bushlyakov (1971), Roslyakov *et al.* (1971*a*, 1972), Petrovskaya (1973), Rusakova and Povarennyk (1973), Nesterov *et al.* (1974*a,b*), Borodaevskaya and Rozhkov (1974), Nestorenko *et al.* (1976) and Roslyakov (1976). In the publication by Borodaevskaya and Rozhkov (1974), the localization of gold and silver in the Maikain 'S' deposit is given. This deposit is a massive pyritic deposit with small amounts of sphalerite, chalcopyrite, galena, tetrahedrite, enargite and bornite. Quartz and barite are the principal gangue minerals. The gossan and oxidized zones provide a gold-silver ore, the two elements being concentrated in the jarositic lower parts of the oxidized zone as shown in Figure 97.