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> Gold is characterized chemically by an
> extreme indifference to the action of all
> bodies usually met with in nature.
> – T.K. Rose and W.A.C. Newman, 1937

# Chapter II. Chemistry, mineralogy and geochemistry of gold

## General chemistry

Gold, Au: atomic no. 79; atomic wt. 196.967; specific gravity 19.32 (20°C); melting point 1063.0°C; valence 1,3.

Comprehensive reviews of the chemistry and physical metallurgy of gold are contained in the works by Mellor (1923), Rose and Newman (1937), Gmelin (1950), Sidgwick (1950), Pascal (1957), Emery and Leddicotte (1961), Badone and Spence (1961), Pourbaix *et al.* (1963), Johnson and Davis (1973) and Myerscough (1973). The summary that follows deals principally with the chemical features of gold as they affect the geochemistry of the element.

Gold is a member of Group IB of the periodic system, which includes copper (Cu), silver (Ag), and gold (Au). Except that the so-called 'coinage metals' exhibit monovalency (oxidation state +1), there is little resemblance to the alkali metals of Group IA. In fact, the differences between the two subgroups are marked, as shown for instance by the general decrease in reactivity of the Group IB elements with increase in atomic number as contrasted with the reverse behaviour of the Group IA elements. As might be expected from electron orbital considerations, there is some similarity between Ni, Pd and Pt (Group VIII) and the corresponding elements of Group IB, namely Cu, Ag and Au. Thus, platinum has only one electron less than gold, and since the energy differences are small in the electronic constitution of the two elements, the differences in the chemical behaviour of the two elements in a few respects are slight. In natural environments, however, there is no close relationship between gold and platinum except that they tend to occur in the native state, and some platinum may be present in certain varieties of native gold and vice versa. There are no particular similarities between gold and mercury, the corresponding element in Group IIB of the periodic system. As is well known, however, gold and mercury form an amalgam, and well-defined compounds occur in the system Au-Hg; natural amalgam is known, but formal Au-Hg compounds do not appear to occur in nature, or if they do they have not been adequately characterized. There are marked differences in the chemistry of silver and gold, a consequence that is attributable to the diminishing effect of the lanthanide contraction between atomic numbers 57 (La) and 79 (Au).

Gold is considered by some to be a transition element of the third series, although it does not fulfil the necessary

Table 1. Energetic properties of copper, silver and gold

| Property | Copper | Silver | Gold |
|---|---|---|---|
| Outer electron configuration | $3d^{10}4s^{1}$ | $4d^{10}5s^{1}$ | $5d^{10}6s^{1}$ |
| Oxidation states (valence) (Those in brackets are uncommon) | 1, 2, (3) | 1, 2, (3) | 1, 3 |
| Electronegativity | 1.9 | 1.9 | 2.4 |
| Ionization potential, eV | Cu(I) 7.724<br>Cu(II)20.29 | Ag(I) 7.574<br>Ag(II)21.48 | Au(I) 9.223<br>Au(III) ~30 |
| Lattice energy coefficient | Cu(I) 215<br>Cu(II)630 | Ag(I)180 | Au(I) ~183 |
| Atomic radius, Å (co-ordination in brackets) | 1.24 (8)<br>1.28 (12) | 1.40 (8)<br>1.44 (12) | 1.40 (8)<br>1.44 (12) |
| Ionic radius, Å (co-ordination in brackets) | Cu(I) 0.96 (6)<br>Cu(I) 1.00 (8)<br>Cu(II) 0.82 (6) | Ag(I) 1.13<br>Ag(I) 1.13 (10)<br>Ag(II) 0.97 (6) | Au(I) 1.37<br>Au(I) 1.37<br>Au(III) 0.78 (4) sq.<br>Au(III) 0.91 (6) |
| Miscellaneous radii, Å | Cu(I) (in fluorides) 1.00<br>Cu(I) (in oxides) 1.05<br>Cu(II) (in fluorides) 0.87<br>Cu(II) (in oxides) 0.97<br>Cu (tetrahedral covalent) 1.35<br>Cu(I) (hydrated) 1.7<br>Cu(II) (hydrated) 3.5 | Ag(I) (in fluoride) 1.33<br>Ag(I) (in oxides) 1.35<br>Ag (tetrahedral covalent) 1.53<br>Ag(I) (hydrated) 1.7 | Au(I) (hydrated) 1.4 |
| Ionic potential, $\frac{Z}{r}$ | Cu(I) 1.00<br>Cu(II) 2.44 | Ag(I) 0.88 | Au(I) 0.73<br>Au(III) 3.30 |

Sources: Szádeczky-Kardoss (1958); Green (1959); Samsonov (1968); Whittaker and Muntus (1970).

Note: The values given for the various radii are approximations at best. Those chosen appear to be the most satisfactory from the viewpoint of the geochemistry of gold, but as is well known all radii should be used with caution, since the radius of an element varies widely depending on the structure of the substance containing the element, the co-ordination configuration of the element and other factors.

electronic conditions[16] that characterize transition elements. Gold is a soft, yellow metal with a moderately high melting point (1063.0°C) and a high electrical and thermal conductivity exceeded only among the elements by silver and copper. It is the most malleable and ductile of metals; 1 oz of gold can be beaten into foil some 300 ft$^2$ in area. Of all the elements, gold in its pure state is undoubtedly the most beautiful, especially when it occurs in crystalline groupings or in dendritic and arborescent arrangements.

The energetic properties of gold, together with those of copper and silver, the two elements with which it is so often associated in nature, are given in Table 1. The thermodynamic properties of the element, its ions and compounds are given in Table 2. The Pourbaix (Eh-pH) diagrams for some of the common gold species are shown in Figure 1, and the cycle of gold interconversions under natural conditions is displayed in Figure 2. Additional data can be found in the publications by Kelley (1960), Wicks and Block (1963), Sillén and Martell (1964), Samsonov (1968), Gedansky and Hepler (1969), Hancock and Finkelstein (1971), Finkelstein and Hancock (1974), and Kubaschewski and von Goldbeck (1975). The vapour pressure of gold has been recently discussed in detail by Paule and Mandel (1972). The vapour pressure of the gold standard is $9.92 \times 10^{-9}$ atm at 1300°K increasing to $1.87 \times 10^{-3}$ atm at 2100°K. The heat of sublimation of gold is given as 87 720 ± 210 cal/mole at 298°K; the corresponding value for silver

Table 2. Thermodynamic data on gold

| Formula | State | ΔH° | ΔF° | S° |
|---|---|---|---|---|
| Au (metal) | c | 0.0 | 0.0 | 11.32 |
| Au(I) | aq |  | 39.0 |  |
| Au (III) | aq |  | 103.6 |  |
| $Au_2O_3$ | c | 19.3 | 39.0 | 30.0 |
| $H_2AuO_3^-$ |  |  | –45.8 |  |
| $HAuO_3^{2-}$ | aq |  | –27.6 |  |
| $AuO_3^{3-}$ | aq |  | –5.8 |  |
| $Au(OH)_3$ | c | –100.0 | –69.3 | 29.0 |
| $Au(OH)_3$ | aq |  | –61.8 |  |
| AuCl | c | –8.4 | –4.2 | (24.)* |
| $AuCl_3$ | c | –28.3 | –11.6 | (35.) |
| $AuCl_3 \cdot 2H_2O$ | c | –167.7 | –123.3 | (54.) |
| $AuCl_4$ | aq | –77.8 | –56.2 | 61. |
| AuBr | c | –4.4 | –3.7 | (27.) |
| $AuBr_2^-$ | aq |  | –27.1 |  |
| $AuBr_3$ | c | –13.0 | –5.9 | (24.) |
| $AuBr_3$ | aq | –9.2 |  |  |
| $AuBr_4^-$ | aq | –45.5 | –38.1 | 75. |
| AuI | c | 0.2 | –0.76 | (28.5) |
| $Au_2P_3$ | c | –24.1 |  |  |
| $Au(CN)_2^-$ | aq | 58.4 | 64.4 | 29.5 |
| $Au(CNS)_2^-$ | aq |  | 57.7 |  |
| $Au(CNS)_4^-$ | aq |  | 130.1 |  |

Sources: Latimer (1952); Handbook of chemistry and physics, 53rd ed.; Chemical Rubber Co., Cleveland, Ohio, 1972.

Notes: ΔH° – the standard heat of formation in kilocalories of the substance or ion from its elements at 25°C

ΔF° – the standard free energy of formation in kilocalories of the substance from its elements at 25°C

S° – the entropy of the substance or ion in cal/degree in its thermodynamic reference state at the reference temperature of 25°C

c – crystalline

aq – in aqueous solutions

*Values in parentheses are estimated.

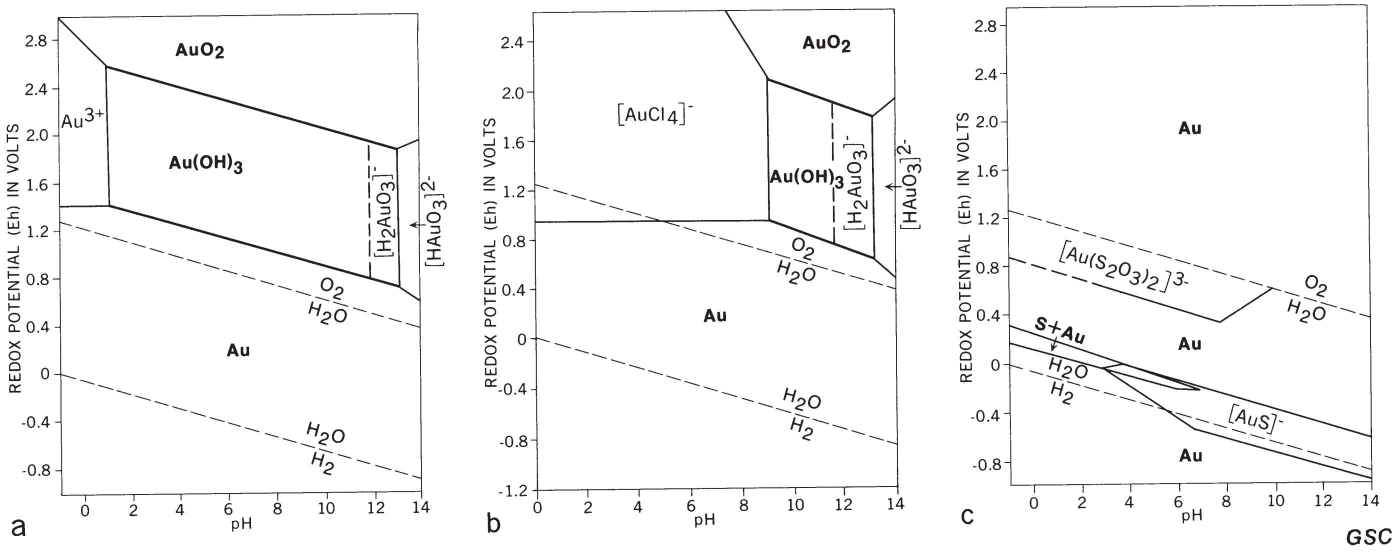

Figure 1. Pourbaix (Eh-pH) diagrams for gold. (a) System Au-$H_2O$ at 25°C and 1 atm total pressure; concentrations of all gold species $10^{-4}$M. (b) System Au-$H_2O$-Cl at 25°C and 1 atm total pressure; concentration of Au(III) = $10^{-2}$M, $C1^-$ = 2M. (c) System Au-S at 25°C and 1 atm total pressure; concentration of all sulphur species = $10^{-1}$M. [Solid species are shown in bold type, dissolved species in lighter type. For details of the thermodynamics of the solution chemistry of gold see the works by Latimer (1952), Pourbaix *et al.* (1963), Tyurin (1965*b*), Garrels and Christ (1965), Goleva *et al.* (1970*b*), Hancock and Finkelstein (1971) and Finkelstein and Hancock (1974).]

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[16] Strictly speaking, the transition elements are characterized by an inner *d* or *f* level, which is not filled to capacity, e.g., nickel. In gold the 5*d* orbital is completely filled.

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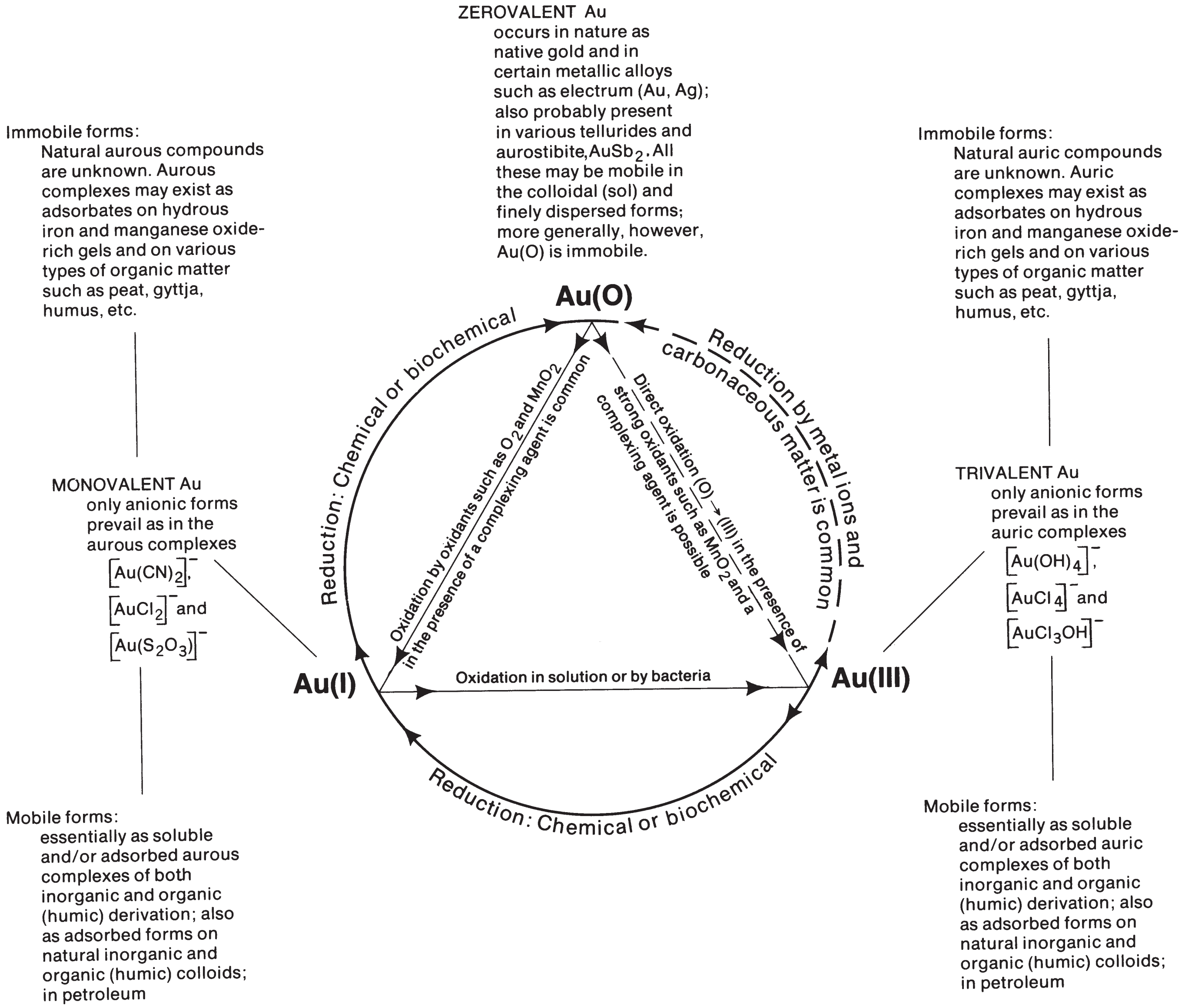

ZEROVALENT Au
occurs in nature as native gold and in certain metallic alloys such as electrum (Au, Ag); also probably present in various tellurides and aurostibite, $AuSb_2$. All these may be mobile in the colloidal (sol) and finely dispersed forms; more generally, however, Au(O) is immobile.

Immobile forms:
Natural aurous compounds are unknown. Aurous complexes may exist as adsorbates on hydrous iron and manganese oxide-rich gels and on various types of organic matter such as peat, gyttja, humus, etc.

MONOVALENT Au
only anionic forms prevail as in the aurous complexes
$[Au(CN)_2]^-$,
$[AuCl_2]^-$ and
$[Au(S_2O_3)]^-$

Mobile forms:
essentially as soluble and/or adsorbed aurous complexes of both inorganic and organic (humic) derivation; also as adsorbed forms on natural inorganic and organic (humic) colloids; in petroleum

Immobile forms:
Natural auric compounds are unknown. Auric complexes may exist as adsorbates on hydrous iron and manganese oxide-rich gels and on various types of organic matter such as peat, gyttja, humus, etc.

TRIVALENT Au
only anionic forms prevail as in the auric complexes
$[Au(OH)_4]^-$,
$[AuCl_4]^-$ and
$[AuCl_3OH]^-$

Mobile forms:
essentially as soluble and/or adsorbed auric complexes of both inorganic and organic (humic) derivation; also as adsorbed forms on natural inorganic and organic (humic) colloids; in petroleum

Figure 2. Cycle of gold interconversions in nature.

is 68 010 ± 300 cal/mole. These figures are of interest in natural systems in that they indicate that silver is the more mobile of the two elements at high temperatures.

Gold is usually found in one of three oxidation states: 0 (native), +1 (aurous) and +3 (auric) designated further as Au, Au(I) and Au(III) in this volume. Au(II) and Au(V) states are also known to occur in certain complex arrangments (Bergendahl, 1975). These appear to be relatively unstable states and probably do not occur in nature, except possibly in some organic-rich or chloride-rich natural waters. Gold in the native state is the most noble of metals. It is chemically unreactive and is not affected by water or most acids, nor attacked by oxygen or sulphur. The halogens react readily with gold as do also solutions that generate them such as aqua regia. Gold dissolves readily in alkali cyanide solutions in the presence of air, sparingly in alkali sulphide solutions, readily in selenic acid at about 225°C, readily in solutions containing telluric and sulphuric or phosphoric acid, readily in sulphuric and hydrochloric acid solutions containing an oxidizing agent such as $MnO_2$, and sparingly in alkali thiosulphate solutions. The element is probably sparingly soluble in solutions containing HCl and $CuCl_2$ in the presence of an oxidizing agent; also sparingly soluble in ferric chloride and ferric sulphate solutions containing an oxidizer. Finely divided gold is said by some investigations to be slightly soluble in alkali hydroxides. These and other reactions are discussed in the sections on natural waters, soils and oxidation processes in gold-bearing deposits. Mercury dissolves or amalgamates about 0.7 per cent by weight of gold at 25°C, and molten tellurium forms an intermetallic compound with the element.

Crystallographically gold belongs to a group that includes gold, silver, copper and lead. All of these metals are isometric, hexoctahedral – $4/m\ \bar{3}\ 2/m$ – and have the copper-type structure with the atoms lying at the points of a face-centred cubic lattice. This structure conforms to the space group F*m* 3*m*, and the unit cell contains 4 atoms. The cell edges for the four pure metals are as follows:

| | Cu | Au | Ag | Pb |
|---|---|---|---|---|
| $a_0$Å | 3.61496(18°C) | 4.07825(25°C) | 4.08548(20°C) | 4.9496(20°C) |

The atomic radius of gold is identical to that of silver (1.44Å), a feature that permits a continuous alloy series with a minimum cell edge at about 20 per cent silver. In nature, however, the series appears to be discontinuous. There is much less similarity in the atomic radii of gold (1.44Å) and copper (1.28Å), and as a consequence most samples of native gold contain relatively small amounts of copper (up to 20% Cu). Native copper, likewise, usually contains only traces of gold. In the laboratory gold forms alloys with a large number of metals, among which the most important are Ag, Cu, Al, Cd, Hg, Co, Pb, Fe, Ni, Pd, Pt, Sn, Ga, Ca, In and Zn. Some of these elements, such as Ag, Cu, Ni, Pd and Pt, are miscible with gold in all proportions. Details of these alloys are given by Badone and Spence (1961), Wise (1964), and Raynor (1976). Natural gold invariably contains some of the elements noted above, particularly Ag, Cu, Al, Fe, Bi, Sn, Pb, Zn, Pd and Pt. The colour of natural gold alloys is largely dominated by silver. With increasing content of silver the golden colour is attenuated until at about 65 per cent silver the colour of the alloy is barely distinguishable from pure silver.

The effect of mercury on gold has been known for centuries. It is usually said that mercury 'dissolves' gold, but this is an error that has crept into the literature and has been repeated for many years (Brown, 1960). In actual fact the solubility of gold in mercury is slight, only 0.13 atomic per cent at 20°C. The amalgamating effect of mercury is essentially the result of mechanical mixing, wetting and surface reactions between gold and mercury, about which we know little. On the other hand gold forms an alloy with mercury, the maximum solid solubility of Hg in Au being approximately 35 atomic per cent. At least three artificial gold-mercury compounds are known in the system Au-Hg – $Au_3Hg$, a second compound somewhat richer in gold than $Au_3Hg$ and an indefinite compound near the composition $Au_2Hg$ (Rolfe and Hume-Rothery, 1967; Berndt and Cummins, 1970). Lindahl (1970) also synthesized a phase $Au_6Hg_5$ at 25 and 80°C. Other phases, such as $AuHg_2$, $Au_2Hg_3$ and $Au_5Hg_8$, also seem to be stable in the system Au-Hg (Shklyar and Kakovskii, 1972). A compound close to $Au_2Hg_3$ and called gold amalgam occurs in nature. Its structure and composition require further work.

In its compounds gold as Au(I) (aurous) and Au(III) (auric) has the electronic configuration of $d^{10}$-type and $d^8$-type respectively and exhibits mainly a covalent character because of the high ionization potentials of the two states of oxidation. This is particularly so in its natural compounds such as the tellurides and the antimonide, $AuSb_2$ (aurostibite). There once was some slight evidence for the existence of Au(II) in certain gold-organic complexes, and compounds with empirical compositions such as AuS and $AuCl_2$ might suggest a (II) oxidation state. It is, however, now generally agreed that compounds such as AuS contain equal numbers of Au(I) and Au(III) species and should be characterized as mixed compounds written as $Au(I)_2S{\cdot}Au(III)_2S_3$. The compound $Cs_2Au_2Cl_6$ also appears to contain gold in both the (I) and (III) states rather than in the (II) state. The possible transitory (catalytic) existence of Au(II) in redox reactions involving $Fe^{2+}$ is discussed by Rich and Taube (1954).

The aqueous chemistry of gold is essentially that of complex ions since the ions $Au^{+1}$ and $Au^{+3}$ are unstable in water because of their high oxidation potentials (Fig. 1). Both Au(I), $d^{10}$, and Au(III), $d^8$, are B-type metal ions, which means that the stability of their complexes tend to decrease with increasing electronegativity of the ligand donor atom. Thus, the stability order for the halogen complexes is $I^- > Br^- > Cl^- > F^-$ where the order of electronegativities is $F^- > Cl^- > Br^- > I^-$. Similarly the stability of the various complexes with the donor atoms in Groups VA and VIA fall in the order Bi > Sb > As > P and Te > Se > S > O. This explains why gold tellurides, gold bismuthide and the antimonide (aurostibite) are stable enough to occur as minerals whereas we do not find natural gold selenides (*sensu strictu*), sulphides, oxides and arsenides. Nevertheless there is a bond between gold and selenium and arsenic since the precious metal is often enriched in deposits containing abundant selenides, arsenides and their oxidized derivatives. Smirnov and Entin (1975) have also noted a bond between gold and phosphorus in genetically diverse phosphatic deposits.

Au(I) generally exhibits linear twofold co-ordination, although tetrahedral fourfold co-ordination is also observed in some aurous substances. Most aurous compounds that are not complexes are insoluble with the exception of AuCN. Aurous oxide, $Au_2O$, and aurous hydroxide, AuOH, are mentioned in the literature, but recent research throws some doubt on their existence. Aurous chloride, AuCl, aurous bromide, AuBr, and aurous iodide, AuI, can be prepared. The chloride slowly disproportionates in water to yield metallic gold and auric chloride. The bromide and iodide behave in a similar manner, although not as rapidly. Aurous fluoride has not been prepared, probably because it is unstable in the presence of water. Aurous chloride dissolves in alkali chloride solutions to form the chloroaurite (I) complex ion $[AuCl_2]^-$. Aurous bromide and iodide behave in a similar manner in solutions containing an excess of bromide or iodide. Aurous cyanide, AuCN, can be easily prepared. It dissolves in alkali cyanide solutions to form the aurous cyanide complex $[Au(CN)_2]^-$. Aurous sulphide, $Au_2S$, is the most stable of the sulphides of the element. It is insoluble in water ($K_{sp} = <10^{-13}$) but may form a colloid; it is insoluble in most acids, soluble in strong oxidizing agents such as aqua regia, soluble in alkali cyanide solutions, and soluble in alkali polysulphide solutions to give thioaurite(I) compounds of the type Na[AuS]. Aurous polysulphides characterized as $Na_4[Au_2S_3]$, $K_3[AuS_2]$ and $K_5[AuS_3]$ are obtained by the action of polysulphide solutions on aurous sulphide and other aurous and auric compounds in solution. These polysulphides are slightly soluble in water. Acidification of a solution containing thioaurite(I) compounds or aurous polysulphides yields aurous sulphide. Treatment of an acidified solution of $K[Au(CN)_2]$ with hydrogen sulphide, likewise, throws down $Au_2S$. Aurous thiosulphates of the type $Na[Au(S_2O_3)]$ can be prepared, but they are not as stable as the fourfold complex $Na_3[Au(S_2O_3)_2]$. Aurous thiosulphate is very soluble in water giving complex ions of the type $[Au(S_2O_3)]^-$ and $[Au(S_2O_3)_2]^{3-}$. The later complex is apparently of the open chain type commonly written as $[O_3S{\cdot}S\text{-}Au\text{-}S{\cdot}SO_3]^{3-}$. By loss of sulphur, complex sulphites of the form

$[O_3S\text{-}Au\text{-}SO_3]^{3-}$ are derived. Oxy-salts of gold(I) are uncommon. There is no simple carbonate or nitrate, and the existence of a sulphate is doubtful. The gold(I) thiocyanate, AuSCN, can be prepared. It is highly insoluble in water.

Summarizing, we observe that gold(I) is characterized by numerous complexes that are stable in aqueous solution. Most of these are monomeric in character, familiar examples being $[AuCl_2]^-$, $[Au(CN)_2]^-$ and $[Au(S_2O_3)]^-$. Crystalline compounds of the type $K[Au(CN)_2]$ can be obtained, and the acid $H[Au(CN)_2]$ can be isolated. Numerous complexes of Au(I) with substituted sulphur, arsenic and antimony ligands are also known. Some of these such as $[AuS]^-$, $[AuS_2]^{3-}$, $[Au_2S_3]^{4-}$, $[AuSb]^{2-}$ and the thioarsenito and thioantimonito complexes, of the type $[Au(AsS_3)]^{2-}$ and $[Au(SbS_3)]^{2-}$, are probably of great importance in the transport of gold in endogenic processes in nature.

Gold(I) also forms a number of organometallic compounds (alkyls, aryls, olefins, etc.) and chelates, but these are much too numerous and complicated to be discussed here. The interested reader should consult the summary by Johnson and Davis (1973) and the specialized reviews by Jack and Powell (1972), Nesmeyanov *et al.* (1974) and Johnson (1976). The organometallic aurous compounds are as a rule not as stable as the corresponding auric compounds. Some of the aurous organometallic compounds such as the phosphine, arsine, mercaptide and methylated complexes and chelates, may occur in natural settings, especially those rich in humus; none of these compounds have, however, been characterized.

Gold(III) commonly exhibits fourfold planar co-ordination, although higher co-ordination numbers, fivefold trigonal bipyramidal and sixfold octahedral, are possible. Some of the complexes of Au(III) are isomorphous with those of Cu(III) and Ag(III). Most of the auric compounds are powerful oxidizing agents. Gold(III) hydroxide, $Au(OH)_3$ is obtained by the addition of alkali hydroxide to solutions containing chloroaurate ion, $[AuCl_4]^-$. The hydroxide is probably not a true hydroxide but rather a hydrated acid hydrate of some form. The hydroxide can be dehydrated to give auric acid $AuO(OH)$ and ultimately the oxide $Au_2O_3$. Both these oxides have amphoteric properties; in acidic solutions they give complexes of the type $[AuCl_4]^-$ and $[Au(SO_4)_2]^-$, and in basic solutions complexes characterized as $[Au(OH)_4]^-$ or $[AuO_2]^-_{aq}$ are stable. The last two are commonly referred to as aurate complexes, the corresponding salts such as, $KAuO_2 \cdot 3H_2O$, being designated aurates. Gold(III) hydroxide when treated with strong alkalies yields another series of aurates characterized by the ion $AuO_3^{3-}$; salts such as $Na_2HAuO_3$ and $Na_3AuO_3$ have been prepared.

Gold(III) forms compounds with all of the halides. Auric fluoride is not stable in water and is rapidly decomposed. The chemistry of the chloride, bromide and iodide is similar. Auric chloride and bromide are soluble in water, in which they are partly hydrolyzed to give species such as $[AuCl_3OH]^-$; excess chloride or bromide ion yields the complex chloraurate or bromoaurate ions, $[AuCl_4]^-$, $[AuBr_4]^-$. Chloroauric acid, $HAuCl_4 \cdot 4H_2O$ and the corresponding bromine compound can be isolated, and well defined salts such as $KAuCl_4$ and $Ca(AuCl_4)_2$ are known. The stability of the auric halide complexes increases in the order $I > Br > Cl > F$. The phase diagram of the gold-chlorine system is discussed by Janssen *et al.* (1976). Two compounds occur in the system – AuCl and $Au_2Cl_6$.

Gold(III) salts of oxyanions are not particularly stable, but solutions containing complex auric nitrates, sulphates, etc., e.g. $[Au(NO_3)_4]^-$, $[Au(SO_4)_2]^-$ can be prepared. Gold selenate, $Au_2(SeO_4)_3$, and gold selenite, $Au_2(SeO_3)_3$, are relatively stable.

Gold(III) cyanides of the type $K[Au(CN)_4] \cdot xH_2O$ are known. In solutions containing excess cyanide they are said to form the various complex ions $[Au(CN)_4]^-$, $[Au(CN)_5]^{2-}$ and $[Au(CN)_6]^{3-}$. Gold(III) thiocyanates are known; the most common of these $K[Au(SCN)_4]$ is insoluble in water.

Gold(III) sulphide, $Au_2S_3$, can be prepared by the action of $H_2S$ on auric salts, but it is readily reduced in water, yielding $Au_2S$ and sulphur. It is soluble in alkali sulphide and polysulphide solutions to give thioaurate(III) compounds, but these are unstable and degrade to the more stable thioaurite(I) species.

Gold(III) forms numerous inorganic complexes, some of which have been mentioned above. Most of these are anionic complexes. Relatively little is known about soluble cationic and neutral gold complexes but Beneš (1967) and Beneš and Riedel (1967) consider that in strongly acid chloride solutions gold exists prevailingly in the form of undissociated $HAuCl_4$. With increasing pH, hydrolysis occurs with the formation of positively charged hydrolytic products (pseudocolloids). Gold(III) also forms a host of organometallic compounds and chelates that are too numerous and complicated to be discussed here. They are reviewed by Jack and Powell (1972), Johnson and Davies (1973) and Nesmeyanov *et al.* (1974). Some of these compounds and complexes may be of importance in the geochemistry of gold in organic (humic) environments, but as yet none have been characterized.

Gold forms a large number of complex compounds in which the state of oxidation of the element is multiple or uncertain. Reference to the sulphide AuS has already been made; it appears to be a compound of $Au_2S$ and $Au_2S_3$. The salt, $Na[AuS] \cdot H_2O$, has been isolated. There are a number of complex double sulphides, including $Ag_3AuS_2$, AgAuS and $Ag_3AuS_2$; a number of tellurides; two selenides AuSe and $Au_2Se_3$; seleno-tellurides of the type $Au_2SeTe$; and mixed selenides and tellurides of the types $Ag_3AuSe_2$ and $Ag_3AuTe_2$; various telluride halides of the type $AuXTe_2$ (where $X = Cl$, Br, I) are also known (Rabenau *et al.*, 1970). Of all these artificial compounds only the tellurides and the silver-gold selenide are known in nature; some of the double sulphides would seem to be stable enough to persist in nature and may occur as minerals. One of these, the double sulphide, $Ag_3AuS_2$, uytenbogaardtite has recently been described. The antimonide, $AuSb_2$, occurs in nature as aurostibite and the silver-gold selenide, $Ag_3AuSe_2$, as fischesserite. The arsenide is unknown as a natural mineral, and as far as the writer can ascertain it has not been synthesized.

Gold has a marked affinity for the elements tellurium and bismuth and less so for antimony. The reason for this is obviously that the various combinations Au-Te, etc. give a particularly stable electronic configuration. The atoms of Te, Bi and Sb have large radii, and this was noted by Goldschmidt (1954) who sought to explain the affinity of gold with these elements as due to their ability to form packings such that gold could be collected (captured) in their interstices. The phenomena are, however, mainly connected with the electronegativity of the donor atoms of the complexes as discussed above. There are a number of gold tellurides in nature, a poorly differentiated bismuthide and an antimonide. Numerous artificial Au-Sb compounds are known (Muller, 1974). Gold does not form a selenide (*sensu strictu*) in nature, but as noted above there is a silver-gold selenide (fischesserite) that occurs in places (*vide infra*). The various phases in the system gold-bismuth-tellurium have been investigated by Gather and Blacknik (1974).

Gold in solution is readily reduced to the metal by nearly all of the metals and metallic ions and by numerous compound substances. Of interest in this respect in natural environments are the ions $Fe^{2+}$ and $Mn^{2+}$ and a great variety of organic compounds including citric and acetic acid and their salts. This feature of the chemistry of gold is discussed in more detail in the sections on soils and natural waters and in the chapter on the oxidation of gold-bearing deposits.

Gold forms a colloid readily when a dilute gold solution is reduced. The particle size is apparently determined by the concentration, temperature and pH. A low pH favours large particles whereas a high pH yields small particles. Gold colloids are hydrophobic and generally carry a negative charge. In a recent study Turkevich *et al.* (1951) have shown that in the formation of gold colloids nucleating agents can be identified with reducing agents which form a mixed polymer with chlorauric ion before the reduction to the gold nucleus takes place. They also showed that the law of growth of the gold colloids is exponential. The average size, the deviation from the average size and the character of the particle size distribution curve are determined by the amount of gold, the nucleation process and the law of growth.

Table 3. Solubility of some gold compounds

| Compound | Solubility in water, g/100cc (25°C) | Solubility in other reagents |
|---|---|---|
| Au | Insoluble | Soluble in aqua regia, KCN, hot $H_2SO_4$; insoluble in acids and alkalies |
| AuBr | Insoluble | Dissociates in acids; soluble in NaCN |
| $AuBr_3$ | Slightly soluble | |
| AuCl | Very slightly soluble | Soluble in HCl, HBr |
| $AuCl_3$ | 68 | |
| AuCN | Very slightly soluble | Soluble in KCN, $NH_4OH$; insoluble in alkalies |
| $HAu(CN_4)\cdot 3H_2O$ | Very soluble | |
| AuI | Very slightly soluble | Soluble in KI |
| $AuI_3$ | Insoluble | Soluble in iodides |
| $H[Au(NO_3)_4]\cdot 3H_2O$ | Soluble, dissociates | Soluble in $HNO_3$ |
| $Au_2O_3$ | Insoluble | Soluble HCl, concentrated $HNO_3$, NaCN |
| $Au_2O_3\cdot xH_2O$ | $5.7 \times 10^{-11}$ | Soluble HCl, NaCN, concentrated $HNO_3$ |
| $Au_2P_3$ | Insoluble | Insoluble in HCl, dilute $HNO_3$ |
| $Au_2Se_3$ | Insoluble | |
| $Au_2S$ | Insoluble | Soluble aqua regia, KCN; insoluble in acids |
| $Au_2S_3$ | Insoluble | Soluble in $Na_2S$ |
| $AuTe_2$ | Insoluble | |

Source: Handbook of chemistry and physics, 53rd ed.; Chemical Rubber Co., Cleveland, Ohio, 1972.

The possible role of gold colloids in the migration of gold in nature is discussed in a subsequent section.

Table 3 lists the solubility constants of some of the common salts and other compounds of gold likely to be encountered in nature.

## Isotopes

Natural gold consists of only one isotope, $^{197}Au_{79}$, whose half life is estimated to be greater than $3 \times 10^{16}$ years (Strominger *et al.* 1958). Some 20 artificial radiosotopes are known; all have short half-lives, none exceeding 185 days. Mauer and Pose (1943) found no evidence of natural fission in gold and concluded that the half-life for the process is longer than $2 \times 10^{15}$ years.

## Abundance and geochemical character: gold in meteorites, tektites and lunar materials

The cosmic abundance of gold as given by Green (1959) from the data of Suess and Urey (1956) is 0.000534 ppm or 0.145 atom of Au per $10^6$ Si atoms. More recent estimated cosmic abundances of gold as given by Cameron (1959), Clayton and Fowler (1961), Baedecker and Ehmann (1965) and Cameron (1968) are respectively 0.145, 0.13, 0.18 and 0.20 atom of Au per $10^6$ Si atoms. These values can be compared with the corresponding value for silver – 0.5 – as given by Cameron (1968). Ehmann and Gillum (1972) give the cosmic atomic abundance of gold as 0.19 ($Si = 10^6$ atoms); that for platinum on the same basis is 1.37 giving an Au/Pt atom ratio for the primitive solar nebula equal to 0.14.

Gold is a trace constituent of meteorites, its abundance in the various types of these objects having a considerable range as shown in Table 4. The iron meteorites (siderites) and the metal phase of chondrites have the highest gold contents indicating the marked siderophilic character of gold. The gold content of the silicate phases of meteorites is low whereas the sulphide (troilite) phase is relatively high, indicating respectively a general poor lithophile tendency and a relatively high chalcophile habit for gold.

In the chondrites the Au/Ag ratio is consistently around 1, whereas in the siderites the average ratio is extremely high, at 40 or more. The ratio in the sulphide (troilite) phase is of the order of 0.05 if the available analyses for silver are reasonably correct. All these data indicate a weak siderophile character and a marked chalcophile nature for silver compared with gold, features that are well known to all chemists.

Some of the correlations of gold with other elements in meteorites are of interest. There is a reasonable correlation between nickel, cobalt and gold in some chondrites and siderites according to the data presented by Goldberg *et al.* (1951) and Vinogradov *et al.* (1973). Linn and Moore (1968), on the other hand, found that the positive correlation of gold concentrations in relation to nickel and to cobalt was not pronounced in their data on iron meteorites. The correlation between gold and iron is not marked in the data on meteorites, although some investigators have observed a positive

Table 4. Gold and silver contents of meteorites, tektites and the moon*

| Type of meteorite, etc. | Element | Number of samples | Range | $\overline{X}$§ | S§ | G§ | $\overline{X}$g§ | Sg§ |
|---|---|---|---|---|---|---|---|---|
| | | | | (ppm) | | | | |
| Chondrites (world) | Au | 246 | 0.0170–1.6000 | 0.2225 | 0.1427 | 0.1998 | -0.6994 | 0.1881 |
| | Ag | 34 | 0.0330–0.5700 | 0.1769 | 0.1464 | 0.1285 | -0.8911 | 0.3542 |
| | Au/Ag | | | 1.2578 | | 1.5549 | | |
| Chondrites, | | | | | | | | |
| Abee† | Au | 1 | 0.25 | | | | | |
| Benton† | Au | 1 | 0.96 | | | | | |
| Holman Island† | Au | 1 | 0.94 | | | | | |
| Chondrites, metal phase (world) | Au | 52 | 0.4480–2.9000 | 1.5085 | 0.6016 | 1.3846 | 0.1413 | 0.1888 |
| Chondrites, nonmetal (silicate) phase (world) | Au | 47 | 0.0004–0.0910 | 0.0199 | 0.0181 | 0.0125 | -1.9030 | 0.4788 |
| Achondrites (world) | Au | 11 | 0.0005–0.2800 | 0.0310 | 0.0830 | 0.0053 | -2.2775 | 0.7186 |
| Siderolites (50% iron, 50% silicate) (world) | Au | 7 | 0.0400–2.000 | 0.9143 | 0.7262 | 0.5318 | -0.2743 | 0.6053 |
| Siderites (irons) (world) | Au | 291 | 0.0550–8.7440 | 1.2050 | 0.8999 | 0.9597 | -0.0179 | 0.3102 |
| | Ag | 87 | 0.0050–0.1320 | 0.0301 | 0.0316 | 0.0174 | -1.7597 | 0.4717 |
| | Au/Ag | | | 40.0332 | | 55.155 | | |
| Siderites | | | | | | | | |
| Annaheim† | Au | 1 | 0.9 | | | | | |
| | Ag | 1 | 0.07 | | | | | |
| | Au/Ag | | 12.85 | | | | | |
| Skookum† | Au | 1 | 0.5 | | | | | |
| | Ag | 1 | 0.15 | | | | | |
| | Au/Ag | | 3.33 | | | | | |
| Madoc† | Au | 1 | 0.7 | | | | | |
| | Ag | 1 | 0.03 | | | | | |
| | Au/Ag | | 23.33 | | | | | |
| Troilite (sulphide phase) (world) | Au | 16 | 0.0700–8.0000 | 0.9787 | 1.9217 | 0.4128 | -0.3842 | 0.5405 |
| | Ag | | | 18‡ | | | | |
| | Au/Ag | | | 0.054 | | | | |
| Tektites (world) | Au | 15 | 0.0003–0.0242 | 0.0081 | 0.0080 | 0.0040 | -2.4020 | 0.6296 |
| | Ag | 8 | 0.2500–0.5000 | 0.4063 | 0.1294 | 0.3856 | -0.4139 | 0.1558 |
| | Au/Ag | | | 0.0199 | | 0.0104 | | |
| Lunar rocks and soils | Au | 529 | 0.0000025–0.08700 | 0.00485 | 0.00855 | 0.00173 | -2.7613 | 0.8021 |
| | Ag | 299 | 0.0001–10.7800 | 0.0980 | 0.6689 | 0.0052 | -2.2819 | 0.9077 |
| | Au/Ag | | | 0.04949 | | 0.3327 | | |
| Lunar rocks | Au | 292 | 0.0000025–0.0870 | 0.0047 | 0.0090 | 0.0011 | -2.9603 | 0.9478 |
| | Ag | 166 | 0.0001–10.7800 | 0.0933 | 0.8440 | 0.0027 | -2.5622 | 0.8602 |
| | Au/Ag | | | 0.0504 | | 0.4074 | | |
| Lunar soils and fines | Au | 237 | 0.000011–0.0737 | 0.0051 | 0.0080 | 0.0031 | -2.5161 | 0.4716 |
| | Ag | 133 | 0.0002–3.0800 | 0.1039 | 0.3458 | 0.0117 | -1.9321 | 0.8445 |
| | Au/Ag | | | 0.0491 | | 0.2650 | | |
| Lunar metal grains | Au | 58 | 0.050–19.000 | 1.5332 | 2.5940 | 0.7737 | -0.1114 | 0.5564 |
| | Ag | 1 | 0.0730 | 0.0730 | | 0.0730 | | |
| | Au/Ag | | | 21.003 | | 10.599 | | |

* Sources of information: *see* the Selected bibliography. Doubtfully high values for gold and silver have been excluded from some of the published data. For details of individual meteorites and bibliographies on meteorites *see* Mason (1962), Middlehurst and Kuiper (1963), Hey (1966), Mason (1971) and Ramdohr (1973). For information on most of the lunar samples see the volumes containing the papers delivered at the 1st, 2nd, 3rd, 4th and 5th Lunar Science conferences held at Houston Texas.

† Analyses done in the Geological Survey of Canada laboratories by precise chemical methods (analyst, J.G. Sen Gupta). (For descriptions of the meteorites *see* Geol. Surv. Can., Pap. 70-66.)

‡ Estimated value.

§ In this and subsequent tables $\overline{X}$, is the arithmetic mean; S, the standard deviation; G, the geometric mean; and $\overline{X}$g and Sg are respectively the mean and standard deviation of the data expressed in $\log_{10}$ units.

correlation in some varieties of meteorites; for instance Ehmann *et al.* (1970) found such a correlation with the total iron content in enstatite chondrites. The relationship of gold with the various platinoids appears to be rather erratic judging from the overall available data, although Ehmann and Gillum (1972) found a positive correlation for platinum and gold within each major chondrite group they investigated. The correlation coefficient was 0.70 which is significant at the 99.9 per cent confidence level. Hintenberger *et al.* (1973) observed an antipathetic correlation between gold and mercury in some Antarctic meteorites. Fouché and Smales (1966) noted a strong correlation between gold and arsenic in iron meteorites and a weak correlation between gold and antimony. Both these correlations extend to terrestrial materials as we shall see later. Similar correlation features were noted for gold, arsenic and antimony in chondritic meteorites by Fouché and Smales

(1967). Other correlations and relationships of gold in meteorites are briefly commented on by Ehmann (1971).

A number of investigators have suggested that an approximation of the average composition of the earth's mantle and even of the entire earth is provided by the composition of the chondrites. Others have suggested that the earth derived from an agglomeration of chondrites. If these theories are valid there is a strange difference, which requires an explanation, in the Au/Ag ratios between chondrites and ultrabasic and basic rocks supposedly derived from the mantle (Table 13). Perhaps primitive differentiation processes in the earth are the reason, the gold settling into the metallic phase (Ni-Fe core) and the silver remaining largely in the mantle. Such a differentiation is perhaps supported by the fact that the Au/Ag ratios in siderites are extremely high. All of this discussion is of course highly speculative to say the least, especially the supposition that the core of the earth is composed of nickel-iron; it may be that chondrites and the other meteorites bear no relationship whatever to the earth in any of its aspects.

The gold and silver data for tektites (Table 4) is similar to that for terrestrial igneous rocks (Table 13). The Au/Ag ratio is, likewise, similar. The significance of these facts is obscure.

The gold and silver data for the lunar rocks and fines (soils) (Table 4) are extensive and are discussed at length by a number of investigators (*see* the list of references in the Selected bibliography). To generalize one notes that the overall gold and silver contents of the lunar materials are not much different from those recorded for igneous rocks on the earth (Table 13). A number of investigators have remarked that the lunar soils are enriched in gold and silver relative to the rocks, the reason being that the soils have a micrometeorite component. The enrichment is, however, not great as can be seen from the statistics recorded in Table 4.

There are no data on the nature of gold in any of the extra-terrestrial materials just described. Presumably in meteorites much of the gold is present in the metallic (mainly Fe-Ni) phases and possibly in part in the sulphide (troilite) phase; also possibly in some of the iron oxides (magnetite, ilmenite) and chromite. In all of these minerals gold may be present as a submicroscopic dispersed phase or in lattice sites in the metal alloys, sulphides and oxides. Ramdohr (1973) mentions the presence of native gold (observed by A.B. Edwards) in the Wedderburn iron meteorite. He also thinks that some osbornite observed in meteorites could be mistaken for gold and vice versa. This possibility should be checked by electron probe.

There is reasonable agreement with respect to the value of the terrestrial abundance of gold. Goldschmidt (1954) gives 0.005 ppm for the lithosphere; Rankama and Sahama (1950) give 0.005 ppm as the average for igneous rocks; Green (1959) gives ~ 0.001 ppm as the average for igneous rocks; Vinogradov's (1962) estimate is 0.0043 ppm for the crust; and Taylor (1964) has given 0.004 ppm as the continental crustal abundance of the element, a mean of the basalt (0.004 ppm) and granite (0.004 ppm) averages. More recently Li and Yio (1966) have given the figures for the abundance of Au, Ag and Pt in the various parts of the earth's crust noted in Table 5. From their estimates the Au:Ag:Pt ratios are 1:20.4:13.2 and the Au/Ag ratio is 0.048. Horn and Adams (1966) computed the abundance of gold in igneous rocks to be 0.00357 ppm; in sedimentary rocks the range was 0.00179 to 0.00457 ppm. The writer estimates the terrestrial abundance of gold and silver to be respectively 0.005 and 0.05 ppm from analyses quoted in this work and a previous report on silver (Boyle, 1968*b*). This gives an Au/Ag ratio of 0.1.

Table 5. Abundance of gold, silver and platinum in domains of the earth's crust*

| Source | Au | Ag | Pt |
|---|---|---|---|
| | | (ppm) | |
| Deep oceanic regions | 0.004 | 0.098 | 0.095 |
| Suboceanic regions | 0.0029 | 0.082 | 0.05 |
| Continental shield regions | 0.0034 | 0.067 | 0.031 |
| Folded belt regions | 0.0038 | 0.062 | 0.022 |
| Oceanic crust | 0.0035 | 0.091 | 0.075 |
| Continental crust | 0.0035 | 0.065 | 0.028 |
| Earth's crust | 0.0035 | 0.075 | 0.046 |
| Crystalline rocks | 0.0036 | 0.077 | 0.049 |
| Sedimentary rocks | 0.0051 | 0.065 | – |

*From Li and Yio (1966).

In the upper lithosphere gold occurs in the native state and as a constituent of a few natural alloys. It is also a trace element in various native metals and semi-metals such as iron, copper and arsenic. These features indicate the strong siderophile character of the element. The metal also combines readily with tellurium, bismuth and antimony, forming a number of mineral species, but its chalcophile character is weak since no natural gold sulphides are known as minerals. The element appears to have no oxyphile character, and there are no known natural gold oxides, salts or basic salts. Maclaren (1908) refers to silicate of gold, but there are no modern investigations to confirm the presence of such a compound. No silicates of gold are known in nature.

Gold combines with a large number of artificial organic compounds, but the occurrence of these in natural environments is largely uninvestigated. The element is a trace constituent of various terrestrial and marine organisms, but its biological role, if any, is unknown. Gold is also a trace constituent of some coals and is found as traces in some petroleum residues and in oil shales.

> Of all metals gold is most
> frequently found native.
> –Richard Kirwan, 1799

# Mineralogy of Gold

## Gold minerals

The minerals of gold are given in Table 6. Of those listed the most common are native gold and the tellurides. For the details of the gold minerals the reader should consult Palache, *et al.* (1944, 1951), Ramdohr (1960), Hey (1962, 1963), Hey and Embrey (1974), Chukhrov (1960–1965) and Berry and Thompson (1962). Occurrences of Canadian gold minerals are noticed by Traill (1970).

*Native gold* crystallizes in a great variety of forms, the most common being parallel groups and twinned aggregates branching at 60 degrees parallel to the edges or the diagonals of the faces of (111); also commonly reticulated, dendritic, arborescent, filiform, wiry, mossy and spongy. Massive forms include rounded fragments (nuggets), flattened grains, scales,

Table 6. Gold minerals

| | |
|---|---|
| *Native elements, alloys and metallic compounds* | |
| Gold | Au |
| Argentian gold (electrum) | (Au,Ag) |
| Cuprian gold (cuproauride) | (Au,Cu) |
| Palladian gold (porpezite) | (Au,Pd) |
| Rhodian gold (rhodite) | (Au,Rh) |
| Iridic gold | (Au,Ir) |
| Platinum gold | (Au,Pt) |
| Bismuthian gold | (Au,Bi) |
| Gold amalgam | $Au_2Hg_3$ (?) |
| Maldonite | $Au_2Bi$ |
| Auricupride | $AuCu_3$ |
| Palladium cuproauride | $(Cu,Pd)_3Au_2$ |
| *Sulphide* | |
| Uytenbogaardtite | $Ag_3AuS_2$ |
| *Tellurides* | |
| Calaverite | $AuTe_2$ |
| Krennerite | $(Au,Ag)Te_2$ |
| Montbrayite | $(Au, Sb)_2Te_3$ |
| Petzite (antamokite) | $Ag_3AuTe_2$ |
| Muthmannite | (Ag,Au)Te |
| Sylvanite | $(Au,Ag)Te_4$ |
| Kostovite | $AuCuTe_4$ |
| Nagyagite | $Pb_5Au(Te,Sb)_4S_{5-8}$ |
| *Antimonide* | |
| Aurostibite | $AuSb_2$ |
| *Selenide* | |
| Fischesserite | $Ag_3AuSe_2$ |
| *Tellurate* | |
| Gold tellurate (?) | |

spangles, sprigs and finely divided particles (flour gold, mustard gold and paint gold). All of these and other forms are figured by Weinig (1960).

The purity of native gold, gold bullion, gold coin, etc. is expressed in terms of fineness, which is commonly defined as the proportion of pure gold in the sample in parts per thousand.[17] Thus, native gold which is 900 fine contains 90 per cent of the element gold. In some deposits native gold is relatively pure, but more generally it contains some silver, copper, and iron and traces to minor amounts of one or several of the following elements: Li, Na, K, Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, B, Al, Ga, In, Sc, Si, Ge, Sn, Pb, Ti, Zr, As, Sb, Bi, V, Se, Te, Cr, Mo, W, Mn, Co, Ni, Rh, Pd, Ir, Pt, U, Th and rare-earths.

There is a vast literature on the composition of native gold in practically all types of deposits in which the mineral occurs. Some of the papers noticed during the compilation of this chapter include those by Warren and Thompson (1944), Ferguson (1950), Perelyaev (1953), Gay (1963, 1964), Denisov *et al.* (1966), Jones and Fleischer (1969), Antweiler and Sutton (1970), Lantsev *et al.* (1971), Desborough *et al.* (1971), Badalova *et al.* (1971), Petrovskaya *et al.* (1971), Berman *et al.* (1973), Semenenko and Latysh (1973), Kuznetsov *et al.* (1973*b*), Petrovskaya (1973), Davidenko (1973*a,b*), Igumnova (1974) and Petrovskaya *et al.* (1976). Some highlights from some of these papers may be mentioned.

There is a great variation in the trace and minor element content of primary and secondary native gold, although within some specific deposits the contents of the various elements appear to range within relatively narrow limits. Native gold in oxidized zones and in associated placers generally contains lesser amounts of silver and a number of other elements compared with the native gold in the corresponding primary ores. Within some specific deposits single crystals and particles of native gold are frequently relatively homogeneous with respect to the distribution of trace and minor elements; in other deposits the native gold is heterogeneous, a silver and/or other elemental zoning being present. In some deposits there is an increase in the silver and other elemental content from the centres of the crystals or particles outward; in other deposits the reverse is the case. In some gold lodes the crystals and particles of native gold contain numerous inclusions, generally associated gangue minerals such as pyrite, magnetite, chalcopyrite, tellurides, etc.; in other lodes the native gold has a scarce assortment of inclusions; and in still others inclusions are virtually absent. Within some single deposits the intergrain variations and differences in trace and minor element contents are often marked; in other deposits the grains and crystals of gold throughout the deposits are relatively homogeneous within narrow limits. An example of the latter is the gold in some of the Witwatersrand ore shoots. Placer gold commonly has thin rims of relatively high purity gold from which, according to some investigators, the silver and other trace elements have been leached. This feature of placer gold is discussed at some length in Chapter III. The gold in the oxidized zones of certain lodes may also exhibit the rim effect; it is uncommon in primary gold ores in most goldfields. Some investigators claim that the types and other features of gold deposits such as temperatures of deposition, nature of the depositing solutions, etc. can be divined from the analyses of native gold samples. Short resumes of some of the papers of the investigations will illustrate their contentions.

Warren and Thompson (1944) considered that by thorough and detailed work it may be possible, by means of spectrographic analysis; to determine the metallogenetic province or zone, and in some cases even the deposit, from which a particular sample of gold originates.

More recently Antweiler and Sutton (1970) report results for 174 quantitative spectrochemical analyses for silver and semiquantitative spectrochemical analyses for 32 other elements in samples of lode and placer gold obtained from 67 localities in eight western states of the continental United States, including Alaska, and from one locality in Brazil. Of the 24 elements detected (besides gold) in the samples, Ag, Cu, Fe and Ti were the most frequently detected. Pb, Pd, Bi, V, Ni and Co were identified more often in lode samples than in placer samples, but Ti, Zr, La, Y and Cr occurred more frequently in placer samples. They concluded that their data could possibly be used in prospecting for deposits of gold and other metals and in determining ore depositional conditions or genetic associations.

Lantsev *et al.* (1971) determined the contents of the following trace elements – As, Sb, Te, Pb, Cu, Fe, Bi, Sn, Ni, Co, Mn, Cr, Ti, Zn, Cd and Ga – in 120 gold samples from 40 endogenic deposits formed under various conditions and at various depths. They concluded that the concentration of trace elements in gold deposits increases as one ascends through ores formed at greater depths to those of near-surface genesis. This tendency was found for all elements, with the exception of Cu, during the passage from great depths to

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[17] Fisher (1945) defines the true gold fineness as the ratio Au/(Au + Ag) × 1000. This definition eliminates the base metal factor.

medium depths and for Sb, Sn, Zn and Mn during the passage from medium to surface depths. This regularity was thought to be caused mainly by diffusion upwards of isomorphous and mechanical admixtures from gold during the process of recrystallization at high temperature.

Research based on polished sections and spectrographic, chemical and electron-probe analyses of native gold from primary deposits and placers carried out by the writer indicates that most of the metallic and semimetallic elements may be lattice constituents of native gold. However, many of the metals and other elements are often contaminants, being present in minute inclusions of the minerals commonly associated with native gold, particularly quartz, carbonates, sericite, sulphides, arsenides, tellurides, selenides, etc. In my experience the following elements exhibit a frequency which suggests that they are predominantly lattice constituents when they are present in pure samples of native gold: Ag, Cu, Fe, Ni, Hg, As, Sb, Bi, Te, Pd and Pt.

Several varieties of native gold are known which contain significant amounts of other metals. These have been given specific mineral names in some cases, but more generally they are referred to by a prefix indicating the contained element, e.g. argentian gold, palladian gold, etc.

*Argentian gold.* Normally all native gold contains some silver generally in the range 5–15 per cent Ag. Most of this silver is a lattice constituent, and there is a complete(?) substitutional series from gold through argentian gold to aurian silver (kustelite) to native silver. *Electrum* has been applied to gold containing 20 per cent or more silver. The name is an ancient one and has been used for centuries, apparently being first applied to the gold won from the famous placers of the Pactolus a small river of ancient Lydia which joined the Hermus (modern Gediz) after flowing through Sardis. Pliny, in his *Historia naturalis,* said "when the proportion of silver in gold is one-fifth, it is called electrum and possesses a pale yellow colour."

The range and significance of the Au/Ag ratio in native gold and in gold deposits is discussed in Chapter III.

*Cuprian gold.* Most samples of native gold contain only traces to minor amounts of copper probably substituting in the lattice in most cases. Cases are known, however, where the copper is apparently plated on the gold (Ferguson, 1950). Some samples of gold mentioned in the literature contain from 0.10 to 20 per cent Cu. One of the copper varieties has been named *cuproauride* and given the formula AuCu. According to Ramdohr (1960) it is rare and requires further investigation. The compound, $AuCu_3$, containing some 40 per cent gold, named *auricupride* is reported by Ramdohr to occur frequently. It has a high metallic lustre and a yellow colour with a reddish tint. Oen and Kieft (1974) describe a new copper-gold alloy with a formula approximating $CuAu_{2.6}$. The alloy occurs in the chromite-niccolite ore from Beni-Bousera, Morocco, as irregular grains mostly along grain boundaries of niccolite and loellingite. In the auriferous ores of the Karabashsk deposit Novgorodova and Tsepin (1976) observed the following phases among the auricuprides, $Cu_3Au$, CuAu and $CuAu_4$. The artificial isomorphous series Cu-Au is complete, but in nature the copper end members with high contents of gold ($>3\%$ Au) have not been recognized.

*Palladian gold* termed *porpezite* in the old literature is said to contain 5 to 10 per cent Pd in solid solution, but samples of this type of gold require restudy to ensure their homogeneity. It has been reported from Porpez, Taguaril and other localities in Minas Geraes and Goyaz, Brazil. Recently, *palladium gold* (Au,Pd) has been described from the Stillwater Complex in Montana by Cabri and Laflamme (1974). The mineral is face-centered cubic ($a = 4.047(1)$Å) and is cream-coloured with a metallic pinkish cast under reflected light in air. It is associated with a number of other rhodium and platinum alloys and minerals including platinian rhodium, rhodian platinum, platinum-iron, and braggite/vysotskite.

*Rhodian gold,* also referred to as *rhodite,* is said to contain 34 to 43 per cent Rh. It requires restudy to determine its homogeneity. Rhodian gold is reported from Colombia and Mexico.

*Iridic gold* is reported in the old literature to contain up to 30 per cent Ir. This type of gold requires restudy to establish its homogeneity. Some of the reported occurrences may be intergrowths of gold and osmium-iridium and platinum as described by Syrovatskii *et al.* (1969).

*Platinum gold* is reported in the old literature to contain up to 10 per cent Pt. It requires reexamination. Some of the reported occurrences may be intergrowths of gold and osmium-iridium and platinum as described by Syrovatskii *et al.* (1969).

*Gold amalgam* is reported by Palache *et al.* (1944) to occur in grains and lumps of white to yellowish colour with metallic lustre in the Mariposa region, California, with platinum in Colombia and in the vicinity of Pleiari, Borneo. The composition of some of the samples analyzed corresponds well with the composition $Au_2Hg_3$, suggesting a compound homologous with the silver mineral, moschellandsbergite, $Ag_2Hg_3$.

*Maldonite or bismuthic gold.* Some samples of native gold contain traces to minor amounts of bismuth (up to 3% Bi) possibly in solid solution. The mineral maldonite was early reported to be an intermetallic compound with the formula $Au_2Bi$. However, microscopic examination of the maldonite from Maldon, Victoria, the type locality, shows a fine myrmekitic intergrowth of gold and bismuth, derived apparently from the breakdown of $Au_2Bi$, which is said to be stable only at high temperatures (Ramdohr, 1953*a*, 1960).

The maldonite from Salsigne (Aude) in France described by Boyer and Picot (1963) averages 64.58 per cent Au and 35.72 per cent Bi, approximating the formula $Au_2Bi$. The sample in this case appears to have been homogenous. Boyer and Picot confirm Ramdohr's opinion that the mineral is formed within a relatively narrow temperature interval and think the mineral is a reliable geothermometer. From the Au-Bi phase diagram they suggest a temperature of deposition below or equal to 373°C.

According to Razin *et al.* (1971) there is some doubt about the existence of *auricupride,* $AuCu_3$. These same authors describe a new mineral, *palladium cuproauride,* in the ores of the Talnakh copper-nickel deposit, U.S.S.R. The mineral is an intermetallic compound with formula $(Cu,Pd)_3Au_2$. It contains traces and minor amounts of Rh, Ag, Bi and Ni.

The physical properties of native gold, the morphology of gold crystals and particles in deposits and the relationship of these parameters to the depositional conditions in gold deposits have been extensively studied by many investigators prior to 1970. Papers reviewed during the compilation of this chapter since that date include those by Korobeinikov (1971), Koroleva *et al.* (1971), Petrovskaya *et al.* (1971*a–d*), Yablokova (1972), Berman *et al.* (1973) and Dzhantuganov (1974). Some of the features brought out by all of these studies, both pre- and post-1970, are summarized briefly below. Only the properties of epigenetic gold and that in the oxidized zones of auriferous deposits are reviewed here; placer gold is discussed in detail in Chapter III.

The morphology of native gold in epigenetic deposits is exceedingly variable, the most common shapes of the particles being nodular and lamellar, lumpy masses, amoeba-shaped masses, simple platy forms, ramifying platy and veinlike masses, dendritic masses, wires, sprigs, spear- and splinterlike forms, crystals, droplike inclusions in sulphides and other minerals, smears on shear planes, pulverulent aggregates (mustard gold), and spongy masses. There appear to be no clear-cut relationships between the shapes of the native gold particles and the types or age of the deposits. In general crystals are rare in the deposits formed at great depth (mainly deposits of Precambrian and Paleozoic age), whereas crystals are relatively common in younger deposits formed near the surface especially in those of Tertiary age. Crystals, wires, dendrites, pulverulent aggregates and spongy masses are especially characteristic of secondary gold found in the oxidized zones of auriferous deposits. Deep-seated deposits, which include most lodes of Precambrian and Paleozoic age, have much more uniformity in the morphology of their native gold particles than near-surface deposits of Mesozoic and Tertiary age. The morphology of the gold particles and crystals in the old (deep-seated) deposits is also generally much simpler than is that of the gold in the younger (near-surface) deposits.

The size of gold particles and crystals in epigenetic gold-bearing deposits varies widely, the usual range being from less than one thousandth of an ounce up to masses weighing a thousand ounces or more. Deposits formed under deep-seated conditions (most Precambrian and Paleozoic deposits) generally are marked by fair uniformity in the size of the gold particles, whereas deposits formed under near-surface conditions (many Tertiary deposits) are often characterized by great variability in the size of the native gold particles and crystals. This variability is said by some investigators to indicate fluctuating conditions during the deposition of the gold. In numerous deposits gold is present in an extremely finely divided form in sulphides, sulphosalts or gauge minerals such as quartz. The division is so fine in some deposits that the gold cannot be seen under the highest magnification in minerals such as arsenopyrite and pyrite. The nature and significance of this submicroscopic gold is discussed subsequently. There are no clear-cut relationships between the size of gold particles and crystals and depth in epigenetic deposits as far as this writer can ascertain from the literature or from his experience. It is of interest to note that the gold of the Witwatersrand is remarkably uniform in its size of particles (av. diameter – 80$\mu$; 0.08 mm), a feature that is discussed in more detail in Chapter III.

Most investigators agree that the morphology and size of gold particles and crystals in most epigenetic deposits are essentially dependent upon the size and shape of the sites of deposition which in turn are predicated on the original or induced porosity of rocks and on structural events such as fracturing, formation of open spaces along faults, shearing etc. In addition there are also various chemical factors which seem to be involved, but about which we have only a superficial knowledge. These include replacement phenomena, exsolution reactions, coprecipitation phenomena and so on.

Native gold contains gaseous inclusions that have recently been studied in some detail by Petrovskaya *et al.* (1971*a*). They found that some 90 per cent of the gas was $CO_2$ and the remainder mainly nitrogen. The pressure in the inclusions studied was estimated at 5 to 20 atm. The authors concluded that the presence of $CO_2$ and $N_2$ (also found in gaseous inclusions in quartz in the same deposits) is due to the adherence of bubbles of $CO_2$ at the surface of hydrophobic gold grains during their growth. Their further conclusion was that carbon dioxide plays a significant role in the crystallization of gold from hydrothermal solutions.

The optical properties of gold have been extensively investigated by Hodgson (1968), and the determination of the silver content of natural gold alloys by reflected-light microscopy is described by Eales (1968) and Eales and Viljoen (1973). A criticism of the first paper has been published by Stumpfl (1969).

Gold is unique among the precious metals in the variety and weight of its placer nuggets. Some have been found that are beautifully metallic and crystallized, whereas others are inconspicuous, being rounded, pitted and covered with black manganese oxides, brown limonite, humic compounds, silica, clay or other nondescript compounds. In weight there are records of nuggets ranging from less than 1 oz up to masses weighing nearly 2400 oz (200 lb troy). Australia has produced many of the largest nuggets, the goldfields of Victoria exceeding all others. Of the nuggets officially recorded from Victoria 12 exceeded 1000 oz, and 33 were between 1000 and 500 oz. The Dunolly district, which is deeply weathered and oxidized, has surpassed all others in the number of nuggets found. The Welcome Stranger weighed slightly more than 2284 oz and was found in detrital material just below the surface at Black Lead, Mt. Moliagul, near Donolly, Victoria. Another nugget, the Welcome, weighed 2217 oz and was found in alluvial material at a depth of 180 ft at Bakery Hill, Ballarat, Victoria. Two others, also found in alluvial gravels in Victoria, the Viscount Canterbury and Viscountess Canterbury, weighed 1114 and 912 oz respectively. In the United States some very large nuggets have been discovered, the one from Carson Hill, Calaveras County, California weighing some 2340 oz (Gaarden, 1940). Another water-worn nugget, the Willard, Dogtown or Magalia nugget, weighing 54 lb troy, was found at Magalia in California in 1859. The discovery of this nugget was the signal for a celebration which has been held annually ever since (Clark, 1970).

Despite the large amount of gold taken from the Klondike, Cariboo and other placer areas of Canada few large nuggets have been discovered. Robinson (1935) mentions an 85 oz nugget from the Klondike, and in eastern Canada a nugget weighing 52 oz, 11 dwt, 6 grains, called the 'Kilgour Nugget' was taken from the Gilbert River (Chaudière), Beauce, County, Quebec. In the same area a nugget weighing 45 oz, 12 dwt called the 'McDonald Nugget' was found on Lot

16, De Lury Concession, Gilbert River, Quebec. Numerous other smaller nuggets weighing a few tens of ounces have been taken from the Klondike, Cariboo and other placers in Canada (Frontispiece).

Gold nuggets have been found in every conceivable geological environment, from birds' nests and crops to potholes in placers. The origin of gold nuggets is discussed in Chapter III.

Certain of the gold tellurides probably occur in minute amounts in most primary gold deposits judging by the frequency with which traces of tellurium are found in gold ores and the nearly universal presence of isolated pockets and veinlets of tellurides in most gold veins and other types of auriferous deposits. In some deposits the tellurides are important ore minerals of both gold and silver. Localities where gold (and silver) tellurides are particularly abundant include Nagyág and Brad, Romania; Kalgoorlie and Mulgabbie, Western Australia; Cripple Creek, Colorado; Kirkland Lake, Ontario; and a number of localities in Japan (Watanabe, 1952); Vatukoula, Fiji; Philippines (Callow and Worley, 1965); and a number of localities in U.S.S.R. (Chukhrov, 1960; Amiryan, 1960; and Pankov and Chukhrov, 1962).

*Krennerite, calaverite, sylvanite, nagyagite, muthmannite* and *petzite* appear to be the most common of the gold tellurides, having been recorded in a large number of places. *Montbrayite* has been recognized only in the Robb-Montbray Mine, Montbray Township, Quebec where it is associated with other tellurides and gold (Thompson, 1949). *Kostovite* is a new mineral and occurs in the copper ore deposit of Chelopech, Bulgaria where it is associated with tennantite, chalcopyrite, pyrite, native tellurium, native gold, tellurides and other minerals (Terziev, 1966). Tunell (1954) has reviewed the main features of the crystal structures of the various gold-silver tellurides.

Thompson (1949) has described most of the known gold and silver telluride occurrences in Canada.

Markham (1960) has discussed the synthetic and natural phases in the system Au-Ag-Te and also his findings with respect to the occurrence of tellurides at Kalgoorlie, Western Australia and Vatukoula, Fiji. He finds that the experimental data are insufficient to indicate a meaningful range of depositional temperatures for any given telluride, but thinks that when the calaverite-krennerite transition is experimentally determined, it should provide a useful geological thermometer. Cloke (1963) and Petersen (1964) have commented on some of the physico-chemical features of Markham's paper.

Shcherbina and Zar'yan (1964) have discussed the parageneses of gold and silver tellurides from Armenian sulphide deposits in terms of the experimentally determined parts of the system Ag-Au-Te. They concluded that the assemblages hessite-petzite-gold and hessite-petzite-krennerite were formed by deposition from hydrothermal solutions during the galena-sphalerite stage of mineralization, and by later replacements. Native silver and tellurium, formed by the decomposition of gold-silver tellurides, occur in some assemblages.

Cabri (1965*a*) recently carried out a systematic investigation of the phase relations in the Au-Ag-Te system and found that krennerite, rather than being a polymorph of $AuTe_2$, should be interpreted as a single mineral entity with the approximate formula $Au_4AgTe_{10}$. It is stable up to its incongruent melting point of 382 ± 5°C, and hence its presence in deposits is not necessarily indicative of a low temperature of formation. The incongruent melting temperature of sylvanite (354 ± 5°C) indicates a maximum temperature for its formation. Cabri also found that hessite and petzite are each characterized by three polymorphs. Continuous solid solution exists between the highest polymorphs and extends to a composition about 7 weight per cent more gold-rich than stoichiometric petzite. A new phase, termed the 'x' phase, was found to be stable along the petzite-hessite join from about 2.5 to 14.5 weight per cent gold within temperature limits of 50 to 415°C. The observations of Forsythe (1968) with respect to the occurrence of tellurides at Vatukoula lend support to some of Cabri's conclusions.

Howie and Veale (1966) have discussed the low temperature synthesis of gold telluride. They could not make gold sesquitelluride by low temperature coreduction and precipitation techniques; sometimes a metastable telluride of composition close to $AuTe_{1.75}$ was obtained. They state that the mineral montbrayite, $Au_2Te_3$, may represent an intermediate step in the ordering of this structure.

The relation between the composition and X-ray diffraction data of gold-silver tellurides is discussed by Cabri and Rucklidge (1968). Stumpfl (1970) has noted considerable compositional variations in the gold content of specimens of gold tellurides from different deposits.

Our semiquantitative and qualitative analyses of the various gold-silver tellurides indicate that most are relatively pure. Traces to minor amounts (tens to thousands of ppm) of S, Se, Sb and As are commonly present in most samples probably replacing Te. In addition to these elements the following are commonly found in traces to minor amounts: Cu, Fe, Ni, Co, Pb, Sn, Hg, W, Mo and Bi. Some of these elements evidently replace Au and Ag, although some of them may be largely in impurities. The platinum metals were not found in any of the samples.

The isotope $^{130}Te$ is radioactive and decays by double beta emission to yield $^{130}Xe$. This feature of tellurium minerals permits age determinations of gold and silver deposits containing tellurium to be made. Srinivasan *et al.* (1972) have determined the half-life for double beta decay of $^{130}Te$ to be $2.83 \pm 0.30 \times 10^{21}$ years from an analysis of xenon and tellurium in the tellurides of Kalgoorlie, Australia. Three telluride samples from different locations (Vakukoula, Fiji; Facebaja, Transylvania, Romania; and Moctezuma, Sonora, Mexico) gave ages consistent with geologic age estimates. The authors conclude that the method is particularly useful in yielding the age of gold and silver mineralization directly.

Some of the facts concerning the occurrence of silver (and gold) tellurides may be noted here. The tellurides seldom if ever are associated with the selenides; for some reason they seem to be mutually exclusive. It may be that observers have failed to recognize the presence of the two types of minerals together, but this seems unlikely considering the amount of mineralogical work that has been done on gold ores. Even in the highly seleniferous gold ores of Salida, Indonesia there are apparently no selenides (or doubtful selenides, naumannite?) associated with the various tellurides (sylvanite, petzite, hessite, altaite). There, the tellurides are invariably associated with galena and the selenium is bound mainly in acanthite, galena and arsenpolybasite (Kieft and Oen, 1973). An alternative reason for the antipathy of selenides and tellurides in deposits may be that the solutions that deposit gold and silver tellurides are inhibited from carrying selenium and vice versa. This, likewise, seems improbable from a chemical viewpoint. There are a number of silver selenides, but no natural gold selenide *sensu strictu* is known. The silver-gold selenide, fischesserite, $Ag_3AuSe_2$, is however, stable. Artificially a stable phase $\alpha$-AuSe can be prepared, and while tellurium does not substitute in the AuSe lattice to a detectable extent, selenium will substitute up to at least 15 atomic per cent of the tellurium atoms in the monoclinic $AuTe_2$ (calaverite) lattice at 400°C (Cranton and Heyding, 1968). There is also at least one ternary phase, $Au_2SeTe$, in the system Au-Se-Te.

The tellurides generally occur in deposits in volcanic assemblages, or in rocks closely associated with andesites, basalts, etc. Particularly notable is their occurrence in Precambrian greenstones, examples being the Kirkland Lake–Noranda–Malartic areas of Ontario and Quebec; Porcupine area, Ontario; Red Lake area, Ontario; Flin Flon, Manitoba; and the famous telluride-gold lodes of Kalgoorlie, Western Australia. In younger (generally Tertiary) volcanic rocks, notable occurrences of gold and silver tellurides are known at Cripple Creek, Colorado; Brad and Nagyag, Romania (Transylvania); Vatukoula, Fiji and elsewhere.

In detail, the gold tellurides occur mainly in quartz and quartz-carbonate veins and in pyritized, silicified and carbonated zones in volcanic rocks. Wall-rock alteration effects characterized by carbonatization, hydration, pyritization and silicification are generally marked in these deposits. Some massive sulphide deposits in volcanic assemblages, particularly those rich in copper, carry gold and silver tellurides but with less frequency than the veins and carbonatized-silicified zones. Skarn deposits do not seem to contain gold and silver tellurides in any abundance according to my investigations, although other tellurides, mainly those of bismuth, may occur in some quantity in such an environment. The minerals most commonly associated with gold and silver tellurides include pyrite, arsenopyrite, pyrrhotite, tetrahedrite-tennantite, native gold, native tellurium (rare in Precambrian but common in Tertiary deposits), other tellurides (particularly coloradoite, HgTe), tellurbismuth, various Cu, Pb, Zn, Ag and Bi sulphides and sulphosalts, tourmaline and fluorite. The paragenesis of deposits containing gold tellurides is often quartz and pyrite followed in turn by base metal sulphides, tellurides and native gold. This sequence is, however, not invariable, gold and tellurides apparently being deposited simultaneously in some deposits, or gold may precede the tellurides.

*Aurostibite* has been recognized in the gold deposits of the Yellowknife and Larder Lake areas in Canada (Graham and Kaiman, 1952), in the deposits of Krasna Hora and Milesov in Czechoslovakia (Sobotka, 1954), in the antimony veins of Costerfield, Victoria, Australia (Stillwell, 1952), in the Lone Hand and Jessie Gold mines, Gwanda district, Rhodesia (Eales, 1962), and in the Indarama Gold-Antimony Mine, Sebakwe area, Que Que, Rhodesia (Mehliss, 1968). It is probably more common than these few occurrences would suggest. According to my observations (Boyle, 1961*a*) aurostibite is generally closely associated with gold in deposits that contain stibnite and other antimony minerals. Aurostibite in these environments frequently rims some of the gold particles and appears to be younger than gold, but good relationships for establishing the paragenesis of the mineral are uncommon. In the Czechoslovakian occurrences aurostibite is said to be younger than the native gold. In the Victoria occurrences the mineral occurs in the quartz-gold-stibnite veins. According to Stillwell (1952) the mineral is best preserved in quartz and, where observed in stibnite, tends to appear as relict areas. Its occurrence in a gold grain containing a gold-aurostibite eutectic led Stillwell to conclude that the mineral formed above 360°C, a higher temperature than that which the younger stibnite was deposited. Stillwell states that aurostibite is a relatively unstable compound and has been largely dissociated in the later stages of vein formation, yielding the dull, rusty, cellular-textured gold that is a common feature of stibnite-bearing veins. The dissociation yields native antimony and gold. The aurostibite in the Gwanda district of Rhodesia contains of the order of 1 per cent nickel and nondetectable amounts of silver. Much of the aurostibite in these deposits rims gold and is probably late, but some of the purer gold in the ore of the Jessie Mine is younger than aurostibite. In the Indarama Mine in Rhodesia the aurostibite was deposited simultaneously with native gold, both minerals being late in the general mineral paragenesis.

The aurostibite in the Bestyube goldfield in northern Kazakhstan, U.S.S.R., forms reaction rims around native gold and is thus a late mineral formed by the reaction of the gold with antimony-bearing solutions in a reducing environment (Naz'mova *et al.,* 1975). Electron microprobe analyses showed the aurostibite to contain Au – 44.52; Ag – 0.12; Cu – 0.08; Sb – 52.73; and As – 1.73 weight per cent. In the Yakutian deposits aurostibite occurs in quartz-stibnite veins where it is intimately intergrown with or rims native gold (Indolev and Zhadanov, 1975). The paragenesis in some samples is native gold followed by aurostibite; in a few others stibnite followed successively by aurostibite and a late generation of native gold. The aurostibite is considered to have formed in the deposits mainly by reactions between early precipitated gold and late stage solutions containing antimony.

Barton (1971) has concluded that aurostibite is stable only under conditions of relatively low sulphur activity, and that the assemblage pyrite + aurostibite is stable only at low temperatures (below about 125°C, but the uncertainties are too large for this to be a useful point on the geothermometric scale). This temperature agrees with the finding of the writer (Boyle, 1954) that late quartz, probably of the same generation as gold and aurostibite, has a temperature of deposition (actually decrepitation temperature and liquid inclusion filling temperature) around 150°C.

*Fischesserite,* the silver-gold selenide, $Ag_3AuSe_2$, is isometric and isostructural with petzite. It occurs in carbonate-quartz veins at Predborice, Bohemia, Czechoslovakia associated with chalcopyrite, naumannite, clausthalite, berzelianite, gold and other selenides (Johan *et al.,* 1971). It appears to be a late mineral in the paragenetic sequence and is commonly situated between the grain boundaries of carbonate minerals. The mineral has also been recognized in certain unusual ores in the Texas Gulf massive sulphide body at Timmins, Ontario.

*Gold tellurate* is reported as a supergene mineral at the Daté Mine, Hokkaido, Japan (Watanabe, 1952). The mineral is evidently derived by the oxidation of gold tellurides. It requires confirmation.

A number of synthetic compounds of gold are relatively stable and may occur as minerals, although they have not yet been identified. These compounds include various selenides, seleno-tellurides, mixed Au-Ag sulphides, the phosphide, the chloride and various telluride halides of the type $AuXTe_2$ ($X$=Cl,Br,I). By analogy with $AuSb_2$ one might also suspect that the compound $AuAs_2$ should occur in nature, although a search by electron-microbe by the writer and his colleagues has failed to find such a mineral in auriferous ores carrying abundant native arsenic, arsenopyrite and other arsenic-bearing minerals. The reason for the nonappearance of $AuAs_2$ in nature may result from the relatively high instability of the mineral at low temperatures due to the unfavourable electronic (electronegativity) relationships discussed previously. (*See further* the discussion under gold in pyrite and arsenopyrite.)

Barton *et al.* (1978) have recently described a double sulphide of silver and gold, *uytenbogaardtite*, $Ag_3AuS_2$, from Tambang Sawah, Benkoelen district, Sumatra, Indonesia; the Comstock Lode, Nevada, U.S.A.; and Smeinogorski, Altai, U.S.S.R. At all three localities uytenbogaardtite occurs as small (up to 100$\mu$) blebs and rims intimately associated with electrum, acanthite, quartz and other minerals.

## Gold in other minerals

Gold is a minor and trace constituent of a great variety of minerals, a feature of the geochemistry of the element that has been extensively investigated for many years. A summary of the status of gold in minerals up to 1969 is contained in the paper by Jones and Fleischer (1969).

The writer's investigations, based on optical and electron microprobe work on polished and thin sections, indicates that the gold in many minerals is present in particulate form, generally as native gold but also as gold tellurides and aurostibite. In some minerals, however, the traces of gold are probably lattice constituents.

### *Gold in silicates*

The older data (prior to 1950) recorded in the literature on the gold content of silicates are sparse and seemingly unreliable since the values recorded range from 0.5 to >0.5 ppm, amounts that are relatively high considering the abundance of gold in nature.

Table 7 records some of the more recent (post-1950) analyses of silicate minerals, a few from the National Mineral Collection of Canada. The latter were specially purified, and the gold in these samples was done by a fire assay–atomic absorption method the detection limit being 0.01 ppm. The silver in the samples was done by spectrographic and atomic absorption methods.

As shown by Table 7 the gold content of silicates ranges from about 0.0002 to 0.924 ppm. There is no strikingly apparent relationship in the gold content of silicates in the series quartz-feldspar-mica-amphibole-pyroxene-olivine, although there is a positive indication that minerals like biotite and amphibole contain a little more gold than the others. This is suggested from recent studies such as those carried out by Zvereva and Gavrilenko (1971). In the dark silicate minerals gold may substitute in the iron sites, although we suspect that much if not all of the gold may be present in microscopic

Table 7. Gold and silver contents of common silicate minerals

| Mineral and locality | Au | Ag | Reference |
|---|---|---|---|
| | (ppm) | | |
| *Quartz* | | | |
| U.S.S.R. | | | |
| Altai and Transbaikal | 0.0006–0.0042<br>(av., 0.0008) | – | 1 |
| Altai-Sayan | 0.011 (av.) | – | 2 |
| Kazakhstan | 0.0011–0.012 | | 4 |
| Altai, Transbaikal and Urals | 0.0016 (av.) | | 5 |
| Urals | 0.0017 (av.) | | 6 |
| U.S.A. | | | |
| Helena, Montana (quartz and feldspar) | 0.006–0.176<br>(av., 0.065) | | 3 |
| Canada | | | |
| Buckingham, Que. | <0.01 | <0.05 | 7 |
| Lansdowne, Ont. (crystals) | <0.01 | <1.0 | 7 |
| *Feldspars* | | | |
| U.S.S.R. | | | |
| Altai and Transbaikal | 0.0002–0.0005<br>(av., 0.0003) | – | 1 |
| Altai-Sayan | 0.0040 (av.) | | 2 |
| Altai-Sayan | 0.018 | | 2 |
| Kazakhstan | 0.0013–0.0052 | | 4 |
| Altai, Transbaikal and Urals | 0.0016–0.0017 | | 5 |
| Urals | 0.0016–0.0017 | | 6 |
| Canada | | | |
| Eau Claire, Ont. (albite) | <0.01 | <0.5 | 7 |
| Villeneuve Tp., Que. (albite) | <0.01 | <0.5 | 7 |
| Bathurst Tp., Ont. (microcline) | <0.01 | <0.5 | 7 |
| Portland Tp., Que. (microcline) | <0.01 | <0.5 | 7 |
| Nain Island, Lab. (Ca feldspar) | <0.01 | <0.5 | 7 |
| *Feldspathoids* | | | |
| Canada | | | |
| Davis Hill, Ont. (nepheline) | <0.01 | <0.5 | 7 |
| Nephton, Ont. (nepheline) | <0.005 | 0.9 | 7 |
| Bancroft, Ont. (sodalite) | <0.01 | <0.5 | 7 |
| *Micas* | | | |
| *Muscovite:* | | | |
| U.S.S.R. | | | |
| Altai-Sayan | 0.0038 (av.) | – | 2 |
| Urals | 0.0109 (av.) | | 6 |
| Canada | | | |
| Eau Claire, Ont. | <0.01 | <0.5 | 7 |
| *Biotite:* | | | |
| U.S.S.R. | | | |
| Altai-Sayan | 0.0040 (av.) | – | 2 |
| Altai | 0.0091 (av.) | – | 2 |
| Kazakhstan | 0.001–0.0119 | – | 4 |
| Altai, Transbaikal and Urals | 0.0019 (av.) | | 5 |
| Urals | 0.0018 (av.) | | 6 |
| U.S.A. | | | |
| Helena, Montana | 0.002–0.924<br>(av., 0.076) | | 3 |
| Canada | | | |
| Douglas, Ont. | <0.01 | <0.5 | 7 |
| *Amphiboles* | | | |
| U.S.S.R. | | | |
| Altai-Sayan | 0.0059 (av.) | – | 2 |
| Kuznetsk, Ala-Tau | 0.077 (av.) | – | 2 |
| Kazakhstan | 0.0026–0.0201 | | 4 |
| Altai, Transbaikal and Urals | 0.0020 (av.) | | 5 |
| Urals | 0.0016 (av.) | | 6 |
| U.S.A. | | | |
| Helena, Montana (hornblende) | 0.003–0.823<br>(av., 0.100) | – | 3 |
| Canada | | | |
| Wilberforce, Ont. | <0.01 | <0.5 | 7 |
| Bathurst Tp., Ont. | <0.01 | <0.5 | 7 |

Table 7. (cont'd.)

| Mineral and locality | Au | Ag | Reference |
|---|---|---|---|
| | (ppm) | | |
| *Pyroxenes* | | | |
| U.S.S.R. | | | |
| Altai-Sayan | 0.016 (av.) | – | 2 |
| Kazakhstan | 0.0137–0.0240 | | 4 |
| Canada | | | |
| Yates Mines, Sandy Creek, Que. | <0.01 | <0.5 | 7 |
| Ball Mines, Haliburton, Ont. | <0.01 | <0.5 | |
| *Chlorite* | | | |
| U.S.S.R. | | | |
| Altai, Transbaikal and Urals | 0.0030 (av.) | | 5 |
| Urals | 0.0025 (av.) | | 6 |
| *Olivine* | | | |
| U.S.S.R. | | | |
| Altai-Sayan | 0.014 (av.) | – | 2 |
| Canada | | | |
| Bigelow Tp., Que. | <0.01 | <0.5 | 7 |
| *Epidote* | | | |
| U.S.S.R. | | | |
| Altai, Transbaikal and Urals | 0.0026 (av.) | | 5 |
| Urals | 0.0025 (av.) | | 6 |
| *Tourmaline* | | | |
| U.S.S.R. | | | |
| Altai-Sayan | 0.012 (av.) | | 2 |
| Canada | | | |
| Portland Tp., Que. | <0.01 | <0.5 | 7 |
| Leduc Mine, Wakefield Tp., Que. | <0.01 | <0.5 | 7 |
| Villeneuve Mine, Villeneuve Tp., Que. | <0.01 | <0.5 | 7 |
| South March, Ont. | <0.005 | 0.1 | 7 |
| *Sphene* | | | |
| U.S.S.R. | | | |
| Altai-Sayan | 0.0039 (av.) | | 2 |
| Altai, Transbaikal and Urals | 0.0029 (av.) | | 5 |
| Urals | 0.0027 (av.) | | 6 |
| *Garnet* | | | |
| Canada | | | |
| Labelle Mine, Que. | 0.01 | <0.5 | 7 |
| Dana Tp., Ont. | <0.01 | <0.5 | 7 |
| U.S.S.R. | | | |
| Urals | 0.0052 (av.) | | 6 |
| *Zircon* | | | |
| Canada | | | |
| Saramac Mines, Ont. | 0.01 | <0.5 | 7 |

References: 1. Anoshin and Potap'yev (1966); neutron activation methods.
2. Shcherbakov and Perezhogin (1964); neutron activation methods.
3. Mantei and Brownlow (1967); neutron activation methods.
4. Zvereva and Gavrilenko (1971); neutron activation methods.
5. Anoshin *et al.* (1970); neutron activation methods.
6. Bushliakov (1971); neutron activation methods.
7. Geological Survey of Canada; assay and atomic absorption methods.

inclusions of pyrite and/or magnetite which these minerals often contain. Biotite and other ferromagnesian minerals devoid of pyrite and/or magnetite contain only very low amounts of gold (<0.01 ppm) in our experience.

### *Gold in native elements*

Gold is a frequent trace and minor constituent in native elements as shown in Table 8. In general the metallic elements contain more gold than the semimetallic and nonmetallic varieties such as graphite, sulphur, etc.

Native arsenic occurs in some gold deposits as does also native antimony. Both minerals contain relatively high contents of gold. My investigations of native arsenic from Bau, Sarawak by polished sections and microprobe show that some of the gold is present as minute inclusions. This gold amounts to about 1/700 of the overall amount determined by assay. It is concluded, therefore, that the remainder of the gold is present as a lattice constituent of the arsenic. The same features prevail in the native antimony from West Gore, Nova Scotia, except that more of the gold is present in the native form.

Bismuth is notably low in gold content according to my analyses. The small amounts present are probably lattice constituents. Graphite contains a little gold, but most of the element is probably present in the small crystals and specks of pyrite, which are invariably present in graphite from veins. The values for diamond given by Mirzaev and Khabirov (1972) are very low.

Copper, silver and the various platinoid metals and alloys invariably contain gold, often in relatively large amounts. Pure native copper from some deposits, mainly in Ontario and Michigan, contains only traces of gold according to my experience. Other deposits, however, appear to have considerable amounts of gold in the native copper according to the published analyses. Probably most of the gold reported in native copper is a lattice constituent. Native silver from Cobalt, Ontario is notably low in gold, but that from Kongsberg, Norway in similar deposits, is relatively enriched in the element according to the published analyses. Aurian silver or kustelite is reported from a number of deposits. In this mineral Au substitutes for Ag, and a complete series extends through argentian gold (electrum) to gold. The various platinoids including native platinum, platiniridium, osmiridium, aurosmiridium, iridosmine, etc. generally contain gold, especially in placers. The quantity of gold varies widely as shown by the analyses in Table 8. In some deposits most of the gold is probably present as a lattice constituent in the native platinoids; in other deposits the platinoids are intergrown with free gold. In a few deposits such as those in the Kuznetsk, Alatau region of U.S.S.R the gold forms thin blooms and films, and more rarely thin crusts on nuggets of osmiridium (sysertskite) and similar platinoids. Small fractures may also contain this type of gold which according to Syrovatskii *et al.* (1969) is definitely secondary and formed within the placers.

Some authors record up to 2.7 per cent Au in native tellurium, but my research on the mineral indicates that little gold is partitioned into pure native tellurium. Samples from Cupra mines, Quebec show only traces of gold, whereas associated tellurides such as altaite and tellurbismuthite are greatly enriched in the element.

The sulphur of gossans on auriferous deposits commonly contains some particulate native gold. A sample of native sulphur from acidic sulphate gossan on cupriferous pyrite deposits on the island of Cyprus is reported to contain 8200 ppm Au (H.A. Tourtelot; U.S. Geol. Surv. Circ. 622, p. 5, 1969). The gold occurs as particles, 10 to 100μ across, and the smaller ones show poorly formed crystal faces. The larger particles are rounded, resembling framboidal pyrite which many geologists believe to be of bacterial origin. The sulphur associated with fumaroles, salt domes and other types of deposits is normally low in gold (<0.01 ppm).

### *Gold in silver and base metal tellurides and selenides*

Gold is a common trace and minor element in practically all of the silver and base metal tellurides and selenides, and in

Table 8. Gold and silver contents of native elements

| Native element and locality | Au | Ag | Au/Ag ratio | Reference |
|---|---|---|---|---|
| | (ppm) | | | |
| *Arsenic,* As | | | | |
| Germany; Andreasberg, Harz | 150 | >1000 | <0.1 | 1 |
| Malaysia; Bau, Sarawak | 20–40 | 30–50 | 0.75 | 3 |
| Germany; Thüringia | 5 | 1 | 5 | 4 |
| *Allemontite,* (As, Sb) | | | | |
| Canada; Atlin, B.C. | 500 | – | – | 4 |
| Canada; Atlin, B.C. | 421 | 294 | 1.43 | 3 |
| *Antimony,* Sb | | | | |
| U.S.A.; Kern County, California | 35.2 | 0.7 | 50.2 | 3 |
| Canada; West Gore, N.S. | 12.0 | 0.3 | 40.0 | 3 |
| *Bismuth,* Bi | | | | |
| Germany; Altenberg, Saxony | 0.03 | 3.5 | 0.008 | 3 |
| Canada; O'Brien Mine, Cobalt, Ont. | 0.050 | 318 | 0.0001 | 3 |
| Australia; New South Wales | 1.8 | 3.5 | 0.51 | 3 |
| *Graphite,* C | | | | |
| Canada; Black Donald Mines, Calabogie, Ont. | 0.035 | <0.5 | >0.07 | 3 |
| Canada; Buckingham, Que. | 0.020 | <0.5 | >0.04 | 3 |
| *Diamond,* C | | | | |
| U.S.S.R., various | 0.00056–0.0031 | | | 4 |
| *Copper,* Cu | | | | |
| Norway; Kviteseid | 200 | >1000 | <0.2 | 1 |
| Canada; Indian Mine, Thunder Bay District, Ont. | 0.02 | 41 | 0.0004 | 3 |
| U.S.A.; Pewabic bed, Keweenaw Peninsula, Michigan | <0.01 | 73.5 | <0.0001 | 3 |
| Various (Chukhrov) | 2–3% | | | 4 |
| *Silver,* Ag | | | | |
| Norway; Kongsberg | 40 | 98.45% | ≪1 | 4 |
| Canada; (Nova Scotia Mine, Cobalt, Ont.) | 3.0 | 99+% | – | 3 |
| Canada; (Castle-Tretheway Mine, Gowganda, Ont.) | 4.1 | 99+% | – | 3 |
| Canada; (Echo Bay Mine, Echo Bay, N.W.T.) | 13.5 | 99+% | – | 3 |
| Aurian silver (kustelite) | 0–30% | – | – | 4 |
| *Iron,* Fe | | | | |
| Greenland; Ovifak, Disko | 1–5 | 5–10 | 0.4 | 2 |
| Germany; Bühl | 0.5 | 5–10 | 0.06 | 2 |
| *Zinc,* Zn | | | | |
| Canada; Keno Hill, Y.T. | nd | tr | – | 3 |
| *Lead,* Pb | | | | |
| Various | tr | tr | – | 4 |
| *Mercury,* Hg | | | | |
| Various | tr–m | tr–m | – | 4 |
| *Iridosmine,* (Os,Ir) | | | | |
| Australia; New South Wales | 800 | – | – | 4 |
| U.S.S.R.; Urals | >1000 | 600 | >1.6 | 1 |
| Various (Chukhrov) | 9000 | – | – | 4 |
| *Osmiridium* (Ir, Os) | | | | |
| Various (Chukhrov) | 19.3% | – | – | 4 |
| *Platinum,* Pt | | | | |
| Brazil | >1000 | >1000 | – | 1 |
| U.S.S.R.; Urals | 500 | 200 | 2.5 | 1 |
| Various (Chukhrov) | up to 3% | – | – | 4 |
| Canada; Similkameen River, B.C. | 300 | 40 | 7.5 | 3 |
| Canada; Horsefly River, B.C. | 240 | 10 | 24 | 3 |
| Canada; North Saskatchewan River, Alta. | 3600 | 1300 | 2.8 | 3 |
| *Platiniridium,* (Pt,Ir) | | | | |
| Brazil | 200 | – | – | 1 |
| *Sulphur,* S | | | | |
| Mexico; San Felipe, Baja California | 0.030 | <0.5 | >0.06 | 3 |
| Italy; Cianciani | <0.01 | <0.5 | – | 3 |
| *Tellurium,* Te | | | | |
| Canada; Cupra Mines, Quebec | <10 | >50 | | 3 |
| Various (Chukhrov) | 0.15–2.78% | | | 4 |

References: 1. Analysis by Noddack and Noddack (1931).
2. Analysis by Goldschmidt and Peters (1932).
3. Analysis by Geological Survey of Canada, Mines Branch and Bondar-Clegg and Co., Ltd., Ottawa.
4. Other sources: Hintze (1889–1968), Doelter *et al.* (1911–1931); Palache *et al.* (1944); Fischer (1958–59); Chukhrov (1960–1965); Mirzaev and Khabirov (1972).

Notes: nd – not detected
tr – trace
m – minor element

some it occurs in considerable quantities (Table 9). From the available data the tellurides appear to contain more of the element than the selenides, but the two types of minerals rarely coexist in one setting, and the partition of gold between the two species is, therefore, relatively unknown. Since natural gold tellurides are common and natural gold selenides *sensu strictu* have not yet been reported one can assume that the bond of gold to tellurium is much more stable than that to selenium in nature. In the double selenide, fischesserite, $Ag_3AuSe_2$, the gold content is 27.4 per cent.

Table 9. Gold and silver contents of silver and base metal tellurides and selenides

| Mineral and locality | Au | Ag | Au/Ag ratio | Reference |
|---|---|---|---|---|
| | (ppm) | | | |
| *Hessite,* $Ag_2Te$ | | | | |
| U.S.S.R.; Krasnyi Klyutsh | 2000 | 62.45% | 0.003 | 1 |
| *Altaite,* PbTe | | | | |
| Australia; Kalgoorlie | 200 | 4300 | 0.05 | 1 |
| U.S.S.R.; Altai | 400 | >1000 | <0.40 | 2 |
| *Melonite,* $NiTe_2$ | | | | |
| Australia | 3220 | 770 | 4.2 | 2 |
| *Clausthalite,* PbSe | | | | |
| Germany; Tilkerode, Harz | 250 | >1000 | <0.25 | 2 |
| *Berzelianite,* $Cu_2Se$ | | | | |
| Sweden; Skrikerum | 100 | >1000 | <0.10 | 2 |
| Czechoslovakia; Bukov | 0.1 | 1460 | 0.00007 | 3 |
| *Umangite,* $Cu_3Se_2$ | | | | |
| Canada; Beaverlodge district, Sask. | 0.3 | 8450 | 0.00003 | 3 |

References: 1. Hintze (1889–1968); Doelter *et al.* (1911–1931); Palache *et al.* (1944); Chukhrov (1960–1965).
2. Noddack and Noddack (1931).
3. Laboratories, Mines Branch and Geological Survey of Canada.

As shown in Table 9 silver tends to predominate over gold in the base metal tellurides and selenides, and the Au/Ag ratio is invariably less than 1, often by several orders of magnitude, especially in the selenides. In the tellurides and selenides gold may replace Ag, Pb, Ni, Bi and Cu, although in many of these minerals, especially the tellurides, small amounts of gold tellurides may be mixed with the base metal varieties.

### *Gold in sulphides, arsenides, antimonides, sulphosalts and similar minerals*

There is a large literature on the gold content of these minerals. The data in Tables 10 and 11 have been compiled up to the end of 1975 from the most significant works on the subject and from the numerous analyses done in the laboratories of the Geological Survey. It is recognized that the data are incomplete, but the ranges shown give an idea of the gold content to be expected in the common sulphides, arsenides, etc.

One of the major problems in ascertaining the role of gold in sulphides, arsenides and allied minerals is the matter of purity of the samples. In a great many occurrences the sulphides, arsenides, etc. are intimately admixed with native gold and gold minerals or contain these minerals as blebs, specks and small crystals. In many cases the investigators do not state whether the minerals are homogeneous or not, and it is impossible to tell if the gold is in the lattices of the minerals or present in one or more admixed gold minerals. Geochemists doing spectrographic and other types of analytical work on sulphides, arsenides and similar minerals should examine their specimens for homogeneity by microscopic methods or better still by means of the electron probe. The data would then be of more significance in ascertaining the extent of replacement of one element by another.

The arsenides and antimonides commonly carry small amounts of gold, those containing the platinum metals (sperrylite) having the highest concentrations according to our analyses. Other arsenides, particularly the copper-bearing species, e.g., domeykite also appear to contain relatively high amounts of gold as shown by the analyses of others. In the arsenides and antimonides gold is probably a lattice constituent and substitutes for the platinum metals and copper and possibly also for cobalt, nickel and iron.

Gold is a common microconstituent in a large number of sulphides and sulphide-arsenides, being concentrated mainly in the copper, silver and antimony species and in pyrite and arsenopyrite. The lead and zinc sulphides and sulphosalts do not normally contain enrichments of gold, although in some deposits galena and sphalerite are indicators of high gold values. Where this occurs the gold is mainly in the native form occurring in close associationship with galena and sphalerite and frequently within these two sulphides as specks and blebs. This has been recently confirmed by the researches of Mincheva-Stefanova and Stefanov (1972) who analyzed some 65 sphalerites from various lead-zinc and polymetallic deposits in Bulgaria. Their values range widely (0.0012–4.08 ppm Au); most of the gold is present in the sphalerite as very finely dispersed inclusions of the native metal. In some sphalerites the dark coloured zones were relatively enriched in gold compared with the lighter zones. The greenish shade of a yellowish green cleiophane (greenish sphalerite with a gold content of 0.0792 ppm) was thought to be due to the presence of very finely dispersed gold throughout the mineral. According to my observations, the case for galena may, however, be somewhat different, since some rather pure galenas contain high contents of gold. In such galenas gold may replace lead, the electronic compensation being provided by tellurium in the sulphur positions. Alternatively these galenas may contain microscopic specks of gold tellurides. Whatever the mechanism it is common to find tellurium in most auriferous galenas.

In a recent paper Parilov and Netaliyeva (1973) carried out a number of leaching experiments on argentiferous sphalerite using $NH_4OH$. Their results indicate that much of the silver in sphalerite is present in the halide form (AgCl), possibly as epitaxitic inclusions because of the similarities in the crystal structures of ZnS and AgCl. Perhaps some of the gold in some sphalerites is, likewise, present in the halide form.

In the various copper, silver and antimony sulphides and sulphide-arsenides gold occurs native and apparently as a lattice constituent. Chalcocite, bornite, chalcopyrite and enargite frequently carry relatively high contents of gold, yet do not exhibit any evidence of the presence of the free metal under the highest magnifications possible with the ore microscope. In this case it seems probable that gold is a lattice constituent substituting in the copper sites. The same situation prevails for a variety of silver minerals, including argentite, freibergite and argyrodite, suggesting that gold in these

Table 10. Gold and silver contents of some common sulphides, arsenides, antimonides, bismuthides and sulphosalts

| Mineral and locality | Au | Ag | Au/Ag ratio | Reference | Remarks |
|---|---|---|---|---|---|
| | (ppm) | | | | |
| *ARSENIDES AND ANTIMONIDES* | | | | | |
| *Niccolite,* $NiAs$ | | | | | |
| Various | 1–10 | 10–100 | <1 | 1 | Purity unknown |
| Canada; Cobalt, Ont. | <0.1 | 7.2 | <1 | 9 | Pure |
| *Smalite,* $[(Co,Ni)As_{3-x}]$ | | | | | |
| Canada; O'Brien Mine, Cobalt, Ont. | 0.045 | 48 700 | <1 | 9 | Contains micro-inclusions of silver |
| *Skutterudite,* $(Co,Ni)As_3$ | | | | | |
| Various | 0.1–5 | 1–1000 | <1 | 1 | Purity unknown |
| Morocco | 8.4 | <0.5 | >1 | 9 | Pure |
| Canada; Cobalt, Ont. | <0.1 | 23 000 | <1 | 9 | Contains micro-inclusions of native silver |
| *Safflorite,* $(Co,Fe)As_2$ | | | | | |
| Various | 0.3–5 | 0.5–100 | <1 | 1 | Purity unknown |
| *Rammelsbergite,* $NiAs_2$ | | | | | |
| Germany; Schneeberg | 0.3 | 5 | 0.06 | 1 | Purity unknown |
| *Domeykite,* $Cu_3As$ | | | | | |
| Mexico; Paracatas | 25 | >1000 | <1 | 2 | Purity unknown |
| *Sperrylite,* $PtAs_2$ | | | | | |
| Canada; Sudbury, Ont. | 40 | 300 | 0.13 | 2 | Purity unknown |
| Canada; Sudbury, Ont. | 700 | 2300 | 0.3 | 9 | Pure |
| *Breithauptite,* $NiSb$ | | | | | |
| Canada; Cobalt, Ont. | <0.01 | 460 | <1 | 9 | Contains micro inclusions of silver |
| *SULPHIDES AND SULPHIDE-ARSENIDES* | | | | | |
| *Chalcocite,* $Cu_2S$ | | | | | |
| U.S.A.; Kennecott Mine, Alaska | <0.02 | 265 | <0.00007 | 9 | Pure |
| U.S.A.; Butte, Montana | 12 | 500 | 0.02 | 2 | Purity unknown |
| U.S.A.; Butte, Montana | 1.05 | 175 | 0.006 | 9 | Pure |
| S.W. Africa; Tsumeb | 0.075 | 93 | 0.0008 | 9 | Pure |
| Canada; Alma, N.B. | 7.0 | 68.2 | 0.10 | 9 | Pure |
| Canada; Dorchester, N.B. | 0.03 | 320 | 0.00009 | 9 | Pure |
| *Bornite,* $Cu_5FeS_4$ | | | | | |
| Germany; Mansfield | 8 | >1000 | <1 | 2 | Purity unknown |
| Canada; Copper Mountain, B.C. | 0.475 | 94.7 | | 9 | Pure |
| Canada; Batachewan Bay, Ont | 0.07 | 31.2 | | 9 | Pure |
| *Galena,* $PbS$ | | | | | |
| U.S.S.R.; Almalyk | 13 | 450 | 0.03 | 3 | Purity unknown |
| U.S.S.R.; Karamazar deposit | 3.0 | 1126 | 0.002 | 8 | Purity unknown |
| Germany; Thuringia | 0.01 | 20–100 | <1 | 4 | Purity unknown |
| South Africa | 30 | >1000 | <1 | 2 | Purity unknown |
| Canada; Keno Hill, Yukon | 0.01–0.19 | 1650–6300 | <1 | 9 | Contains minor amounts of tetrahedrite |
| Canada; Walton, N.S. | <0.02 | 355 | <1 | 9 | Pure; assay |
| Canada; Carleton Place, Ont. | 0.015 | 32 | 0.0004 | 9 | Pure; assay |
| Canada; Hudson Bay Range, B.C. | trace | 2257 | <1 | 12 | 98% pure |
| *Sphalerite,* $ZnS$ | | | | | |
| Germany; Silesia | 3 | 150 | 0.02 | 2 | Purity unknown |
| Germany; Bühl | 0.5 | 5 | 0.10 | 1 | Purity unknown |
| U.S.S.R.; Chukotka | 500 | | | 5 | Purity unknown |
| U.S.S.R.; Karamazar deposit | 3.3 | 364 | 0.009 | 8 | Purity unknown |
| U.S.S.R.; Uzbekistan | 1.3 | 75 | 0.017 | 8 | Purity unknown |
| Canada; Keno Hill, Y.T. | 0.3–0.5 | 10–5000 | <1 | 9 | Some specimens contain tetrahedrite |
| Canada; Yellowknife, N.W.T. | <10 | 10–100 | | 9 | Pure; spectrographic analyses |
| Canada; Hudson Bay Range, B.C. | 3.4 | 68.4–342.0 | 0.01–0.05 | 12 | 94–97% pure |
| Canada; Orchan Mine, Que. | 0.55 | 38.3 | 0.014 | 10 | Mill concentrate |
| Canada; Normetal Mine, Que. | 0.41 | 50.95 | 0.008 | 10 | Mill concentrate |

Table 10. (cont'd.)

| Mineral and locality | Au | Ag | Au/Ag ratio | Reference | Remarks |
|---|---|---|---|---|---|
| | (ppm) | | | | |
| *Chalcopyrite,* $CuFeS_2$ | | | | | |
| Germany; Clausthal | 20 | 800 | 0.025 | 2 | Purity unknown |
| Germany; Zwickau | 0.2 | 100–1000 | <1 | 1 | Purity unknown |
| Germany; Thüringia | 0.02 | ~10 | <1 | 4 | Purity unknown |
| U.S.S.R.; Almalyk | 22 | 0.02 | 1100 | 3 | Purity unknown |
| U.S.S.R.; Karamazar deposit | 4 | 927 | 0.004 | 8 | Purity unknown |
| U.S.S.R.; Uzbekistan | 8 | 90–212 | <1 | 8 | Purity unknown |
| Canada; Yellowknife, N.W.T. | <10 | 10–1000 | <1 | 9 | Pure; spectrographic analyses |
| Canada; Keno Hill, Y.T | 0.9 | 1280 | 0.0007 | 9 | Pure; assay |
| Canada; Walton, N.S. | 0.17 | 1300 | 0.0001 | 9 | Pure; assay |
| Canada; Hudson Bay Range, B.C. | 6.84 | 694.2 | 0.009 | 12 | 97% pure |
| Canada; Horne Mine, Noranda, Que. | 22.26 | 56.08 | 0.39 | 10 | Mill concentrate |
| Canada; Opemiska Mine, Que. | 4.44 | 102.6 | 0.04 | 10 | Mill concentrate |
| Canada; Orchan Mine, Que. | 2.32 | 533.5 | 0.004 | 10 | Mill concentrate |
| Canada; Campbell-Chibougamu Mine, Que. | 20.00 | 85.50 | 0.233 | 10 | Mill concentrate |
| Canada; Normetal Mine, Que. | 8.2 | 399.11 | 0.020 | 10 | Mill concentrate |
| *Pyrrhotite,* $Fe_{1-x}S$ | | | | | |
| Norway; Frøysa | 2 | 100 | 0.02 | 2 | Purity unknown |
| Germany; Bühl | 0.5 | 5 | 0.1 | 1 | Purity unknown |
| U.S.S.R.; Chukotka | 2 | – | – | 5 | Purity unknown |
| East Greenland | 0.003 | – | – | 6 | Analysis by neutron activation |
| Canada; Buckingham, Que. | 0.1 | <1 | <1 | 9 | Pure; assay sample from pegmatite |
| Canada; Yellowknife, N.W.T. | <10 | <1 | – | 9 | Pure; spectrographic analysis |
| Canada; Hudson Bay Range, B.C. | 22.2 | 44.4 | 0.5 | 12 | 98% pure |
| *Pentlandite,* $(Fe,Ni)_9S_8$ | | | | | |
| Norway; Espedalen | 6 | 140 | 0.04 | 2 | Purity uncertain |
| Germany; St. Blasien | 0.5 | 10–100 | <1 | 1 | Purity uncertain |
| *Stannite;* $Cu_2FeSnS_4$ | | | | | |
| England; Cornwall | 2–5 | 100 | <1 | 1, 2 | Purity uncertain |
| Czechoslovakia; Zinnwald | 0.2 | 100–1000 | <1 | 1 | Purity uncertain |
| *Argentite* (Acanthite), $Ag_2S$ | | | | | |
| Germany; Freiberg | 200 | – | | 2 | Purity uncertain |
| Canada; Cobalt, Ont. | 0.130 | – | | 9 | Pure |
| Canada; Thunder Bay district, Ont. | 0.380 | – | | 9 | Pure |
| Canada; Echo Bay, N.W.T. | 0.320 | – | | 9 | Pure |
| *Cinnabar,* HgS | | | | | |
| Spain; Almaden | 0.020 | <0.5 | | 9 | Pure |
| U.S.S.R.; Khaydarkan deposit | 0.070 | <0.5 | | 9 | Pure |
| U.S.A.; New Almaden, Calif. | 0.180 | <0.5 | | 9 | Pure |
| *Stibnite,* $Sb_2S_3$ | | | | | |
| Germany; Thüringia | 0.9 | 2 | 0.45 | 4 | Purity unknown |
| U.S.S.R.; Chukotka | 20 | | | 5 | Purity unknown |
| Canada; Yellowknife, N.W.T. | 10–20 | 100–1000 | <1 | 9 | Impure; contains native gold, aurostibite, tetrahedrite, etc. |
| Japan | 0.025 | 0.6 | 0.04 | 9 | Pure |
| *Bismuthinite,* $Bi_2S_3$ | | | | | |
| Canada; Wakefield Tp., Que. | 0.025 | 28 | 0.0009 | 9 | Pure |
| Hungary; Bánát Mines | 3300 | – | – | 11 | Contains inclusions of native gold |
| *Molybdenite,* $MoS_2$ | | | | | |
| Various | 0.05–10 | 10–>100 | <1 | 1 | Purity unknown |
| Germany; Thüringia | 0.02 | >100 | <1 | 4 | Purity unknown |
| Canada; Yellowknife, N.W.T. | 0.145 | <1 | | 9 | Pure |

Table 10. (cont'd.)

| Mineral and locality | Au | Ag | Au/Ag ratio | Reference | Remarks |
|---|---|---|---|---|---|
| | (ppm) | | | | |
| *Pyrite,* $FeS_2$ | | | | | |
| South Africa (Rand) | 0.18 | 0.10 | 1.8 | 9 | Probably contains inclusions of gold |
| East Greenland | 0.016 | | | 6 | Purity unknown |
| Germany; Thüringia | 0.2 | 5 | 0.04 | 4 | Purity unknown |
| Norway; various | 0.4 | 10–70 | <1 | 2 | Purity unknown |
| Italy; various | 0.12–200 | | | 7 | Purity unknown |
| U.S.S.R.; Almalyk | 3.5 | 36 | 0.097 | 3 | Purity unknown |
| U.S.S.R.; Chukotka | 10 | | | 5 | Purity unknown |
| U.S.S.R.; Karamazar deposit | 27 | 141 | 0.191 | 8 | Purity unknown |
| U.S.S.R.; Uzbekistan | 40–187 | 37–232 | – | 8 | Purity unknown |
| Canada; Hudson Bay Range, B.C. | 4.8 | 78.6 | 0.06 | 12 | 80% pure |
| *Alabandite,* MnS | | | | | |
| Roumania; Nagyág | 2 | 30 | 0.07 | 2 | Purity unknown |
| *Marcasite,* $FeS_2$ | | | | | |
| Germany; Westphalia | 4 | 100 | 0.04 | 2 | Purity unknown |
| *Siegenite,* $(Co,Ni)_3S_4$ | | | | | |
| Germany | 1 | >1000 | <1 | 1 | Purity unknown |
| *Arsenopyrite,* FeAsS | | | | | |
| Norway; Skutterud | 8 | 90 | 0.09 | 2 | Purity unknown |
| Germany; Saxony | 0.5 | 10 | 0.05 | 1 | Purity unknown |
| Germany; Thüringia | 0.5 | 15 | 0.03 | 4 | Purity unknown |
| U.S.S.R.; Chukotka | 200 | | | 5 | Purity unknown |
| U.S.S.R.; Karamazar deposit | 1.5 | 318 | 0.004 | 8 | |
| U.S.S.R.; Uzbekistan | 40–559 | 44–160 | – | 8 | |
| Canada; Hudson Bay Range, B.C. | 12.9–20.5 | 3.4–17.1 | 0.75–5.9 | 12 | 99% pure |
| *Cobaltite,* CoAsS | | | | | |
| Canada; Cobalt, Ont. | 5 | 5 | 1 | 1 | Purity unknown |
| Norway; Skutterud | 10 | 200 | 0.05 | 2 | Purity unknown |
| Norway; Skutterud | 0.5 | 1 | 0.5 | 1 | Purity unknown |
| Sweden; Tunaberg | 0.5 | 10 | 0.05 | 1 | Purity unknown |
| Germany; various | 0.3–3 | 5–10 | <1 | 1 | Purity unknown |
| Germany; Thüringia | 5 | 20 | 0.25 | 4 | Purity unknown |
| Canada; Cobalt, Ont. | 0.04 | 50 000 | <1 | 9 | Contains microinclusions of silver |
| *Gersdorffite,* NiAsS | | | | | |
| Germany; various | 5–100 | 1–100 | | 1 | |
| *Ullmannite,* NiSbS | | | | | |
| Germany; various | 0.5–20 | 10–1000 | <1 | 1 | |
| Germany; Thüringia | 1 | 10 | 0.1 | 4 | |
| *SULPHOSALTS* | | | | | |
| *Tetrahedrite,* $Cu_{12}Sb_4S_{13}$ | | | | | |
| England; Cornwall | 8 | >1000 | <1 | 2 | Purity unknown |
| Austria; Tyrol | 60 | >1000 | <1 | 2 | Purity unknown |
| Germany; Thüringia | 0.02 | 20–100 | <1 | 4 | Purity unknown |
| U.S.S.R.; Karamazar deposit | 91 | 15 097 | 0.006 | 8 | Purity unknown |
| Canada; Yellowknife, N.W.T. | 10–100 | 10–>1000 | <1 | 9 | Pure |
| Canada; Keno Hill, Y.T. (freibergite) | 10.9–44.8 | 5–17% | <1 | 9 | Pure |
| Canada; Clyde Forks, Ont. | 0.8 | 762 | 0.001 | 9 | Pure |
| Canada; Hudson Bay Range, B.C. | 71.8 | 25–27% | <1 | 12 | |
| *Tennantite,* $Cu_{12}As_4S_{13}$ | | | | | |
| Canada; Walton, N.S. | <0.03 | 785 | <1 | 9 | Pure |
| *Boulangerite,* $Pb_5Sb_4S_{11}$ | | | | | |
| Canada; Keno Hill, Y.T. | 0.5 | 230 | 0.002 | 9 | Pure |
| *Jamesonite,* $Pb_4FeSb_6S_{14}$ | | | | | |
| Canada; Dublin Gulch, Y.T. | 0.7 | 240 | 0.003 | 9 | Pure |
| *Germanite,* $Cu_3(Ge,Ga,Fe,Zn)(As,S)_4$ | | | | | |
| S.W. Africa; Tsumeb | 40 | 800 | 0.05 | 2 | Purity unknown |

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2. Noddack and Noddack (1931).
3. Badalov and Terekhovich (1966).
4. Fischer (1958–1959).
5. Sidorov (1966).
6. Vincent and Crocket (1960).
7. Minguzzi (1947).
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9. Analyses by laboratories, Geological Survey of Canada, Mines Branch, and Bondar-Clegg and Co. Ltd., Ottawa.
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11. Koch, S. (1948), Acta Mineral. Petrog. vol.2, p. 4.
12. Kirkham (1968).

Table 11. Gold and silver contents of pyrite, pyrrhotite and arsenopyrite from some Canadian mineral deposits and rocks

| Mineral and locality | Au | Ag | Au/Ag ratio | As | Sb | Remarks |
|---|---|---|---|---|---|---|
| | (ppm) | | | (ppm) | | |
| *Pyrite:* | | | | | | |
| Buckingham, Quebec (composite sample) | <0.01 | 0.2 | <1 | 16 | 5 | In pegmatites |
| Richardson Mine, Eldorado, Ont. | 0.5 | 2 | | 56 | <1 | In skarn |
| Keno and Galena Hills, Y.T. (6 samples from Pb-Zn-Ag Deposits) | 0.08–6.1 | <10–200 | <1 | 1100–6760 | 10–265 | Not associated with arsenopyrite. No gold seen in polished sections. Minor tetrahedrite in some samples |
| Keno and Galena Hills, Y.T. (3 samples from gold-quartz deposits) | 2.6–15.7 | <10–200 | <1 | 2900–6500 | 10–1020 | Associated with arsenopyrite. No gold seen in polished sections. Minor tetrahedrite and other sulphosalts in some samples |
| Yellowknife, N.W.T. | 1–5 | 5–20 | <1 | 100–500 | 5–50 | In gold-quartz deposits |
| Walton, N.S. (1 composite sample) | <0.01 | 172 | <1 | 5600 | 40 | Associated with chalcopyrite, galena, sphalerite and tennantite in Pb-Zn-Ag orebody |
| Blind River, Elliot Lake, Ont. | 0.41 | 7.5 | 0.05 | 300 | 6 | Pure, from uraniferous ore |
| Geco Mine, Manitouwadge, Ont. | 1.52 | 400 | 0.003 | – | – | Massive sulphide body |
| Flin Flon Mine, Man. | 0.75 | 33 | 0.02 | – | – | Massive sulphide body |
| Kidd Creek Mine (Texas Gulf Sulphur), Timmins, Ont. | 0.01 | 8 | 0.001 | – | – | Massive sulphide body |
| Nigadoo Mine, Bathurst, N.B. | 0.005 | 140 | <0.001 | – | – | Massive sulphide body |
| Heath Steele Mine, N.B. | 1.00 | 28 | 0.035 | – | – | Massive sulphide body |
| Horne Mine, Noranda, Que. | 2.00 | 20 | 0.10 | – | – | Massive sulphide body |
| Faro Mine, Y.T. | 1.00 | 58 | 0.017 | – | – | Massive sulphide body |
| Weedon Pyrite Mine, Que. | 0.15 | 5 | 0.03 | – | – | Massive sulphide body |
| Louvem Mine, Val d'Or, Que. | 0.23 | 5 | 0.046 | – | – | Massive sulphide body |
| New Calumet Mine, Que. | 1.36 | 750 | 0.002 | – | – | Skarn |
| Cobalt area, Ont. | 0.160 | 5 | 0.03 | 1400 | 10 | In pyritiferous graphitic schist and slate interbedded with greenstone. Minor amounts of chalcopyrite, pyrrhotite and other sulphides |
| Keno-Galena Hills, Y.T. | 0.06–1.9 | 2–14 | <1 | 500–1100 | 15–34 | In quartzite, phyllite and schist remote from veins |
| Walton, N.S. (10 composite samples) | <0.02–0.17 | 0.34–4.0 | <1 | 230–940 | 26–124 | In shales; well removed from mineralized zones |
| Walton, N.S. (3 composite samples) | 0.06–0.37 | 1.7–112.8 | <1 | 70–1600 | 5–28 | In coalified plant zones near minor faults |
| Ovens, N.S. (2 composite samples) | 0.15 | 1.16 | 0.13 | 200 | 6–21 | In slates and greywacke |
| Rawdon area, N.S. (composite sample) | <0.01 | 0.5 | <1 | 6400 | 7 | In slates |
| Wabana, Nfld. (composite sample) | 0.08 | 1.4 | 0.06 | 620 | 30 | Pyritiferous zone in iron beds |
| Florence area, Ont. | 0.02 | 0.17 | 0.1 | 1600 | 41 | In Devonian shales |
| Port Hood, N.S. | 0.04 | 0.17 | 0.23 | 190 | 9.6 | In coal |
| Stonehaven, N.B. | 0.02 | 12 | 0.001 | 1200 | 16 | In pyritiferous coal-bearing sandstone. Minor amount of galena present |
| Champlain Lookout, Gatineau Park, Que. | 0.025 | 1 | 0.02 | – | – | Pyrite cubes in Grenville gneiss |
| *Pyrrhotite:* | | | | | | |
| South of Bancroft, Ont. | 0.012 | 6.1 | 0.001 | 300 | 7.5 | In quartzites |
| Buckingham, Que. | 0.01 | <1 | <1 | – | – | In pegmatites |
| Yellowknife, N.W.T. | <10 | <1 | – | – | – | In gold-quartz veins (spectrographic analyses) |
| St. Stephen, N.B. | 0.105 | 6.2 | 0.017 | 160 | <15 | In nickel deposit |
| Argenteuil Co., Que. | 1.010 | 6.0 | 0.168 | 196 | – | |
| Noranda, Que. | 0.980 | 6.0 | 0.163 | 130 | <15 | In Cu-Zn deposit; minor chalcopyrite |
| Hastings County, Ont. MacDonald Mine, | 0.020 | 2.7 | 0.007 | 76 | <15 | Pegmatite |

Table 11. (cont'd.)

| Mineral and locality | Au | Ag | Au/Ag ratio | As | Sb | Remarks |
|---|---|---|---|---|---|---|
| | (ppm) | | | (ppm) | | |
| *Pyrrhotite (cont'd.):* | | | | | | |
| Garson Mine, Sudbury, Ont. | 0.220 | 3.6 | 0.061 | 61 | <15 | Massive sulphide deposit |
| Alexo Mine, Cochrane, Ont. | 0.220 | 5.0 | 0.044 | 58 | <15 | Massive sulphide deposit |
| Leroi Mine, Rossland, B.C. | 2.110 | 88.0 | 0.024 | 61 | <15 | Massive sulphide deposit |
| *Arsenopyrite:* | | | | | | |
| Keno-Galena Hills, Y.T. | 9.7–17.3 | 10–400 | <1 | >40% | 380–1160 | In gold-quartz veins |
| Dublin Gulch area, Y.T. | 2.4 | 2–20 | <1 | >40% | 170–190 | In gold-quartz veins |
| Yellowknife, N.W.T. | 10 | 5 | 2 | >40% | 10–100 | In gold-quartz veins |
| West Lake Gold Mine, Mt. Uniacke, N.S. | >500 | 48 | >10 | >40% | 330 | In gold-quartz veins |
| Marmora Tp., Hastings County, Ont. | 3.75 | 2.8 | 1.34 | >40% | 45 | Gold-quartz prospect |
| Howry Creek Gold Mine, Curtin Tp., Sudbury district, Ont. | 17.85 | 2.5 | 7.14 | >40% | 50 | In gold-quartz veins |
| Ovens area, N.S. | 2.05 | 0.5 | 4.1 | >40% | 12–200 | In slates and greywacke |
| Molega area, N.S. | 5.95 | 0.8 | 7.4 | >40% | 180 | In slates and greywacke near gold-quartz veins |

*Analyses by Laboratories, Geological Survey of Canada and Bondar-Clegg and Co. Ltd., Ottawa.

minerals occupies some of the silver sites in the lattice. The situation with stibnite is complex. Pure stibnite from Japan appears to contain relatively little gold and silver. In other deposits, however, the mineral is gold- and silver-bearing as at Yellowknife and Red Lake in Canada and in the Chukotka deposits, U.S.S.R. In the Canadian deposits examined by the writer the stibnite is intimately intergrown with tetrahedrite which is gold-bearing and with aurostibite and finely divided native gold which cannot effectively be separated from the antimony sulphide prior to analysis. Hand picked blades of stibnite from these deposits, however, generally contain only a little gold. These facts suggest that relatively little gold enters the stibnite lattice, and that if gold is present in stibnite it occurs predominantly in the native form, as aurostibite, or in admixed sulphosalts. It is of interest to note, however, that Dickson *et al.* (1975) found that synthetic stibnite, orpiment and realgar took up considerable amounts of gold from the gold tubes used in their synthetic studies: stibnite from 1000 to 2000 ppm Au; orpiment from 100 to 2000 ppm Au; and realgar from 50 to 200 ppm Au. The exact nature of the gold in the sulphides was not determined.

Of the various sulphosalts, the tetrahedrite-tennantite series is the most consistently enriched in gold. Only rarely can native gold or other gold minerals be detected in pure auriferous tetrahedrite-tennantite samples suggesting that most of the gold in these minerals is a lattice constituent substituting for copper. That gold prefers the copper sulphosalts has been shown by the writer at Keno Hill (Boyle, 1965*a*). There, tetrahedrite (freibergite) contains from 11 to 45 ppm Au whereas the closely associated lead sulphosalts, boulangerite and jamesonite, contain of the order of 0.5 ppm Au. In a qualitative way the same is true at Yellowknife, although here great difficulty is encountered in obtaining pure separates of each mineral.

Gold is commonly found in pyrite and arsenopyrite, especially in auriferous deposits, a feature of the element which has been known for a long time. Commonly associated elements in the pyrite of both host rocks and deposits are silver, arsenic and antimony and in arsenopyrite, silver and antimony, as shown in Table 11. With respect to pyrite there is no consistent relationship between the arsenic and antimony contents and the gold content; the same is true as regards the antimony and gold contents in arsenopyrite. In pure pyrite the Au/Ag ratio is generally less than 1 in all types of occurrences according to our analyses and those published in the literature. Only rarely have we found exceptions to this generalization, and these are obvious such as in samples where the pyrite contains visible gold as blebs or in late fractures. In samples of pyrite from the Rand ores we have analyzed we have noted an Au/Ag ratio generally greater than 1, but some samples give ratios less than 1. Those having the high ratios generally have specks of native gold which cannot be physically separated from the pyrite. Many investigators have commented upon the close association of gold and pyrite in the Rand among whom Pelletier (1940), Liebenberg (1955) and Saager (1969) should be mentioned as having made detailed studies. It is of interest to note that the Au/Ag ratio in the pyrite in the relatively nonauriferous Blind River–Elliot Lake quartz-pebble conglomerates have a low ratio (0.05) (Table 11). The Au/Ag ratio in arsenopyrite appears to be erratic judging from some of my data and those in the literature. However, in a number of Nova Scotia deposits where I have carefully examined coexisting pyrite and arsenopyrite, both devoid of secondary gold in fractures, the ratio is generally greater than 1 in arsenopyrite and less than 1 in pyrite. This suggests a tendency for arsenopyrite to concentrate gold whereas pyrite tends to take up silver.

The problem of the nature of gold (and silver) in pyrite and arsenopyrite is an old one that first appeared when metallurgists sought to deal with certain gold ores that are not directly amenable to cyanidation processes. Most of these ores are arsenical and usually contain abundant arsenopyrite, which contains most of the gold. Some, such as those in the Bau area, Sarawak, contain the bulk of the gold in native arsenic and minor arsenopyrite. Others are characterized mainly by gold-bearing pyrite, and still others contain gold-bearing arsenopyrite, sulphosalts and pyrite. Visible and microscopic native gold is present in most of these deposits but often makes up only a small proportion of the total amount of gold in the ores. The remainder of the gold is in an 'invisible' form and can only be won by roasting the ores, which liberates the gold in a state amenable to cyanidation. In some gold ores such as those in Fiji and southeastern Ontario practically all of the gold is 'invisible' in either arsenopyrite or pyrite.

Investigations on the nature of gold (and silver) in pyrite and arsenopyrite have been carried out in the past by Bürg (1930, 1935), Head (1934, 1935*a,b*), Haycock (1937), Van Aubel (1939), Kurauti (1941), Maslenitsky (1944) and Stillwell and Edwards (1946) and more recently by Edwards (1958), Clark (1960), Boyle (1961*a*, 1965*a*), Aubert *et al.* (1964), Tyurin (1965*a*), Schweigart (1965), McPheat *et al.* (1969), Korobushkin (1970), Kalitkina (1971), Badalov (1972), Sakharova *et al.* (1972), Wells and Mullens (1973), Klempert *et al.* (1973) and Gavrilov *et al.* (1974). Two views predominate, one that the gold is present in chemical combination in the pyrite and arsenopyrite, and the other that the gold is present in a finely divided (colloidal?), often submicroscopic state ($<0.1\mu$). The former view appears the more probable as will be shown in the following.

Examination of most polished sections of gold-bearing pyrite and arsenopyrite at high magnifications generally reveals the presence of minute blebs or stringers of native gold or other gold minerals that frequently appear to be of a secondary (exsolved) nature. Calculations of the amount of gold present in these forms generally agree with the assay values within the experimental errors inherent in such work. There are, however, a number of deposits where the assay values of pyrite and arsenopyrite, particularly the latter, greatly exceed the amount of gold minerals visible at the highest magnifications under the microscope. This gold is generally not amenable to cyanidation and, in my experience, can only be recovered, by complete breakdown of the pyrite or arsenopyrite lattice either by roasting or by attack with nitric acid or aqua regia. Under the microprobe, domains or points of high gold content in the pyrite and arsenopyrite can rarely be made out, although in some specimens from Châtelet, France, Aubert *et al.* (1964) were able to distinguish gold-rich areas in arsenopyrite. Microscopic and microprobe work, therefore, suggest that much of the 'invisible' gold in pyrite and arsenopyrite is present in a submicroscopic form, probably a lattice constituent of these two minerals. This view is confirmed by recent research using a microprobe and other techniques on auriferous pyrite (0.065 oz/ton) by McPheat *et al.* (1969). They found that 0.02 to 0.03 oz/ton gold was in solid solution and the balance of the metal was finely dispersed as grains throughout the pyrite. Wells and Mullens (1973), however, opted for the particulate gold theory in the Carlin and Cortez ores of Nevada. Using a microprobe they found that much of the gold in the deposits was present in a submicroscopic form ($<0.5\ \mu$) in tiny grains ($<0.005$ mm) of arsenian pyrite and in the thin rims of larger pyrite grains; also in small grains of arsenopyrite where it is present. They concluded that since the gold content varies widely within the interior of large pyrite grains, within pyrite rims and within the disseminated pyrite and arsenopyrite – some pyrite and arsenopyrite is barren – that the gold possibly occurs as submicron particles of native gold or of a gold mineral.

Some synthetic and detailed analytical studies have been done on the problem of the state of gold in pyrite and arsenopyrite. Burg (1930, 1935), who first investigated the problem, showed that when natural gold-bearing pyrite from Brad is heated to 600°C in a vacuum and the liberated sulphur vapour is removed, the pyrite is converted to pyrrhotite, and the gold aggregates into small visible particles. If the sulphur vapour is retained, the gold reacts with it to form a gold sulphide with variable stability features. Burg thought that his results suggested solid solution of gold in the pyrite. Kurauti (1941) and Maslenitsky (1944) synthesized gold-bearing pyrite in which the gold could not be detected microscopically. Maslenitsky found that his synthetic pryrite, containing some 340 ppm gold, when heated in vacuo at 600°C behaved in a similar manner to the natural pyrite used by Burg. He also observed inclusions of gold sulphide in his heated synthetic pyrite, and he was also able to synthesize $Au_2S_3$ and determine its optical properties and etching behaviour. Kurauti's results are especially significant since he found that up to 2000 ppm gold could be substituted in the pyrite lattice, and further that the lattice constant of pyrite decreased with increasing gold content, a feature that proves solid solution of gold in pyrite. Tyurin (1965*a*), on the other hand, found in some experiments that gold concomitantly precipitated with pyrite was present in discrete particles that did not exceed $3\mu$ in size. Clark (1960) also found that the solubility of gold in arsenopyrite at 600°C was insufficient to measurably affect the 131 spacing of the mineral. He did not rule out, however, the possibility of a small gold solubility in arsenopyrite, for example 0.1 per cent (1000 ppm or approximately 30 oz Au/ton of arsenopyrite). In a survey of research for 1969 (U.S.G.S., Prof. Pap. 650-A, p. A108) it was reported that P.B. Barton has found that chalcopyrite can dissolve more than 1.6 weight per cent Au at 650°C and that much of this gold is exsolved on cooling. In the 600–700°C temperature range, galena dissolves between 0.1 and 0.5 weight per cent Au. Bismuth increases the solubility of gold, whereas silver decreases it. This suggests that the mechanism for the incorporation of gold in galena involves Au(I) rather than Au(III). In the same range of temperatures, the solubility of gold in pyrite, pyrrhotite and arsenopyrite is less, perhaps much less, than 0.1 weight per cent. Korobushkin (1970) determined by selective chemical methods that gold in gold-bearing pyrite and arsenopyrite in a deposit in western Kazakhstan was present in two forms – in a cationic form, the gold substituting isomorphously for iron, and in an anionic form, the gold substituting for atoms of arsenic–because of the similarlity of the atomic radii of the two elements (Au, 1.44Å; As, 1.39Å). This view has been reiterated by Badalov (1972). Finally, Kirillov *et al.* (1970) experimented with iron monosulphide and dithiosulphatoaurate, $Na_3[Au(S_2O_3)_2]$ in an attempt to synthesize auriferous pyrite at low temperatures. Their results indicate that the thiosulphate complex disproportionates in aqueous solution in the presence of FeS and that gold passes into the precipitate. The precipitate evidently consisted of FeS grains covered by films of auriferous $FeS_2$. They write equations for the reactions as follows:

$$2Na_3[Au(S_2O_3)_2] + 4H_2O \rightarrow 2Au + S + 3Na_2SO_4 + 3H_2S$$

$$FeS + S \rightarrow FeS_2$$

Extensive chemical and microscopic work on both auriferous pyrite and arsenopyrite by Haycock (1937), Stillwell and Edwards 1946, Edwards (1958) and McPheat *et al.* (1969) on Canadian, Fijian and Australian gold ores strongly suggest solid solution of gold in the lattice of both pyrite and arsenopyrite. The writer's research on gold-bearing pyrite and arsenopyrite from Yellowknife, N.W.T.; Keno Hill, Yukon; southeastern Ontario; and Nova Scotia suggests the same phenomenon.

There are theoretical reasons for suspecting that gold (and silver) enter the structure of pyrite and arsenopyrite. In pyrite (and the closely related arsenopyrite) each iron atom is covalently bonded to six sulphur atoms at the corners of a nearly regular octahedron. In addition there is also a moderate degree of metallic bonding (Fe-Fe) indicated by the metallic lustre, especially of arsenopyrite. The octahedral covalent radius of ferrous iron in pyrite is 1.23Å, and for gold in aurostibite, $AuSb_2$, a mineral isostructural with pyrite, the octahedral radius is 1.40Å. There is also a similarity in the covalent radius of arsenic (1.39Å) and gold (1.40Å). Gold will form three rather unstable artificial sulphides, AuS, $Au_2S$ and $Au_2S_3$ indicating that the bond to sulphur although weak is nonetheless possible. These considerations suggest that some gold may substitute in the iron sites of pyrite and arsenopyrite mainly because of similar octahedral radii, a certain affinity for sulphur, and the isostructural relationship of the two minerals pyrite and aurostibite.[18] There may also be some substitution of gold for arsenic in arsenopyrite because of the similar radii and charges of the two elements. In addition the metallic binding in the sulphides, especially arsenopyrite, confers certain alloying properties on them, permitting other metals such as gold and silver to reside in the lattices without excessive distortion especially at high temperatures. Another reason why pyrite is commonly auriferous may be due to certain epitaxial relationships which take place when pyrite and gold are precipitated in veins. Thus, Amosov and Gureev (1970) noted that gold forms thin crystalline crusts on pyrite and concluded that the crystalline data for gold and pyrite suggest epitaxy as a possibility. Further investigations by Amosov *et al.* (1975) indicate the cocrystallization of pyrite and native gold. They suggest that the cocrystallization phenomenon is not the trapping of gold particles by pyrite but the deposition of gold on the surface of the growing pyrite crystals. Research by Sakharova *et al.* (1972) on gold-bearing sulphides (pyrite, arsenopyrite, chalcopyrite and pyrrhotite) from the Darasun deposit in East Transbaikal further confirms the exsolution hypothesis. They found that during heating tests of polished sections of the various sulphides that the finely dispersed ('invisible') gold aggregated into larger particles around 250 to 300°C. A disintegration of some of the larger 'visible' gold particles was also noted in some cases. They concluded that over a long period of time, gold in the sulphides could be redistributed at relatively low temperatures (150–250°C) during the late stage of hydrothermal processes in veins. Kalitkina (1971) also found experimentally that gold migrated relatively rapidly by diffusion in the solid state, preferably along fractures and grain boundaries, in both pyrite and arsenopyrite. During heating tests Klempert *et al.* (1973), likewise, observed exsolution of gold from the auriferous ('invisible' gold) pyrite of the Terek deposit in Uzbekistan. Narseev and Starova (*in* Petrovskaya, 1974) noted that some 95 per cent of the gold in the Kalba deposits of eastern Kazakhstan was dispersed in pyrite and arsenopyrite. After heating the pyrite for 20 min. at 250°C enlarged gold particles and a decrease in the cell parameter of the pyrite took place (from 5.4275 to 5.4095). They suggested that point defects in the lattice of pyrite occur at the sites of the dispersed gold. The decreased microhardness found for the auriferous pyrite was considered to be due to linear dislocations. For the auriferous arsenopyrite the investigators noted a tendency to fine acicular to finely prismatic habit, increased cell parameters *a* and *b* and decreased microhardness. Other details of the auriferous pyrite and arsenopyrite should be sought in the original paper.

Having regard to the above discussion one can postulate, therefore, that early formed high temperature pyrite and arsenopyrite probably take up gold and silver largely in solid solution, or as atomic layers on the growing faces of the sulphide minerals, features that appear to be common in some of the deposits studied by the writer (e.g., Yellowknife; Boyle, 1961*a*). These features are also commented on by Haycock (1937), Stillwell and Edwards (1946), Edwards (1958) and McPheat *et al.* (1969). At lower temperatures the presence of foreign constituents such as gold and silver distort the pyrite and arsenopyrite lattices, with a consequent rise in the free energy of the crystals. In order to reduce the free energy of the system to a minimum under the prevailing conditions gold and silver migrate to nearby low chemical potential sites such as fractures and grain boundaries where they crystallize as silver-bearing native gold. This appears to explain the frequent occurrence of much 'invisible' gold and silver in relatively unfractured and unrecrystallized pyrite and arsenopyrite; where reworking, recrystallization and fracturing are evident the gold is largely present in the native form, although small amounts may remain within the lattice of the two minerals. The exsolution phenomenon described above is probably largely the result of diffusion processes, a conclusion supported by the experimental work of Clark (1960) who found that gold diffused rapidly through arsenopyrite at temperatures of 660°C and higher.

### *Gold in halides, carbonates, sulphates, oxides and similar minerals*

Data on the gold content of some halides, carbonates, sulphates, oxides, etc. are given in Table 12. The nature of gold in many of these minerals is difficult to determine, particularly in those of supergene derivation because of their finely divided, often pulverulent habit, and their common intermixture with a variety of other supergene minerals.

The common halides contain very little gold, generally less than 0.01 ppm. Seeland (1973*a,b*) noted the presence of gold in only one halite sample from Paleozoic rocks in Michigan. The average gold content in the halite was 0.06 ppm. There appear to be no published analyses of the gold content of the various silver halides, nor of the mercury, copper and lead-copper halides and complex carbonate or

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[18] Note that practically all pyrite and arsenopyrite (Table 11) contains antimony – sufficient it would seem to bind the gold in the pyrite and arsenopyrite lattice, thus neutralizing any charge differences.

Table 12. Gold and silver contents of some halides, carbonates, sulphates, phosphates, arsenates, antimonates, nitrates, tungstates and oxides.

| Mineral and locality | Au | Ag | Au/Ag ratio | Reference | Remarks |
|---|---|---|---|---|---|
| | (ppm) | | | | |
| *HALIDES* | | | | | |
| *Halite,* NaCl | | | | | |
| England; Cheshire | 0.103 | nd | – | 1 | Purity unknown |
| Germany; Stassfurt | 0.132 | nd | – | 1 | Purity unknown |
| Canada; Pugwash, N.S. | <0.01 | <0.5 | – | 21 | Pure |
| U.S.A.; Michigan | 0.06 | – | – | 20 | |
| *Sylvite,* KCl | | | | | |
| Germany; Mecklenburg | 0.003 | nd | – | 2 | Purity unknown |
| Germany; various | 0.0001–0.0034 | nd | – | 14 | Potassium salts |
| *Carnallite,* $KMgCl_3\cdot 6H_2O$ | | | | | |
| Germany; Bernburg | 0.012 | nd | – | 2 | Purity unknown |
| *Sylvite,* KCl, *and Carnallite,* $KMgCl_3\cdot 6H_2O$ | | | | | |
| Canada; Ormiston, Sask. | <0.01 | <0.5 | – | 21 | Pure |
| *Fluorite,* $CaF_2$ | | | | | |
| Canada; St. Lawrence, Nfld. | <0.01 | <0.5 | – | 21 | Pure |
| Canada; Sandy Creek, Que. | <0.01 | <0.5 | – | 21 | Pure |
| Canada; Madoc, Ont. | 0.01 | <0.5 | – | 21 | Pure |
| *Chlorargyrite,* AgCl | | | | | |
| Chile; Chanarcillo | <10 | 75% | – | 21 | Pure |
| Australia; Broken Hill, N.S.W. | <10 | 75% | – | 21 | Pure |
| *CARBONATES* | | | | | |
| *Siderite,* $FeCO_3$ | | | | | |
| Canada; Keno Hill, Y.T. | 0.17 | <1 | – | 21 | Pure |
| *Dolomite,* $CaMg\ (CO_3)_2$ | | | | | |
| Canada; Portage du Fort, Que. | <0.01 | <0.5 | – | 21 | Pure |
| Canada; Bancroft, Ont. | <0.01 | <0.5 | | 21 | Pure |
| Canada; Actinolite, Ont. | <0.01 | <0.5 | – | 21 | Pure |
| *Calcite,* $CaCO_3$ | | | | | |
| Canada; Pinks Lake, Que. | 0.010 | <0.5 | – | 21 | Pure |
| Canada; Brompton Lake, Que. | 0.015 | <0.5 | – | 21 | Pure |
| Mexico; Chihuahua | <0.01 | <0.5 | – | 21 | Pure |
| *Calcite* (marble) | | | | | |
| Canada; Carleton Place, Ont. | <0.01 | <0.5 | – | 21 | Pure |
| *Malachite,* $Cu_2(OH)_2(CO_3)$ | | | | | |
| Zaire; Katanga | 0.015 | <0.1 | – | 21 | Pure |
| U.S.A.; Bisbee, Ariz. | 0.01 | 106 | 0.00009 | 21 | Pure |
| *Azurite,* $Cu_3(OH)_2(CO_3)_2$ | | | | | |
| Southwest Africa; Tsumeb | 0.190 | <0.1 | – | 21 | Pure |
| U.S.A.; Bisbee, Ariz. | 0.210 | 29 | 0.007 | 21 | Pure |
| *SULPHATES* | | | | | |
| *Anhydrite,* $CaSO_4$ | | | | | |
| Germany; Plömnitz | 0.007 | nd | – | 2 | Purity unknown |
| *Gypsum,* $CaSO_4\cdot 2H_2O$ | | | | | |
| United States; Michigan | 0.02 | – | – | 20 | |
| United States; Grand Rapids, Mich. | 0.083 | nd | – | 3 | Purity unknown |
| United States; Salina, N.Y. | 0.083 | nd | – | 3 | Purity unknown |
| Canada; Keno Hill, Y.T. | <0.005 | <0.005 | – | 21 | In lead-zinc-silver veins and lodes |
| Canada; Walton, N.S. | 0.085 | 0.51 | 0.16 | 21 | Evaporite beds, minor pyrite in some samples |
| *Kainite,* $KMg(SO_4)Cl\cdot 3H_20$ | | | | | |
| Germany; Plömnitz | 0.003 | nd | – | 2 | Purity unknown |
| *Barite,* $BaSO_4$ | | | | | |
| Canada; Keno Hill area, Y.T. | 0.08 | <1–5 | – | 21 | In veins (secondary?) |
| Canada; Madoc, Ont. | <0.01–0.01 | <0.5 | – | | Pure |
| Canada; Walton, N.S. | <0.01 | <0.5 | – | 21 | Pure |
| *Anglesite,* $PbSO_4$ | | | | | |
| Canada; Keno Hill, Y.T. | 0.17–0.5 | >1000 | <1 | 21 | Oxidation product of galena |
| Canada; Bathurst, N.B. | <0.01–0.01 | 44 | <1 | 21 | In oxidized zone of massive sulphide deposits |
| *Jarosite,* $KFe_3(SO_4)_2(OH)_6$ | | | | | |
| Various localities | up to 7900 | up to 18% | <1 | | Gold probably largely present in finely divided native form in most samples |
| *Various sulphates of iron, zinc, etc.* | | | | | |
| Canada; Keno Hill area, Y.T. | up to 0.08 | 41.72 | <1 | 21 | Derived from oxidation of pyrite, siderite, etc. |

Contents

Table 12. (cont'd.)

| Mineral and locality | Au | Ag | Au/Ag ratio | Reference | Remarks |
|---|---|---|---|---|---|
| | (ppm) | | | | |
| *PHOSPHATES, ARSENATES, ANTIMONATES* | | | | | |
| *Apatite,* $Ca_5(PO_4)_3(F,Cl,OH)$ | | | | | |
| Canada; Sandy Creek, Que. | <0.01 | <0.5 | – | 21 | Pure |
| Canada; Sebastopol Tp., Ont. | <0.01 | <0.5 | – | 21 | Pure |
| Canada; Cantley, Que. | <0.01 | <0.5 | – | 21 | Pure |
| U.S.S.R.; various | 0.003–0.03 | nd | – | 15 | Bone phosphate |
| *Triplite,* $(Mn,Fe)_2(PO_4)F$ | | | | | |
| South West Africa; Sandamab | 0.5 | 5 | 0.1 | 4 | Purity unknown |
| *Pyromorphite,* $[Pb_5(PO_4,AsO_4)_3Cl]$ | | | | | |
| Canada; Keno Hill area, Y.T. | 0.17 | 100–1000 | <1 | 21 | Contains some cerussite, otherwise pure |
| Germany; Schwarzwald | 18–21 | 200 | 0.1 | 16 | Purity unknown |
| *Scorodite,* $(Fe,Al)(AsO_4)\cdot 2H_2O$ | | | | | |
| Canada; Keno Hill area, Y.T. | 0.5–10.26 | 1–50 | <1 | 21 | Oxidation product of gold-quartz-arsenopyrite veins |
| *Beudantite,* $PbFe_3(AsO_4)(SO_4)(OH)_6$ | | | | | |
| Canada; Bathurst, N.B. | 0.425 | 87 | 0.004 | 21 | In oxidized zone of massive sulphide deposits, pure |
| *Bindheimite,* $Pb_2Sb_2O_6(O,OH)$ | | | | | |
| Canada; Keno Hill area, Y.T. | 0.7 | 100–1000 | <1 | 21 | Alteration product of galena and freibergite |
| *NITRATES* | | | | | |
| *Soda-Niter,* $NaNO_3$ | | | | | |
| Chile | 0.110 | nd | – | 1 | Purity unknown |
| *TUNGSTATES* | | | | | |
| *Wolframite,* $(Fe,Mn)(WO_4)$ | | | | | |
| Canada; Keno Hill area, Y.T. | 0.17 | <1 | – | 21 | Pure |
| *Scheelite,* $Ca(WO_4)$ | | | | | |
| Canada; Keno Hill area, Y.T. | 0.03 | <1 | – | 21 | Pure |
| *OXIDES* | | | | | |
| *Magnetite,* $FeFe_2O_4$ | | | | | |
| United States; Helena, Mont. | 0.003–0.329 (av., 0.037) | nd | – | 7 | Range and average of 44 analyses |
| U.S.S.R.; Altai-Sayan | 0.048 | nd | – | 8 | Average of seven analyses |
| U.S.S.R.; Kazakhstan | <0.001–0.0120 | – | – | 13 | In rocks |
| U.S.S.R.; Urals | 0.0036 | nd | – | 17 | Average in granitoid rocks |
| U.S.S.R.; Altai, Transbaikal and Urals | 0.0034 | nd | – | 18 | Average in granitoid rocks |
| Canada; Marmora, Crowe Lake, Ont. | 0.03 | <0.4 | – | 21 | In skarn orebody |
| Canada; Hull, Que. | <0.01 | <1 | – | 21 | Composite of magnetite body in skarn |
| *Ilmenite,* $FeTiO_3$ | | | | | |
| U.S.S.R.; Altai, Transbaikal and Urals | 0.0019 | – | – | 18 | Average in granitoid rocks |
| U.S.S.R.; Urals | 0.0022 | – | – | 17 | Average in granitoid rocks |
| Canada; St. Urbain, Que. | <0.01 | 0.4 | <1 | 21 | Pure |
| *Hematite,* $Fe_2O_3$ | | | | | |
| Canada; Yellowknife, N.W.T. | 0.005 | <0.04 | – | 21 | In giant quartz veins |
| Canada; Walton, N.S. | <0.01 | 7.5 | – | 21 | In oxidized zones of barite deposits |
| Canada; Balderson, Ont. | <0.01 | <0.5 | – | 21 | Pure |
| Canada; Plummer Tp., Ont. | <0.01 | <0.5 | – | 21 | Pure |
| *Pyrolusite,* $MnO_2$ | | | | | |
| Czechoslovakia; Platten | 0.2 | 4 | 0.05 | 5 | Purity unknown |
| *Psilomelane,* $BaMn^{2+}Mn_8^{4+}O_{16}(OH)_4$ | | | | | |
| Germany: Harz | 2 | 50 | 0.04 | 5 | Purity unknown |
| *Hausmannite,* $Mn^{2+}Mn_2^{3+}O_4$ | | | | | |
| Sweden: Langban | 0.1 | 10 | 0.01 | 5 | Purity unknown |
| *Wad,* Mn Oxides | | | | | |
| Germany; Thuringia | 0.01 | 5 | <1 | 6 | Purity unknown |
| United States; various | <100 | 30–300 | – | 9 | Purity unknown |
| Various (U.S.A.; Sumatra, etc.) | 8–35 | up to 1000 or more | 1 | 10 | Purity unknown |
| United States; Arkansas | 0.7 | 23 | 0.03 | 11 | Purity unknown |
| Canada; Keno Hill, Y.T. | 0.08 | 100–1000 | <1 | 21 | In oxidized zones of Pb-Zn-Ag deposits |

Contents

Table 12. (cont'd.)

| Mineral and locality | Au | Ag | Au/Ag ratio | Reference | Remarks |
|---|---|---|---|---|---|
| | (ppm) | | | | |
| *Wad (cont'd.)* | | | | | |
| Canada; Walton, N.S. | <0.01 | 0.8–1.4 | <1 | 21 | Nodules in limestone |
| Canada; Walton, N.S. | 0.34 | 0.68 | 0.5 | 21 | Spring precipitates (average) |
| Oceans, manganese nodules | 0.003 | – | – | 12 | Average |
| Canada; Nova Scotia lakes, manganese nodules | 0.004 | – | – | 12 | Average |
| *Limonite,* iron oxides | | | | | |
| Various | 1–35 | 1–1000 or more | <1 | | General estimate from world literature. All in oxidized zones of polymetallic deposits |
| Canada; Keno Hill area, Y.T. | 0.08 | 100–1000 | <1 | 21 | In oxidized zones of Pb-Zn-Ag deposits |
| Canada; Walton, N.S. | <0.01 | 0.5 | <1 | 21 | In oxidized zones of barite deposits |
| Canada; Bathurst, N.B. | <0.01–21.2 | 0.5–500 | <1 | 21 | In gossans of massive sulphide deposits |
| *Cassiterite,* $SnO_2$ | | | | | |
| Various localities | 0.2–0.5 | 1–100 | <1 | 4 | Purity unknown |
| Canada; Keno Hill area, Y.T. | <0.01 | 1–5 | <1 | 21 | Pure |
| *Uraninite,* $UO_2$ | | | | | |
| Norway; Brevik | 0.1 | 2 | 0.05 | 5 | Purity unknown |
| Czechoslovakia; Jáchymov | 0.03 | 5 | 0.006 | 5 | Purity unknown |
| *Pitchblende,* $UO_2$ | | | | | |
| Canada; Great Bear Lake, N.W.T. | 0.025 | 5.0 | 0.005 | 21 | Pure |
| *Thorianite,* $ThO_2$ | | | | | |
| Ceylon | 0.05 | 2 | 0.02 | 5 | Purity unknown |
| *Columbite,* $(Fe,Mn)(Nb,Ta)_2O_6$ | | | | | |
| Norway; Arendal | 0.05 | 2 | 0.02 | 5 | Purity unknown |
| *Chromite,* $FeCr_2O_4$ | | | | | |
| Various localities | 0.2 | 1 | 0.2 | 4 | Purity unknown |
| Canada; Bird River, Man. | <0.01 | 3 | <1 | 21 | Pure |
| *Samarskite, tantalite, ilmenorutile* | | | | | |
| Various localities | 0.02–0.65 | 0.2–0.3 | – | 19 | Purity unknown |

Note: nd – not determined

References:
1. Liversidge (1897*a*).
2. Friedrick (1906).
3. Lincoln (1911*b*).
4. Goldschmidt and Peters (1932).
5. Noddack and Noddack (1931).
6. Fischer (1958–1959).
7. Mantei and Brownlow (1967).
8. Shcherbakov and Perezhogin (1964).
9. Hewett, Fleischer and Conklin (1963).
10. Clevenger and Caron (1925).
11. Foley (1960).
12. Harriss *et al.* (1968).
13. Zvereva and Gavrilenko (1971).
14. Goubeau and Birckenbach (1938).
15. Yasyrev (1969).
16. Schmidt (1919).
17. Bushliakov (1971).
18. Anoshin *et al.* (1970).
19. Lunde (1927) and Lunde and Johnson (1928).
20. Seeland (1973*a,b*).
21. Laboratories, Geological Survey of Canada and Bondar-Clegg and Co., Ltd., Ottawa.

hydroxide halides. Analyses of chlorargyite, AgCl, in laboratories of the Geological Survey show gold to be generally less than 10 ppm, indicating that there is little enrichment of the precious metal in silver halides.

All of the common carbonates have a very low gold content, generally much less than 0.01 ppm. This is probably due to the fact that the bond of gold to the carbonate radical is very weak or nonexistent. The complex copper carbonates can apparently accommodate small amounts of gold, probably substituting in the copper sites.

Among the simple sulphates investigated the largest amounts of gold have been noted in anglesite from Keno Hill, Yukon. Its presence in the mineral from this area, however, appears to be spurious; the element is probably largely present in admixed scorodite, bindheimite and beudantite which cannot be physically separated from the anglesite. The anglesite from the Bathurst area is relatively pure and contains on the average only 0.01 ppm Au.

Hand-sorted concentrates of supergene sulphates of copper and iron from underground workings of mines in the Empire district, Colorado, are reported to contain as much as 11.7 ppm Au, 10 ppm Te and 0.60 ppm Hg, all well above background amounts for the area (Lakin, 1969*a*). Higher-than-background amounts of manganese, bismuth, cobalt, nickel and zinc were also detected in the samples. Seeland (1973*a,b*) noted the presence of gold in one sample of gypsum-anhydrite from Paleozoic rocks in Michigan. The amount recorded was 0.02 ppm Au.

As noted above halite and the common sulphates contain only minor traces of gold. Friend and Allchin (1939), however, report 49 ppm Au in pale blue celestite and 85 ppm Au in deep red celestite from Yate, Gloucestershire, England. Colourless crystals contained no detectable gold. In a later paper the same authors (Friend and Allchin, 1940) found up to 4 ppm Au in blue anhydrite from Cropwell Bishop, Nottinghamshire and an average of 23 ppm Au in deep blue Stassfurt halite. They attributed the various colours of these minerals to the presence of colloidal gold. The gold values recorded in these halite and sulphate samples are exceptionally high and should be confirmed. The writer has been unable to find more than a trace of gold (<0.01 ppm) in orange gypsum from Nova Scotia and in most coloured halite, celestite and anhydrite samples from various localities. However, one sample of blue halite from Heringen, Germany, and a sample of blue celestite from Wogau, Germany contained 0.125 and 0.110 ppm Au respectively. The corresponding silver contents were 2.8 and 0.4 ppm.

The basic sulphates of ferric iron and other elements, the jarosites, frequently contain relatively high amounts of gold. Knopf (1915) recorded up to 7900 ppm Au (234 oz/ton) in plumbojarosite from the Boss Mine, southern Nevada, and Head and Miller (1928) found up to 89 ppm Au (2.6 oz/ton) in jarosite from Beatty, Nevada and Marysvale, Utah. In U.S.S.R. Chukhrov *et al.* (1940) report gold- and silver-bearing jarosites from the Maikain deposit, central Kazakhstan, and Friedrich (1960) found gold in jarosite in the Rodalquilar deposit, Spain. In all of these deposits most of the gold is apparently present in the native state as finely divided particles. Despite this feature it would seem from my observations that the jarosites, particularly plumojarosite and argentojarosite, can accommodate some gold in their lattices. Argentojarosite may contain up to 18 per cent silver, a feature proving considerable substitution of the metal in the alkali sites of the jarosite lattice. One can suppose, therefore, that where mobile gold is present in the solutions from which jarosite is crystallized that there may be some substitution of Au(I) (1.37Å) for Ag(I) (1.13Å) because of somewhat similar radii and similar electronic configurations.

There is relatively little gold in any of the apatites investigated in laboratories of the Geological Survey, but the phosphates, pyromorphite and triplite, can apparently accommodate some gold in their lattices probably substituting in the lead or iron sites. Some of the sedimentary bone phosphates in U.S.S.R. carry small amounts of gold. Smirnov and Entin (1975) have noted a bond between gold and phosphorus in a number of genetically diverse phosphatic deposits in U.S.S.R. In certain apatites from these deposits they recorded up to 0.030 ppm Au.

Scorodite from gold-bearing arsenopyrite veins invariably contains gold, frequently in amounts up to 10 ppm or more. In my experience most of this is present in finely divided native gold, although some pure specimens of scorodite in which gold cannot be seen microscopically nor removed either physically or chemically (by cyanide solutions) appear to contain the metal in lattice sites, probably substituting for iron. Beudantite and bindheimite, likewise, invariably contain gold, some of which cannot be removed physically nor chemically. Some of this gold (together with silver) probably substitutes in the lead sites of the lattices of these minerals. It is interesting to note that gold tends to concentrate in the supergene arsenates and antimonates, a feature which suggests a definite coherence between the metal and arsenic and antimony. This coherence is of course well known in hypogene mineral assemblages.

Both of the tungstates, wolframite and scheelite, may contain small amounts of gold. The nature of the gold is unknown. Probably most of it resides in microscopic particles of the native metal. It is worth noting that there is a general association of tungsten, gold and silver in many types of gold deposits.

In rocks and in a few auriferous deposits magnetite carries gold. Some values are given in Table 12; others are quoted in subsequent sections on gold in rocks. The amount of gold in magnetites can range up to 0.05 ppm. The element apparently substitutes for iron in the magnetite lattice since free gold can rarely if ever be seen in the mineral. Platinum group metals accompany gold in some magnetites from rocks in the Urals (Fominykh and Znamenskii, 1974).

Of the various supergene oxides, limonite and wad tend to be the most common carriers of gold, especially where they occur either in or near gold deposits. The presence of gold (and especially silver) in wad (up to 1.3 oz/ton Au and 100 oz/ton Ag or more) is an old problem discussed in great detail in the years past by Clevenger and Caron (1925) and numerous others. The reasons for the extended study were mainly metallurgical since the manganiferous silver-bearing ores and some wad ores containing gold are highly refractory and only yield their silver to cyanide solutions after intensive reduction. After much study Clevenger and Caron and others concluded that much of the silver in wad is held as silver manganite of uncertain composition. More recent work concerning silver in these ores is discussed by Boyle (1968*b*). With respect to gold in wad-silver ores Clevenger and Caron concluded that the gold in some of these ores is amenable to direct cyanidation, and hence its extraction is not increased by reduction. In other ores the gold follows silver, and is more or less refractory; on reduction the recovery of gold is increased from such ores to an even higher percentage than the silver. More recent papers on the occurrence of gold in manganese oxides include those by Foley (1960) who found up to 0.02 oz/ton Au in the manganese ores of Polk County, Arkansas; Harriss *et al.* (1968) who recorded the gold contents in manganese nodules shown in Table 12; and Hrytsyk *et al.* (1969) who found native gold in the earthy manganese ores of the Chyvchyn Mountains, U.S.S.R.

The occurrence of gold in limonite and other iron oxides, especially in the gossans of precious and base metal deposits, is well known and has been repeatedly described in innumerable publications (*see also* Chapter IV).

In recent years the writer has investigated the nature and distribution of gold (and silver) in wad and limonite from a variety of gold-bearing deposits, mainly in Yukon, Northwest Territories, New Brunswick and Nova Scotia. The results of the research concerning the silver have been published (Boyle, 1968*b*). The principal results with respect to gold include the following:

1. Some samples of wad and limonite have the gold (and silver) uniformly distributed throughout the mineral complexes; in other samples the gold (and silver) is erratically distributed.
2. Most of the gold- and silver-bearing wads and limonites carry considerable quantities of silica, alumina, titanium, phosphorus, arsenic and antimony (*see,* for instance, Tables 42, 56 and 60 in Boyle, 1965*a*).
3. In most samples of wad and limonite gold is present in the native state and can be superpanned from samples of the minerals or leached by potassium cyanide. In some samples of wad and limonite the gold follows silver and is tightly bonded to the manganese and iron complexes and is not readily soluble in potassium cyanide or potassium thiosulphate. This

gold may be present as an adsorbed constituent or as a gold manganite, or ferrite although its constitution is apparently amorphous (colloidal?) since no distinct X-ray patterns can be discerned from those of the wad and limonite minerals. In certain samples with a relatively high organic content, the gold may be bound in organic (humic) complexes of manganese and iron. In still other samples, particularly in gossans, the gold (and silver) appear to be an integral part of admixed minerals such as plumbojarosite or argentojarosite, beudantite, bindheimite, scorodite and anglesite.

One of the reasons for the enrichment of gold (and silver) in wad and limonite, especially in gossans, is the fact that the simple soluble species of the two elements are readily reduced to the metals by ferrous and manganous salts. This feature is discussed further in Chapter IV.

Another reason for the enrichment of gold (and silver) in wad and limonite is probably due to the colloidal behaviour of hydrous manganese dioxide and hydrous ferric oxide. Hydrous manganese dioxide sols and gels carry a negative charge and strongly adsorb cationic gold (and silver) to their surfaces. With aging, the gold may partake of the structure of the manganese dioxide complex, giving a gold manganite or some other similar compound. Alternatively the gold may simply remain in an adsorbed state either at the grain boundaries of the microcrystals of the complex or perhaps in interstitial positions. On recrystallization, after long periods of aging, some of the gold may also be split out of the complex giving nuclei of native gold. Silica sols and gels and humic colloids, likewise, carry negative charges and tend to adsorb cationic gold to their surfaces. Hence, the presence of these colloids in wad would also tend to increase the amount of gold precipitated in the wad-silica-humic complex. Some gold thus precipitated could conceivably also be bound as gold-manganese-iron organic complexes. Under other conditions the manganese dioxide colloids may present a positively charged surface due to adsorption of a variety of cations. This then permits the adsorption and/or coprecipitation of negative anionic complexes of gold or negative gold colloids. Another possibility may also account for the adsorption of gold on manganese colloids. The hydrated manganous oxide (hydroxide), $MnO{\cdot}H_2O$, appears to form during the initial stage of precipitation of manganese under a low oxidation potential, and this gelatinous precipitate is later oxidized to hydrated manganese dioxide, $MnO_2{\cdot}H_2O$. The hydrated manganous oxide (hydroxide) adsorbs anions strongly and would, therefore, tend to adsorb and/or coprecipitate the available negative anionic complexes of gold or negative gold colloids.

Ferric oxide hydrosols and gels tend to carry a positive charge and thus adsorb and precipitate various negative ionic complexes of gold, e.g., $[AuCl_2]^-$ and the negatively charged colloids of gold. With aging of the gels the gold is commonly split out as the native metal, but in many cases the gold is an intimate constituent of the limonitic complex.

In a milieu where manganese, iron, lead, silica, alumina, sulphate, phosphate, arsenate, antimonate, etc. are present in solution in oxidizing zones, the colloidal reactions must be very complex indeed. There, normal adsorption phenomena undoubtedly play a part, but hydrolytic reactions, especially those involved in the hydrolysis of iron and manganese sulphates, soluble arsenates, antimonates and phosphates, etc., also come into play. During these reactions gold is coprecipitated with argentojarosite, plumbojarosite, beudantite, bindheimite and other hydrolytic products, all of which may be intimately associated with the wad and limonite gels. On aging the wad-limonite complex tends to segregate out native gold and other gold- and silver-bearing minerals.

> As for the earth . . . it hath dust of gold.
> –Job 28:5–6

## Geochemistry of gold in terrestrial materials

Summary accounts of the various aspects of the geochemistry of gold in most terrestrial materials are contained in a large number of works including those by Maclaren (1908), Crane (1908), Emmons (1917), Mellor (1923), Clarke (1924), Dunn (1929), Goldschmidt and Peters (1932), Lindgren (1933), Van Aubel (1934), Emmons (1937), Fersman (1939), Zvyagintsev (1941), Gmelin (1950–1954), Bateman (1950), Rankama and Sahama (1950), Smirnov (1951), Friedensburg (1953), Goldschmidt (1954), Routhier (1963), Shcherbakov and Perezhogin (1964), Smirnov (1965), Foss (1966*a,b*), Ziauddin (1970), Uklonskii (1970), Machairas (1970*a*), Shcherbina (1972), Allmann and Crocket (1972), Petrovskaya (1973), Simons and Prinz (1973) and Smirnov (1974). There is a selected annotated bibliography on the geochemistry of gold by Cooper (1971).

In the following sections there are numerous tables on the content of gold in the various earth materials. During the compilation of these tables considerable difficulty was encountered in deciding which analytical data in the literature should be used in the calculations because of the different analytical procedures employed, rock nomenclature, possible presence of gold mineralization and so on. These problems are familiar to all geochemists who attempt to calculate normal or background abundance figures. I have been selective in compiling the tables, utilizing only those data which in my opinion have been obtained by reliable modern analytical procedures on earth materials, which seemed to me from the descriptions of the samples to be well removed from the effects of gold mineralization. Admittedly this is a rather subjective procedure, and I would stress the fact that the abundance figures given in the tables are only estimates at best. All of the data sources are given in the Selected bibliography at the end of the bulletin.

### Gold in igneous-type[19] rocks

The gold content of igneous-type rocks is given in Table 13. The table has been compiled from analyses in the literature and from analyses done for the Geological Survey of Canada. Excessively high values have been arbitrarily omitted from some of the data as have also the gold contents of rocks that are highly altered or have closely associated sulphide and gold deposits.

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[19] The term igneous-type is used to avoid the controversy on the origin of granites, ultrabasic rocks and various types of porphyries included in the tables.

Table 13. Gold content of igneous-type rocks

| Rock type | Number of samples | Range | $\bar{X}$ | S | G | $\bar{X}g$ | Sg | Ag* $\bar{X}$ | Au/Ag ratio |
|---|---|---|---|---|---|---|---|---|---|
| | | | (ppm) | | | | | (ppm) | |
| *Ultrabasic rocks* | | | | | | | | | |
| Dunite, peridotite, pyroxenite, kimberlite, anorthosite, etc. | 1185 | 0.0002–0.7800 | 0.0114 | 0.0474 | 0.0045 | –2.3424 | 0.4899 | 0.08 | 0.1425 |
| *Lamprophyres* | | | | | | | | | |
| Camptonite, minette, etc. | 15 | 0.0007–0.0020 | 0.0016 | 0.0004 | 0.0015 | –2.8117 | 0.1235 | – | – |
| *Basic rocks* | | | | | | | | | |
| Intrusives: gabbro, norite, diabase, etc. | 1493 | 0.0003–0.6800 | 0.0230 | 0.0631 | 0.0068 | –2.1686 | 0.5621 | 0.14 | 0.1643 |
| Extrusives: basalt, etc. | 1752 | 0.0001–0.2300 | 0.0174 | 0.0180 | 0.0076 | –2.1215 | 0.6636 | 0.11 | 0.1582 |
| *Intermediate rocks* | | | | | | | | | |
| Intrusives: granodiorite, syenite, monzonite, diorite, etc. | 4710 | 0.0001–0.3500 | 0.0075 | 0.0126 | 0.0042 | –2.3769 | 0.4170 | 0.05 | 0.1500 |
| Extrusives: andesite, trachyte, dacite, latite, etc. | 1359 | 0.0001–0.0650 | 0.0129 | 0.0126 | 0.0068 | –2.1680 | 0.5476 | 0.08 | 0.1613 |
| *Acid rocks* | | | | | | | | | |
| Intrusives: granite, aplite, etc. | 3454 | 0.0002–2.9000 | 0.0114 | 0.0796 | 0.0028 | –2.5518 | 0.5233 | 0.05 | 0.2280 |
| Extrusives: rhyolite, obsidian, etc. | 372 | 0.0001–0.1130 | 0.0037 | 0.0074 | 0.0017 | –2.7699 | 0.5248 | 0.05 | 0.0740 |
| *Alkali-rich rocks* | | | | | | | | | |
| Nepheline syenite, phonolite, etc. | 99 | 0.0001–0.0135 | 0.0034 | 0.0032 | 0.0021 | –2.6775 | 0.4764 | 0.10 | 0.0340 |
| All ultrabasic rocks | 1185 | 0.0002–0.7800 | 0.0114 | 0.0474 | 0.0045 | –2.3424 | 0.4899 | 0.08 | 0.1425 |
| All lamprophyres | 15 | 0.0007–0.0020 | 0.0016 | 0.0004 | 0.0015 | –2.8117 | 0.1235 | – | – |
| All basic rocks | 3245 | 0.0001–0.6800 | 0.0200 | 0.0449 | 0.0072 | –2.1432 | 0.6193 | 0.12 | 0.1667 |
| All intermediate rocks | 6069 | 0.0001–0.3500 | 0.0087 | 0.0128 | 0.0047 | –2.3302 | 0.4579 | 0.06 | 0.1450 |
| All acid rocks | 3826 | 0.0001–2.9000 | 0.0106 | 0.0757 | 0.0027 | –2.5730 | 0.5274 | 0.05 | 0.2120 |
| All alkali-rich rocks | 99 | 0.0001–0.0135 | 0.0034 | 0.0032 | 0.0021 | –2.6775 | 0.4764 | 0.10 | 0.0340 |
| All igneous rocks | 14 439 | 0.0001–2.9000 | 0.0119 | 0.0474 | 0.0044 | –2.3564 | 0.5414 | 0.07 | 0.1700 |

* The arithmetic mean for silver is taken from a previous compilation by Boyle (1968*b*). It does not refer to the samples quoted in the column-number of samples.

Some of the variations in the data on gold analyses of igneous rocks are evidently due to analytical rather than natural causes, a feature that is difficult to assess. Most of the data from the literature compiled in Table 13 are based on neutron activation analyses, which in my experience are not always satisfactory for some types of rocks. Most of the Geological Survey analyses have been done by a combined fire assay–atomic absorption method, which uses several tens of grams of rock powder. While not as sensitive as activation analyses in some respects the method does give more uniform reproducible results and tends to smooth out errors due to sample inhomogeneities.

There is considerable uncertainty about trends in the concentration of gold in the sequence – ultrabasic-basic-intermediate-acidic rocks. Some investigators, including Shilin (1968) and Shcherbakov (1968), maintain that mafic rocks are enriched in gold relative to acidic rocks. In central Kamchatka, Shilin, for example, found the older magmatic rocks of basic composition to contain more gold than the younger acid rocks of the same Miocene magmatic epoch. Others, including De Grazia and Haskin (1964), Anoshin and Potap'yev (1966) and Voskresenskaya *et al.* (1970) find a near uniformity of concentration of gold in all igneous rock types. Gottfried *et al.* (1969) report that gold is not concentrated in residual liquids during magmatic differentiation. In general they found gold contents in felsic members of the batholiths sampled to be lower than in the related mafic members and noted that relatively higher gold concentrations are associated with earlier crystallizing phases (e.g., magnetite, mafic silicates, etc.). They remarked that this was consistent with the trend of progressive depletion of gold from mafic to silicic rocks of calc-alkalic suites. Volarovich and Shilin (1971) report that gold gradually increases in the differentiation series gabbro to aplite, although the distribution of the element in the various rock types is frequently irregular. Most of the gold is said to be dispersed in igneous rocks in the native state. They also claim an increase in gold with increase in potassium content during differentiation, and suggest that during the postmagmatic stage potassium-rich solutions appear enriched with gold, from which gold deposits are formed. In the Kurile-Kamchatka volcanic province, however, Anoshin and Kepezhinskas (1972) found statistically that the gold content is independent of the basicity of the volcanic rocks; elevated gold contents were found, nevertheless, in potassium-rich volcanics in the basalt-andesite-liparite series. The authors concluded that generally there is no significant difference in gold content among the groups of volcanic rocks related to a single differentiation series. In other words gold is inert during differentiation of basalt magma. In the central Kyzylkum, Khamrabaev *et al.* (1972) noted that there was a general tendency for Pb, U and Th to increase in the granitic series from older granodiorites to younger granites. Gold showed an opposite tendency. Ivensen *et al.* (1974) indicate that gold is fractionated in magmas during differentiation and crystallization. They found an inverse correlation between the gold content and the amount of alkali feldspars. The gold content was also found to increase with an increase in the basicity of the rock and the Na content. In a recent paper Kashirin *et al.* (1975) noted a significant increase in the gold content from the first to the last differentiates of the granitic intrusions in the Lena gold-bearing region. Higher gold contents were found in the endocontact and apical parts of the intrusions as well as in parts of the intrusions that were altered (beresitized and sericitized). The granitic bodies were also found to be surrounded by extensive exocontact aureoles, the belt with the maximum gold contents being located some 500 m from the granitic contact.

Shcherbakov and Perezhogin (1964) find that in the Altai-Sayan folded belt of the U.S.S.R. gold is more abundant in extrusive rocks than in their intrusive equivalents. This trend is also apparent in the data of other investigators. There is also more gold in oceanic basalts than in those of terrestrial occurrence according to some investigators (De Grazia and Haskin, 1964; Anoshin and Emel'yanov, 1969).

In recent years a number of investigations have been conducted on the gold content of layered basic intrusives and ultrabasic masses to define the differentiation trend of the element. Vincent and Crocket (1960) postulated that the initial magma from which the Skaergaard rocks crystallized contained 0.0046 ppm Au. All the rocks throughout the differentiation series, including the acid granophyres, are within a factor of 2 of this amount. The ferrogabbro phase with a relatively high copper sulphide content contained ten times the gold content (0.028 ppm) of the average rock; ferrogabbros with iron sulphides contained relatively little gold (0.0029 ppm). Rowe (1969) investigated the differentiated Great Lake tholeiitic dolerite sheet in Tasmania and found that the gold content of parts of the core is related to the mafic index $[(FeO + Fe_2O_3) \times 100/FeO + Fe_2O_3 + MgO]$. The variation of gold content with depth and mafic index was found to be similar to that of copper, indicating in Rowe's opinion that gold and copper probably crystallized concomitantly from the magma. Crocket and Chyi (1972) noticed considerable fractionation of gold between dunite, peridotite and their serpentinized equivalents in the Mount Albert pluton, Gaspé, Quebec. In the peridotites and dunites the gold content averaged $0.0011 \pm 0.0004$ ppm whereas in the serpentinites the average was $0.0024 \pm 0.0007$ ppm. Gold is concentrated (0.0034 ppm) in the accessory chrome spinels in peridotites and dunites. In late deuteric chromitite veinlets the gold content was only 0.00083 ppm.

Voskresenskaya *et al.* (1970) found that the distribution of gold in the layered Zlatogorsk intrusion of ultrabasic and basic rocks was relatively uniform around 0.0012 ppm. An exception was the leucocratic norites (0.0049 ppm Au). The Zlatogorsk intrusion is characterized by a substantially lower content of gold compared with the Skaergaard and Anakit intrusions. Shcheka *et al.* (1971) examined the gold contents of various intrusive basic and ultrabasic bodies in U.S.S.R., Korean People's Democratic Republic and the Indian Ocean and found that the rocks of the ultrabasic dunite-harzburgite clan were richest in the element (0.021 ppm). Rocks of the gabbro clan had considerably less gold (0.004 ppm). Their data led them to the conclusion that gold is fairly uniformly distributed throughout the rocks during differentiation and auto-metasomatic processes of ultrabasic and basic suites; a notable concentration of the element, however takes place during the Cu-Ni sulphide stage. Examination of rocks near contacts indicated that reworking by granitic magmas of basic and ultrabasic rocks leads to considerable loss of gold from the invaded rocks. Moiseenko and Fat'yanov (1972) developed this thesis further, pointing out that the primary source of gold in the earth's crust is derived from basic and ultrabasic magmatic formations arising in the mantle. During granitization and metamorphism of basic and ultrabasic rocks gold is released, is transferred to melts and hydrothermal solutions, migrates and is deposited in any available local structures.

Anoshin *et al.* (1971) examined the Upper Paleozoic to Lower Mesozoic traprock (tholeiite-basalt) intrusions in the Tungusian and Putoransk subprovinces of U.S.S.R. and found an average gold content of 0.007 ppm; the minimum and maximum contents were 0.002 and 0.074 ppm respectively. In one of the differentiated sills they found an average of 0.008 ppm, which they thought represented the initial content of the undifferentiated magma. In the gabbro-dolerite horizon of the sill, containing abundant sulphides and magnetite, and enriched in copper, they found an average of 0.020 ppm Au. Other rocks in the differentiated sequence contained relatively uniform contents of gold (~0.004 ppm Au). These facts led them to the conclusion that gold is concentrated during the sulphide and hydrothermal formation stages of the differentiation of traprock magmas. The study of Noril'sk type differentiated intrusives (Talnakh and Noril'sk) in U.S.S.R by Godlevskii *et al.* (1970) indicates a similar trend. Gold is concentrated in the layered phases of the intrusives impregnated with sulphides (up to 0.42 ppm); associated layered differentiates such as gabbros and dolerites have gold contents ranging from 0.03 to 0.06 ppm, an order of magnitude higher than that for basic rocks in general.

Certain ultrabasic rocks appear to be greatly enriched in gold. Borisenko and Uskov (1971) found the following values in the Gusevogorsk Massif, Urals, U.S.S.R.

| | Au content | |
|---|---|---|
| Rock | Range | Average |
| | (ppm) | |
| Diallage and hornblende pyroxenite | 0.004–1.3 | 0.14 |
| Olivine pyroxenites | 0.002–0.5 | 0.08 |
| Wehrlites | 0.004–0.6 | 0.08 |
| Hornblendites | 0.020–0.3 | 0.12 |

Some of the gold is in the native form and as electrum, both associated with native platinum. The highest gold contents were found in layers and zones of the ultrabasic rocks enriched in sulphides (pyrite, chalcopyrite, bornite) and characterized by increased contents of hornblende.

In another paper, Borisenko *et al.* (1972) state that the irregular distribution of the gold content of ultrabasic rocks is due to the presence in these rocks of discrete inclusions of native gold and electrum. The remainder of the gold, which is rather uniformly distributed, occurs in the form of neutral atoms adsorbed by rock-forming and ore minerals. In the Noril'sk type of differentiated intrusives (Talnakh and Noril'sk) in U.S.S.R., Godlevskii *et al.* (1970) state that the gold is present in both the native form and as an isomorphic replacement in the rocks and associated ores.

Dodin *et al.* (1973) examined the platinoid and gold contents of a number of basic intrusives in U.S.S.R., some nickel-bearing of the Norilsk-Talnakh type. They found that the content of platinoids in both rock-forming minerals and the rocks and their various ratios were indicative of economic nickeliferous intrusives; the gold contents on the other hand were independent of the type of intrusion and hence not indicative of economic nickel-bearing massifs.

Ultrabasic inclusions in a kimberlite pipe in northern Yakutia were analyzed by Ukhanov and Pchelintseva (1972).

Low gold contents were found in garnetiferous peridotite (av. 0.0012 ppm) and garnetiferous pyroxenite (av. 0.0015 ppm). Eclogites contained increased amounts (up to 0.0045 ppm). The authors noted an increase in the gold content with the ferruginous character of the eclogite but no correlation with the various oxides. A direct correlation of gold with vanadium was also indicated. They concluded from their preliminary data that the gold is largely contained in clinopyroxene.

In another study of kimberlite rocks and ultrabasic inclusions Rozhkov *et al.* (1973) found the gold content to range from 0.001 to 0.010 ppm. They concluded that none of the kimberlite rocks are gold concentrators. They further remarked that their values did not confirm the supposition that the gold in ultrabasic rocks is heterogeneous, nor the hypothesis of an irregular content of the noble metal in the upper mantle on a regional basis.

Serpentinization may reduce the gold content of ultrabasic rocks according to the data of Li and Kornev (1972). In the ultramafic rocks of the Yenisei Range the initial gold content averages about 0.0041 ppm; in the serpentinites the gold content is 0.0017 ppm, a moderate decrease.

The distribution of gold in batholiths and stocks of intermediate to granitic composition appears to be highly variable although some general trends are apparent. Mantei and Brownlow (1967) showed that the Marysville quartz diorite stock in Montana has an appreciably higher gold content in and near the periphery where it averages 0.071 ppm; elsewhere it averages about 0.01 ppm. Voskresenskaya and Zvereva (1968) observed small but statistically significant differences in the average contents (0.0011, 0.0016, 0.0021 ppm) of gold in three granitic complexes in northern Kazakhstan. Hybrid rocks of the endocontact zones of the complexes contained from 1.5 to 4.5 times as much gold as the granitic rocks. Davletov and Dzhakshibayev (1970) used neutron activation analysis to determine the distribution of gold between the minerals in various igneous rocks. Feldspars were found to be the main carriers of gold (50% of the metal in the rock), whereas biotite was also observed to be a consistent concentrator mineral. The carriers and concentrators showed a progressive increase in Au content from the centre of an intrusion to the periphery and from the deep parts to the apical parts. Bushliakov (1971) found that the gold content decreases with increasing rock acidity in the granitoids of the Verkh-Isetsk massif in the Urals. Uvarov *et al.* (1972) examined the gold content (0.0006–0.003 ppm) from three granitic complexes on the Kalba-Narymsk region of eastern Kazakhstan. They found a general uniformity of gold contents in single complexes but significant differences in the level of the gold values of the three complexes. Antipin *et al.* (1969), however, found no difference in the content of gold (and molybdenum) in granitoids of different ages and geological settings in the East Transbaikal region of U.S.S.R. From this they reasoned that gold is relatively inert during the processes of magmatic differentiation of multi-phase intrusions. A somewhat similar conclusion was reached by Li and Datsenko (1973) who investigated the gold content of a variety of metasomatic and palingenic granitoids of the South Yenisei Range, U.S.S.R. They noticed a slight enrichment (up to 0.150 ppm Au) in the endocontact and central zones of the Taraksk and Posolnensk granitoid massif. In the rocks of the Nizhnekansk massif they found no significant differences in the gold contents (~0.002 ppm) of the different phases. They interpreted this behaviour as due to the inert character of gold during palingenesis. Shcherbakov and Perezhogin (1963) examined the gold content of granites and other rocks and their accessory magnetites in the Altai-Sayan gold belt. They noted that the average gold content in the granitic masses was higher in the peripheries, in the apical parts and in the region of the exocontacts.

The data in the literature suggest regional variations in the gold content of igneous rocks, and there may well be distinct gold geochemical provinces. The variations are, however, small in most cases, and it is not possible to determine whether they are real or due to analytical variance between investigators. Nevertheless, the gold contents of some suites of igneous rocks within certain specific areas exceeds the norm by factors as high as 10. With respect to gold content there appears to be no universal difference between batholiths and stocks with associated gold deposits and those that are barren. Shcherbakov and Perezhogin (1964) could find no clear-cut difference between the gold content in 'gold bearing' and other intrusives, a feature that agrees with most of our data. Mantei and Brownlow (1967) and others have, however, indicated that some stocks with associated gold deposits have higher than average gold contents. Shilin (1968) noted that certain Miocene magmatic rocks in central Kamchatka have gold contents one order of magnitude greater than others in the same region. He postulated a Miocene magmatic hearth enriched in gold below central Kamchatka. In the Rice Lake–Beresford Lake area of southeastern Saskatchewan Stephenson and Ehmann (1971) found evidence to indicate that the mafic intrusions may be the source rocks of the gold deposits. Some varieties of monchiquite, camptonite, odonite and other lamprophyric rocks appear to be enriched in gold (and silver) in some areas. Buturlinov and Latysh (1970) found up to 0.08 ppm Au and 3.6 ppm Ag in some of these basic lamprophyric rocks in the Donets Basin, U.S.S.R. Our experience with lamprophyric rocks is that they may contain up to 0.05 ppm Au or more where they contain abundant pyrite or where they are albitized and altered.

Gottfried *et al.* (1969, 1972) and Tilling *et al.* (1973) have concluded, following an extensive study of gold in igneous rocks that:

> The available data provide little support for the view that gold is concentrated in the residual liquids during magmatic differentiation in any of the calc-alkalic or alkalic provinces. The variation trends indicate that gold either remains relatively constant or decreases during differentiation processes.
>
> The gold content in suites of unaltered igneous rocks spatially associated with gold mineralization from selected areas – Boulder batholith region, Montana; Cornwall, Pa.; Jerome district, Arizona; Bullfrog district, Nevada; Mother Lode, California – is virtually the same as petrographically equivalent rocks from provinces devoid of mineralization. The relatively high concentration of gold that exceeds background levels for a given region invariably occurs only locally in altered rocks and may be ascribed to remobilization or secondary introduction. Geochemical abundance data alone neither provide unique criteria in identifying broad segments of the crust favorable for gold mineralization nor specify processes that resulted in the economic concentration of gold. Thus, in any exploration program, geologic factors, such as petrologic, structural and tectonic setting, must be considered in conjunction with purely geochemical abundance factors.

Against this view we have the research by Kushmuradov (1970), who worked in a gold-bearing area in Uzbek, U.S.S.R. and found an average of 0.01 ppm Au in the granitoids of the North Nuratau Mountains, a value some 2 to 3 times higher than the average abundance of gold in such rocks. Altered (albitized and silicified) granitoids and sedimentary rocks near the Charmitan, Karaulkhon Latta and Koktonly gold deposits contained 2 to 3 times more gold (0.02 ppm) than the unaltered rocks. Dyke rocks, including lamprophyres, granite porphyries and diorite porphyries, were relatively enriched in gold averaging 0.026 ppm. However, a study of a number of intrusive granitoid bodies in U.S.S.R. with diverse associated ore mineralization, carried out by Anoshin *et al.* (1970) found no significant statistical difference in the gold content between bodies with associated gold ores and those that are barren. These researchers also found similar gold contents in different phases of granitoid bodies with associated gold mineralization. They suggested that the increased amounts of gold in some intrusions in gold belts was secondary, that is, the metal was introduced or rearranged during the hydrothermal stage. In the Chatkal zone of the Tien Shan, Davletov (1974) finds that relatively high contents of gold occur in igneous intrusives spatially associated with the gold mineralization of this zone.

Wolfe (1975) gives interesting data on barren and auriferous granitoid bodies from six Early Precambrian felsic intrusions in Ontario. These range in size from 4 to 88 km². Four – Dome stock, Red Lake area; Larder Lake stock; Lebel stock, Kirkland Lake area; and Cairo stock, Matachewan area – have associated gold deposits and two (Kabenung Lake and Coyle Lake) are barren. Wolfe observed that the gold levels in unmineralized stocks are consistently below the 5 ppb detection limit of the analytical method used. In contrast, analyses of samples from stocks with associated gold mines within their borders and in nearby metavolcanic-metasedimentary host rocks show a strongly skewed trace element gold population with a substantial percentage of gold values exceeding 5 ppb and ranging as high as 320 ppb. Further details on this research are given in Chapter V.

In the granitic rocks and their contact haloes in the auriferous Lena region, Kashirin *et al.* (1975) observed that the former carried from 0.0016 to 0.0047 ppm Au whereas the latter contained from 0.0007 to 0.0139 ppm Au. They noted that the concentration of gold increased in the late-stage differentiates of the granitic magma and in rocks altered by autometasomatic processes. An enrichment of gold was also observed in the endocontact and apical facies of the granitic bodies.

In the recent symposium edited by Petrovskaya (1974) there are a number of papers referring to the abundance of gold in igneous rocks and the presence of auriferous deposits. One by Trunilina and Yakovlev notes that the content of gold in unaltered magmatic rocks of the Charka River Basin (northeastern Yakutia) increases with the sulphur content and that these rocks have a high gold content (0.0086–0.0205 ppm) when auriferous mineralization is present in the area. An accumulation of gold in peripheral parts of granitic massifs and in selvages of dykes is also noted, features that are ascribed to magmatic differentiation.

The writer concludes from this diversity of findings and opinion that the relationship between the gold content of igneous rocks and the presence or absence of gold deposits is unresolved. Part of the problem would seem to be the difficulty in obtaining an adequate sample in that gold is distributed extremely nonuniformly in unaltered igneous-type rocks. Even those that are equigranular and massive were found by Rozhkov *et al.* (1970) to display this habit. The sampling problem is even more troublesome in slightly altered rocks where the gold content can range widely from sample to sample.

To summarize the facts on the general distribution of gold in igneous rocks as shown in Table 13 and from the more detailed data in the numerous publications and in my files one can say that the variation from the mean gold content of igneous rocks is never great. The data suggest that on the average the ultrabasic and basic rocks have slightly more gold than other igneous-type rocks, but the excess amount is not great as shown by the geometric mean. In places there is evidence of some trends in the sequence ultrabasic-basic-acidic rocks with a general depletion in gold toward the acid end of the sequence. This trend is, however, not marked and a general uniformity of gold content seems to be present in many sequences. Specific observations indicate few definite trends except in rocks which contain relatively high contents of sulphides, especially pyrite and chalcopyrite. Such rocks are generally enriched in gold regardless of type. We have also noted relatively high gold contents in some quartz-feldspar porphyries containing pyrite and other sulphides, but the origin of these porphyries and their contained sulphides is somewhat controversial. They may in some cases be of metamorphic rather than igneous origin. There is a suggestion that some of the alkali-rich syenites and similar rocks are higher than normal in gold but only by a small amount. On the basis of the available data nepheline syenites and phonolites appear to be normal within a range 0.0001 to 0.0135 ppm Au. The nepheline syenites of Ontario are low in gold (<0.005 ppm), and the alkali basalts investigated by Gottfried *et al.* (1972) appear to have a distinctly lower gold content (~0.0006 ppm) than most Hawaiian and continental basalts of the tholeiitic magma type with a gold content ranging from 0.002 to 0.0035 ppm. Certain highly alkaline Permian magmatic rocks investigated by Lisogor and Babakhodzhaev (in Petrovskaya, 1974) are, however, enriched in gold compared with others in the Karamazar region of U.S.S.R.

The distribution of gold in some regional suites of igneous rocks is lognormal in nature; in others lognormal with a marked skew; and in still others the distribution is polymodal. The last type of distribution suggests addition of gold to the rocks during mineralization processes.

There is considerable difference of opinion on the distribution and nature of gold in igneous rocks. Most investigators are agreed that gold is distributed in a nonuniform manner in igneous rocks; in fact in some rocks its distribution can be said to be quite erratic according to our investigations. Rozhkov *et al.* (1970) comment at length on this particular feature after applying statistical principles to their data. Three views seem to be prevalent with respect to the nature of the gold in igneous rocks. One holds that the gold is present in the native form or as electrum; another that the element is dispersed throughout the rocks and constituent minerals in the form of neutral atoms; and a third that the gold is present as

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an atomic and/or ionic substitution in the lattice sites of minerals. Probably all three are correct depending on the type of rock, mineral composition and other factors. Mineral separates from igneous rocks show gold to be present in practically all of the minerals although the amounts vary, but generally only within narrow limits. Data from the literature and the writer's analyses indicate the following ranges in ppm to be expected: quartz, 0.0008–0.002; feldspars, 0.0003–0.002; biotite, 0.002–0.007; hornblende, 0.0005–0.003; pyroxene, 0.0005–0.004; olivine, 0.001–0.01; sphene, 0.004–0.009; magnetite, 0.003–0.1; and pyrite and other accessory sulphides, up to 0.5 or more. Considerably higher values for biotite, hornblende and magnetite are reported in some igneous rocks by Mantei and Brownlow (1967) and others. In some suites of rocks the sialic minerals, mainly the feldspars, carry the highest contents of gold. Khairullin *et al.* (1968) found the highest amounts of gold in the heavy fractions (e.g., biotite and magnetite), and Davletov and Dzhakshibayev (1970) found that biotite is the principal mineral concentrator of gold, but the feldspars contain the bulk of the element in igneous rocks (up to 50% of the total amount of gold present). Mantei and Brownlow (1967) and Zvereva and Gavrilenko (1971) noticed that the dark minerals including pryoxene, hornblende, biotite and magnetite are enriched in gold compared with quartz and feldspar, although the latter investigators emphasize the point that the magnetite is not always richer in gold than other minerals and that its gold content varies within broad limits. Anoshin *et al.* (1970) for instance state that in granitoids the gold content of the rock-forming minerals is relatively uniform, and that the differences are statistically insignificant. Their table indicates, however, that quartz and feldspar (0.0016 ppm) have lower average gold contents than biotite, amphibole, magnetite, sphene, etc. (0.0019, 0.0020, 0.0034, 0.0029 ppm Au respectively). Bushliakov (1971) gives the average gold content in rock forming minerals in the granitoids of the Urals as determined by activation analyses as follows: quartz, 0.0017 ppm; plagioclase, 0.0017 ppm; microcline, 0.0016 ppm; hornblende, 0.0016 ppm; biotite, 0.0018 ppm; muscovite, 0.0019 ppm; magnetite, 0.0036 ppm; ilmenite, 0.0022 ppm; sphene, 0.0027 ppm; apatite, 0.0024 ppm; garnet 0.0052 ppm; epidote, 0.0025; ppm; and chlorite, 0.0025 ppm. Sobolev *et al.* (1974) record the following ranges in parts per million for the various minerals in basic and ultrabasic formations in the Urals: olivine, 0.003–0.010; pyroxene, 0.0006–0.001; plagioclase, 0.0005–0.003; and hornblende, 0.0004–0.0007. Gottfried *et al.* (1972) found by material balance calculations that in most igneous rocks, even the very freshest, the gold measured in the rock tended to be greater than that indicated by the summation of the gold contribution from the principal rock-forming minerals. This suggested to them that some of the gold may reside elsewhere in the rock, possibly in phases volumetrically small but comparatively rich in gold (for example, sulfides) or even as intergranular native gold. Keays and Scott (1976) found that the gold contents of the glass rims of oceanic pillow basalts (av. 0.0015 ppm) to be some 5 to 7 times greater than those of the associated crystalline interiors (av. 0.0005 ppm). They considered that the hosts for the bulk of gold in basalts are probably (1) early separated oxide and silicate phases such as Cr-spinel and olivine and (2) sulphide phases.

The gold (and platinum content) of magnetites in rocks can apparently be used to differentiate igneous rocks of different genesis. In the Urals the granitoids have two origins – one as differentiates of basaltic magma and the second derived from sialic material (by granitization). In an interesting paper on the subject Fominykh and Znamenskii (1974) observed an increased content of gold in the magnetites from granitoids of the granite (sialic) formation, with which are often associated hydrothermal gold-bearing deposits. The gold content of magnetites of this formation ranged from 0.018 to 0.035 ppm; in addition an increased gold content (0.035 ppm) was noted in magnetites from more basic varieties of rocks (quartz diorites and diorites). Magnetites in the granitoids of the gabbro (basaltic) formation differ in gold content from magnetites of the granite formation by an order of magnitude and contain the same amount of gold regardless of the rock composition (av. 0.006 ppm).

Platinum group elements are also distributed differentially in magnetites from the different groups of granitoids. A high platinum content was noted in magnetites from the gabbro group of granitoids, the maximum amounts being found in magnetites from diorites, quartz diorites, granosyenites and syenodiorites. In the magnetites of the granitoids derived from sialic material the platinum content was low and did not depend on the rock composition.

Finally, experiments carried out by Davletov *et al.* (1973) on the phase leaching of gold from intrusive rocks and mineral carriers of gold in these rocks indicates that gold is not distributed evenly in the mineral carriers as should be the case with isomorphic replacement. Rather, the metal occurs in microcracks and lattice discontinuities in the minerals and in microfractures and along intergrain boundaries in the rocks. These features are of interest in theories of metamorphic secretion since gold in microfractures and grain boundaries can be easily mobilized (extracted) from these sites. This circumstance is referred to later in the section on the origin of epigenetic deposits in Chapter III.

The writer's investigations generally confirm the findings of a number of workers that the dark minerals, magnetite, ilmenite and particularly pyrite and chalcopyrite contain the highest amounts of gold in igneous rocks. In our work on igneous rocks we have not been able to separate free gold from large quantities of rock nor have we seen free gold in polished sections of mineral concentrates of magnetite, pyrite, chalcopyrite and other sulphides from fresh (unaltered) igneous rocks. There are, however, numerous older references in the literature (e.g., Blake, 1897; Spurr, 1903, 1904; Weed, 1904*a, b*; Brock, 1904) of free gold in supposedly fresh (unaltered) granites, diabase, etc. Some of the descriptions given are, however, suspicious of alteration or impregnation since many are in or near gold mines or sulphide deposits.

Correlations of gold with other elements in igneous rocks are imperfect and seemingly erratic in many cases. Shcherbakov and Perezhogin (1964) claim to have found a correlation of gold with the following metals and metal oxides in decreasing order of correlation as follows: Cu, $Fe_2O_3$, MgO, V and FeO. They found no correlation with Zn, Pb and other metals. Rowe (1969), as noted above, found a correlation with the mafic index and with copper in the Great Lake tholeiitic dolerite sheet in Tasmania. Zvereva and Gavrilenko (1971) could find no correlation of gold with iron in the minerals examined in their study. Gottfried *et al.* (1969, 1972) concluded that their data suggest a negative correlation between gold content and abundance of some 'residual' trace elements (e.g., Th, U and Nb) but a gross positive correlation with chalcophilic elements such as copper. Shcherbakov *et al.* (1972) carried out an extensive series of gold analyses (over 2000) on a large number of rock types. They found a definite correlation between the iron and gold contents of igneous and sedimentary rocks, the higher gold contents being present in rocks with high iron contents. The main gold concentrator mineral in granitoids was found to be magnetite; in skarn, hornfels and schists the gold was contained mainly in the femic minerals. Hamrabaev and Urunbaev (1971) noted positive correlations of gold with ferrous iron and copper in the igneous rocks of Uzbekistan. A possible correlation of gold and sodium was also noticed. Keays and Scott (1976) analyzed a number of oceanic pillow basalts from the mid-Atlantic Ridges; in the fresh crystalline interiors of the pillows they noted correlations between gold and Cr, Ni and MgO.

Studies by the writer on the correlation of gold with other elements in igneous rocks suggest a positive correlation with Fe and possible positive correlations with Cu, Ag, S, As and Sb, but the relationships are often erratic. I think the positive correlation with sulphur is genuine, and I have noted a general tendency for gold to be enriched in igneous rocks rich in pyrite, pyrrhotite or chalcopyrite. The correlation with arsenic, likewise, seems highly probable most of the arsenic being present in the sulphides, especially pyrite (Boyle and Jonasson, 1973). In the basic-ultrabasic suites of rocks there appears to be a weak positive correlation between gold and the various platinoids, and perhaps with chromium, although at the time of writing my research on the platinum group is not complete. It further appears that certain ultrabasic rocks are enriched in both the platinoids and gold compared with more acidic suites of rocks.

Goldschmidt (1954) estimated the abundance of gold in igneous rocks (lithosphere) to be 0.005 ppm. Others (*see* the section above on abundance) have given abundances, based mainly on igneous rocks, ranging from 0.001 to 0.0043 ppm. Calculations based on the data given in Table 13 yield an abundance of 0.0044 ppm (geometric mean) for igneous rocks. Like all abundance calculations this figure should be taken as a rough estimate until more accurate figures are available on the quantity of each igneous rock type in the earth.

## Gold in sedimentary rocks

The gold content of a variety of unconsolidated sedimentary rocks is given in Table 14, and similar data for consolidated sediments are contained in Table 15.

The data are not extensive for most types of unconsolidated sediments, but those available indicate that certain types of tuffs (volcanic ash) and organic sediments may be enriched in gold. Some of the sediments associated with oceanic ridges and rises appear also to contain slightly higher than average amounts of gold. Crocket *et al.* (1973) consider that the gold in the sediments of the East Pacific Rise had a submarine volcanic exhalative origin. Piper and Graef (1974) on the other hand think that much of the gold in the flank sediments of this rise had a lithogenic origin (not precipitated from seawater). In the crestal sediments, however, where the gold is significantly higher in content, they considered that a fraction of the gold had a volcanogenic (exhalative) source (precipitated from seawater).

The Red Sea metalliferous sediments (Hendricks *et al.,* 1969) are enriched in gold (and silver) (Table 14). These sediments exhibit a wide variation in physical appearance and in chemical composition, from oxidized red muds to dark sulphide-rich muds and a few light-coloured carbonate-rich samples. Hendricks *et al.* (1969) found extreme variations in composition between adjacent sample sites, and considerable variation was noted even within different splits from the same core. Extreme vertical variations in the cores were also recorded, sometimes within a few centimetres of depth.

The data provided by Koeberlin (1934) on the gold content of the volcanic ash in central Chile is interesting, in that there may be areas where such deposits (both unconsolidated and indurated) may be of economic interest. Goodchild (1918) also mentions the fact that certain ash flows associated with the volcano La Sufral in Colombia contain from 0.42 to 1.71 ppm Au. Silver, likewise, has been found to be enriched in certain falls of volcanic ash in Ecuador, South America (Mallet, 1887,1890). Taken together these two facts are of prime importance considering the frequent occurrence of gold-silver deposits in or associated with tuffs (sedimented volcanic ash) or porphyries (crystallized volcanic material) in the Canadian Shield, Tertiary terranes, etc. These types of rocks in the Canadian Shield are enriched in both gold and silver and a variety of other associated elements (Boyle, 1968*a,b*) (Table 15). Such rocks would seem to be an adequate source for the derivation of gold-silver veins and other deposits by a metamorphic secretion mechanism. (*See* the section on origin of gold deposits in Chapter III.)

Anoshin *et al.* (1969) carried out an extensive investigation of marine sediments in the Atlantic Ocean basin with the results given in Table 14. Their main findings can be summarized in point form as follows: (Details should be sought in the original paper.)

1. The average gold content in modern sediments is a little higher than the average content in felsic, mafic and ultramafic rocks, but considerably lower than the content in oceanic basalts. The most frequent occurring concentrations of gold (0.003–0.006 ppm) fall within the range of consolidated sedimentary rocks or are slightly higher (*see also* Table 15).
2. The highest gold contents were in coquinoid limestones from the Black Sea, the lowest in sands and gravels from the Baltic Sea and Atlantic Ocean and in some pyroclastic sediments from the vicinity of Iceland.
3. In the clastic sediments the gold content increases with decrease in grain size. The correlation of gold content with the pelitic (clay) fraction is weak in some types of sediment but significant in others.
4. The distribution of gold in the unconsolidated sediments coincides closely with the distribution of uranium, an element often closely associated with organic matter.
5. In carbonate sediments very low and very high values were encountered. The highest contents are apparently concentrated in molluscan shells.
6. In general the concentration of gold in biogenic carbonate sediments is not dependent on the content of

Table14. Gold content of some Recent unconsolidated sedimentary rocks

| Rock Type | Au (range) | Au (av.) | Ag (av.) | Au/Ag ratio | Reference |
|---|---|---|---|---|---|
| | | (ppm) | | | |
| Volcanic ash, Chile | 0.1–5 | – | – | – | 1 |
| Deep sea red clay, volcanic ash, etc., Atlantic region | 0.015–0.267 | 0.108 | 0.737 | 0.146 | 2 |
| Red clay | | | | | |
| Brazilian Basin | 0.0042–0.0310 | | – | | 3 |
| Lutites | | | | | |
| Argentinian Basin | 0.0031–0.0173 | | – | | 3 |
| Recent carbonates | | | | | |
| Florida Coast | | 0.0039 | – | | 3 |
| Recent coral | | | | | |
| Florida Coast | | 0.0008 | – | | 3 |
| Terrigenous sediments (silt, clay, sand, gravel) (30% $CaCO_3$) | | | | | |
| Baltic Sea | 0.0001–0.0054 | 0.003 | – | | 4 |
| Black Sea | 0.002–0.024 | 0.006 | – | | 4 |
| Mediterranean Sea | 0.0011–0.009 | 0.0038 | – | | 4 |
| Atlantic Ocean | 0.0006–0.0042 | 0.0013 | – | | 4 |
| Biogenic and chemical sediments (coquinoids, sand, silt, clay) ($>$30% $CaCO_3$) | | | | | |
| Black Sea | 0.0046–0.150 | 0.0204 | – | | 4 |
| Mediterranean Sea | 0.0011–0.0065 | 0.0031 | – | | 4 |
| Atlantic Ocean | 0.0007–0.0034 | 0.0015 | – | | 4 |
| Volcanic sediments (silts; 10% pyroclasts) | | | | | |
| Atlantic Ocean (near Iceland) | 0.0005–0.015 | 0.0042 | – | | 4 |
| Mediterranean Sea (Santorini Lagoon) | | 0.0140 | – | | 4 |
| Oceanic sediments; Arctic, Antarctic, Pacific, and Indian Oceans | 0.00064–0.0076 | 0.00274 | – | | 5 |
| Oceanic sediments: East Pacific Rise | 0.00036–0.00282 | 0.00134 | | | 6 |
| Red Sea metalliferous sediments | 0.0210–5.6000 | 0.6594 | 28.3973 | 0.0232 | 7 |
| Shelf sediments Carolina Coast, U.S.A. | 0–0.006 | | | | 8 |
| Alluvial placers (stream, river and marine) | <0.01–200+ | – | 0.1–20+ | | 9 |

References:
1. Koeberlin (1938).
2. Wagoner (1908).
3. De Grazia and Haskin (1964).
4. Anoshin *et al.* (1969).
5. Crocket *et al.* (1973).
6. Piper and Graef (1974).
7. Hendricks *et al.* (1969).
8. Pilkey and Bornhold (1970).
9. Estimated.

Table 15. Gold content of unconsolidated and consolidated (lithified) sedimentary rocks

| Rock type | Number of Samples | Range | $\bar{X}$ | S | G | $\bar{X}g$ | Sg | Ag* $\bar{X}$ | Au/Ag ratio |
|---|---|---|---|---|---|---|---|---|---|
| | | | (ppm) | | | | | (ppm) | |
| Unconsolidated sediments, oceans | 299 | 0.0003–2.5000 | 0.0523 | 0.2761 | 0.0035 | –2.4615 | 0.6792 | – | – |
| Sandstone, arkose, conglomerate and sedimentary breccias | 3474 | 0.0002–0.4300 | 0.0570 | 0.0499 | 0.0263 | –1.5807 | 0.7139 | 0.2 | 0.2850 |
| Greywacke and subgreywacke | 38 | 0.0010–0.1000 | 0.0132 | 0.0192 | 0.0076 | –2.1207 | 0.4303 | 0.2 | 0.0660 |
| Witwatersrand and similar auriferous quartz-pebble conglomerates | | 0.4–230 | 8.0 | | | | | 0.8 | 10.0 |
| Shale, mudstone, siltstone, argillite | 1356 | 0.0001–0.8000 | 0.0080 | 0.0266 | 0.0039 | –2.4061 | 0.4730 | 0.2 | 0.0400 |
| Sulphidic-schists, pyritic greywacke, pyritic black shale, pyritic tuff, etc. | 19 | 0.0025–2.1000 | 0.1320 | 0.4778 | 0.0143 | –1.8442 | 0.7228 | 0.6 | 0.2200 |
| Tuffs | 97 | 0.0005–0.1120 | 0.0069 | 0.0163 | 0.0023 | –2.6341 | 0.5737 | 0.3 | 0.0230 |
| Limestone, dolomite | 440 | 0.0002–0.0889 | 0.0070 | 0.0128 | 0.0034 | –2.4706 | 0.4648 | 0.1 | 0.0700 |
| Evaporites: | | | | | | | | | |
| 1) Gypsum, anhydrite | 18 | 0.0050–0.0850 | 0.0208 | 0.0169 | 0.0172 | –1.7644 | 0.2683 | <0.1 | <0.*n* |
| 2) Halite, sylvite, etc. | 15 | 0.0005–0.0300 | 0.0238 | 0.0109 | 0.0178 | –1.7505 | 0.4880 | <0.1 | <0.*n* |
| *(See also* Table 12) | | | | | | | | | |
| Chert | 3 | 0.0050–0.0400 | 0.0167 | 0.0202 | 0.0100 | –2.0000 | 0.5214 | 0.2 | 0.0835 |
| Phosphorite | 1 | | 0.0072 | | | | | | |
| Manganese nodules | 1 | | 0.0002 | | | | | | |
| All sedimentary rocks | 5761 | 0.0001–2.5000 | 0.0403 | 0.0831 | 0.0122 | –1.9125 | 0.7632 | 0.3 | 0.1343 |

* The arithmetic mean for silver is taken from a previous compilation by Boyle (1968*b*). It does not refer to samples quoted in the column–number of samples.

$CaCO_3$ but probably on the organic content since there is a general positive correlation between gold and organic matter ($C_{org}$). This suggests that gold is probably absorbed by organisms (principally plankton) from seawater which on their death are sedimented in the clays and other marine sediments. Another process is concerned with the precipitation of gold in organo-metallic compounds absorbed on clays and clastic material.

7. The distribution of gold in some marine sediments appears to depend on the types of rocks in the provenance areas and on the mineral composition of the marine sediments.

The gold content of modern eluvial and alluvial (placer) deposits may be high enough to provide an economic source of the element. The lowest economic unit for exploitation of these deposits varies from region to region and from deposit to deposit. Roughly it is about 0.1 ppm Au. Most of the gold in eluvial and alluvial deposits is particulate. Its origin is probably due to both mechanical and chemical processes. These concepts, and descriptions of the deposits, are discussed in greater detail in the section on placers in Chapter III.

In normal types of consolidated sedimentary rocks the highest amounts of gold unquestionably occur in the conglomerate, sandstone, greywacke suite and in the black shales, carbonaceous argillites, alum shales, oil shales and some phosphorites. Only small amounts of gold occur in normal shales, limestone, evaporites and other sedimentary rocks. Certain consolidated sandstones and conglomerates are greatly enriched in gold. Most of these constitute fossil placers; they are discussed in some detail under this heading in Chapter III.

Minnitt *et al.* (1973) analyzed three suites of essentially argillaceous sediment from the Wolkberg Group and the Black Reef–Dolomite transition zone (Transvaal Supergroup, northeastern Transvaal) for gold, using instrumental neutron activation analysis. The average gold content of the argillaceous rocks was found to be 0.0025 ppm, while the more arenaceous sediments carried, on the average, some 0.022 ppm gold. Sediment samples from the old workings on the Crags had an average gold content of 0.061 ppm; a value of 0.131 ppm was determined for one sample from these workings. Minnitt *et al.* (1973) concluded from their investigation that the background gold concentration in argillites is, on average, about 10 times lower than in more arenaceous sediments. An important exception was found in a carbonaceous silt-shale rock from the Dolomite–Black Reef transition zone, which carried nearly 0.090 ppm gold. Such a sediment they thought could act as proto-ore for gold-quartz reefs of the Pilgrims Rest-type, which are very often intimately associated with the carbonaceous shale beds in the Dolomite.

Certain terranes of sedimentary and derived metamorphic rocks appear to be greatly enriched in gold. Thus Li and Shokhina (1974 *a,b*) noted that the Proterozoic (sedimentary and derived metamorphic) rocks of the Yenisey Range are characterized by higher than normal contents of gold, in some cases by an order of magnitude of the clarke value (0.004 ppm). Particularly enriched are certain sandstones and quartzites and carbonaceous and graphitic phyllites and schists.

Certain oil shales and other types of bituminous sediments contain small amounts of gold in excess of the average for normal shales. Varley (1922) has described an investigation involving recovery of gold from such rocks in Wyoming (Green River Formation) and Utah. He records values ranging from 0.3 to 0.6 ppm (0.01–0.02 oz/ton Au). Cook (1973) in a later paper on the Green River oil shale gives the gold content as <0.1 ppm. The nature of the gold in the shales could not be determined by Varley. Korotayeva and Polikarpochkin (1969) also noted enriched contents of gold in the organic-rich rocks of the Nerchinsk Zavod region of eastern Transbaikal, U.S.S.R. The enrichment was two- to threefold and in places ten- to fifteenfold compared with the light (organic free) shales and siltstones. In other papers by Polikarpochkin *et al.* (1969) and Gapon (1970) the maximum gold values recorded in organic (carbonaceous) rocks was 200 ppm with some 50 per cent of the samples containing 5 ppm and more. These authors ascribe the enrichment of gold in the carbonaceous rocks to physico-chemical processes and calculated that some 50 per cent of the gold in the rock was precipitated from solution. In samples of the Athabasca tar sands we found less than 0.005 ppm Au.

Phosphorites appear to be enriched in gold in places. Yasyrev (1969) found from <0.01 to 0.15 ppm in the Mesozoic nodular phosphate deposits of the Russian Platform. Some 10 to 35 per cent of the gold was in the free state; the remainder was combined in a chemical form. In fossil reptile bones and sawfish teeth the amounts of gold ranged from <0.01 to 0.085 ppm. Yasyrev found a correlation of gold content in phosphorites with a number of other trâce elements including Ti, Zr, etc. This might suggest that detrital processes were the prime factors in the concentration of gold in these deposits, but our observations indicate that such elements are also subject to marked hydrolysis phenomena (as is also gold in solution) causing their precipitation. In the United States and Morocco the marine phosphorites appear to be low in gold. Samples of marine phosphate rock from Florida, Montana, North Carolina and Morocco contained only up to 0.003 ppm Au as determined by the neutron activation–fire assay method (Z.S. Altschuler, U.S. Geol. Surv. Circ. 622, p. 11).

Evaporites are notably low in gold and silver. Goubeau and Birckenbach (1938) found a general average of 0.0014 ppm total precious metals (Ag, Au, Pt, etc.) in various potassium salts (sylvanite, carnallite, etc.) in Germany. Our analyses show that all salt deposits including halite, sylvite, etc. generally have less than 0.001 ppm Au. Gypsum and anhydrite from the Walton area, Nova Scotia, likewise, generally has less than 0.001 ppm Au. Pyrite in evaporites may, however, be enriched in gold (up to 0.01 ppm). Seeland (1973 *a,b*) reports higher than average amounts of gold in certain samples of gypsum, anhydrite and halite from Paleozoic rock formations south of the Great Lakes in United States. Twelve per cent of the gypsum and anhydrite samples analyzed contained detectable gold, the mean being 0.020 ppm; a similar percentage of halite samples reported gold with a mean of 0.061 ppm.

Popov (1975) investigated the gold content in the Upper Jurassic Halogenous Formation in the southern part of Russian Turkestan. In all some 120 samples were analyzed. The average gold values found were: rock salt – 0.0012 ppm;

sylvanite – 0.0017 ppm; and sylvanite-carnallite – 0.0031 ppm. The content of gold in the associated limestones and anhydrite was lower. The order of increasing concentration of gold in the various rocks was found to be anhydrite–anhydrite-limestone–rock salt–potassium salts, indicating that gold was precipitated in increasingly larger amounts from waters of increasing salinity.

There appear to be only limited data on the gold content of oxidate sediments. The gold and silver contents of a number of iron-formations and associated sedimentary rocks in Canada are shown in Table 16. It will be noted that the sulphide-bearing members are the most enriched in the two elements. The Algoma (Archean) type iron-formations generally contain more gold than the Superior (Proterozoic) type. The Ordovician iron-formation in the Bathurst area of New Brunswick contains only low gold contents, from <0.005 to 0.01 ppm. Analyses of fossiliferous sedimentary magnetite beds (Lower Devonian) in the Nictaux Falls area of Nova Scotia indicate that the gold contents are less than 0.005 ppm. Hematite beds at the base of the Nepean sandstone (Cambrian) near Delta, Ontario generally contain less than 0.005 ppm Au. Seeland (1973 *a,b*) noted that certain glauconitic sandstones (Franconia Sandstone in Wisconsin) were slightly enriched in gold. Some 17 per cent of the samples analyzed reported gold with a mean content of 0.031 ppm.

Rozhkov *et al.* (1971*a*) have provided some data for the

Table 16. Gold and silver content of Canadian Precambrian* and Paleozoic iron-formations

| Locality, type and age | Description | Au | Ag | Au/Ag ratio |
|---|---|---|---|---|
| | | (ppm) | | |
| Temagami, Ont.<br>Algoma-type iron-formation†<br>Precambrian (Archean) | Banded pyrite-magnetite chert | 0.050 | 2.4 | 0.02 |
| | Banded chert with conformable pyrite layer | 0.020 | 0.7 | 0.03 |
| | Banded chert with minor disseminated pyrite | 0.060 | 1.1 | 0.05 |
| | Jasper and chert with pyrite | 0.020 | 2.0 | 0.01 |
| | Pyritic chert-magnetite breccia | 0.055 | 0.8 | 0.07 |
| Balmer Lake, Ont.<br>Algoma-type iron-formation<br>Precambrian (Archean) | Magnetic laminated grey chert | <0.005 | 0.6 | <0.008 |
| Kukatush, Sudbury district, Ont.<br>Algoma-type iron-formation<br>Precambrian (Archean) | Magnetite-carbonate-chert iron-formation | <0.005 | 0.9 | <0.005 |
| | Thinly banded carbonate iron-formation | <0.01 | 1.6 | <0.006 |
| | Jasper-magnetite-hematite iron-formation | <0.01 | 0.4 | <0.02 |
| Geraldton, Ont.<br>Algoma-type iron-formation<br>Precambrian (Archean) | Magnetite-carbonate-quartz iron-formation | 0.01 | 1.0 | 0.01 |
| | Magnetite-carbonate-quartz-pyrite iron-formation | 0.01 | 1.1 | 0.009 |
| | Magnetite-carbonate-quartz-pyrite iron-formation | 0.085 | 0.9 | 0.09 |
| | Carbonate-quartz-pyrite iron-formation | 1.030 | 2.0 | 0.51 |
| | Oxide-carbonate facies iron-formation | <0.005 | 0.8 | <0.006 |
| Schreiber, Ont.<br>Algoma-type iron-formation<br>Precambrian (Archean) | Massive pyrite in iron-formation | 0.070 | 2.2 | 0.03 |
| | Massive pyrrhotite in iron-formation | 0.040 | 3.6 | 0.01 |
| | Massive pyrite, pyrrhotite, minor galena in iron-formation | 0.050 | 4.7 | 0.01 |
| Michipicoten, Ont.<br>Algoma-type iron-formation<br>Precambrian (Archean) | Buff siderite | <0.01 | 2.1 | <0.004 |
| | Black siderite, minor disseminated pyrite | <0.005 | 1.4 | <0.003 |
| | Black siderite with pyrite in quartz-ankerite vein | 0.005 | 1.6 | 0.003 |
| | Siderite-chert iron-formation, minor pyrite | <0.01 | 1.0 | <0.01 |
| | Magnetite-siderite-chert iron-formation | 0.025 | 1.4 | 0.02 |
| | Magnetite-siderite-pyrrhotite-chert iron-formation | <0.005 | 1.1 | <0.004 |
| | Siderite-pyrite-chert iron-formation | 0.005 | 1.8 | 0.003 |
| Hearne Lake, N.W.T.<br>Algoma-type iron-formation<br>Precambrian (Archean) | Recrystallized chert-magnetite iron-formation | <0.005 | 0.5 | <0.01 |
| | Silicate facies (quartz-chlorite-pyrite and minor chalcopyrite) | 0.235 | 1.9 | 0.12 |
| Kaminak Lake area, N.W.T.<br>Algoma-type iron-formation<br>Precambrian (Archean) | Laminated magnetite iron-formation | <0.005 | 0.3 | <0.016 |
| | Magnetite iron-formation, some pyrite | 0.015 | 0.8 | 0.018 |
| | Pyritic cherty iron-formation | 0.010 | 1.4 | 0.007 |
| | Massive pyrrhotite in iron-formation | 0.015 | 2.8 | 0.005 |
| | Pyritic interflow | 0.065 | 2.3 | 0.028 |
| | Massive carbonate, some pyrite and arsenopyrite | 0.090 | 1.1 | 0.081 |
| | Massive carbonate | 0.025 | 1.5 | 0.016 |
| | Pyritic interflow | 0.430 | 1.3 | 0.330 |
| | Pyritic graphitic-interflow | 0.005 | 0.4 | 0.125 |
| | Cherty carbonate iron-formation | 0.005 | 1.3 | 0.003 |
| | Cherty iron-formation | 0.005 | 0.4 | 0.012 |
| | Magnetite chert bands | 0.005 | 0.4 | 0.012 |
| | Pyritic interflow, some chalcopyrite | 0.180 | 13.0 | 0.013 |
| | Pyritic cherty carbonate interflow | 0.150 | 2.4 | 0.062 |
| | Carbonate-rich tuff | 0.060 | 0.9 | 0.066 |
| | Siderite | <0.005 | 0.8 | <0.006 |
| | Cherty pyritic interflow | <0.005 | 0.9 | <0.005 |
| | Pyritic bands in iron-formation | 0.020 | 1.2 | 0.016 |
| | Cherty pyritic bands | 0.020 | 1.4 | 0.014 |
| | Cherty pyritic bands silicate iron-formation | 0.760 | 1.5 | 0.506 |

Table 16. (cont'd.)

| Locality, type and age | Description | Au | Ag | Au/Ag ratio |
|---|---|---|---|---|
| | | (ppm) | | |
| Kirkland Lake, Ont.<br>Algoma-type iron-formation | Magnetite-chert | 0.031 | 0.5 | 0.06 |
| Precambrian (Archean) | Chert and fine-grained quartz | <0.01 | 0.1 | <0.1 |
| Schefferville, Labrador-Quebec | Nonmagnetic silicate-carbonate iron-formation, Ferriman section | <0.01 | 0.4 | <0.02 |
| Superior-type iron-formation† | Silicate-carbonate member of iron-formation, Wishart section | <0.01 | 0.9 | <0.01 |
| Precambrian (Proterozoic) | Silicate-carbonate member of iron-formation, French section | <0.01 | 0.8 | <0.01 |
| | Oxide facies; Lower Red cherty member of iron-formation, French section | <0.01 | 0.9 | <0.01 |
| | Oxide facies; Pink Cherty member of iron-formation, French section | <0.01 | 0.6 | <0.02 |
| | Oxide facies; Grey Cherty member of iron-formation, French section | <0.005 | 0.5 | <0.01 |
| | Oxide facies; Brown Cherty member of iron-formation, French section | <0.015 | 0.7 | <0.02 |
| | Oxide facies; Upper Grey member of iron-formation, French section | <0.010 | 0.6 | <0.02 |
| Bathurst district, N.B.<br>Austin Brook area | Magnetite-chert-chlorite (composite sample) | <0.01 | 3.7 | 0.003 |
| Algoma-type iron-formation<br>Ordovician | Magnetite-chert-chlorite-pyrite (composite sample) | 0.075 | 4.1 | 0.018 |
| Nictaux Falls area, N.S.<br>Nictaux-Torbrook Formation<br>Metamorphosed Clinton-type iron-formation<br>Upper Devonian | Magnetite-hematite (composite sample) | 0.023 | 1.9 | 0.012 |

*The samples in these suites of iron-formations were kindly provided by G. A. Gross, R. H. Ridler and J.B. Henderson, Geological Survey of Canada; and H. Lovell, Division of Mines, Ontario Ministry of Natural resources.

†For classification of the types of iron-formations *see* G.A. Gross (1965), Geology of iron deposits of Canada, vol. 1; Geol. Surv. Can., Econ. Geol. Rep. no. 22, p. 116.

Krivoi Rog ores of U.S.S.R. as shown in Table 17. It will be noted that the gold contents are an order of magnitude higher than the contents in most sedimentary rocks. The gold tenor in all rocks and ores of the iron-formations was found to be 0.0*n* ppm. Some of the iron ores are relatively rich in gold; for example martite ore – 0.7 ppm, magnetite concentrate – 0.4 to 0.8 ppm. This suggested to the authors that some ore horizons were enriched in gold by sedimentary or metamorphic processes. Data provided by Pletnev (1972) for the Krivoi Rog siliceous ferruginous formations of Lower Proterozoic age show that in vertical profile the rocks range in gold content from 0.02 to 2 ppm. Two types of gold were recognized – one related to original sedimentation processes and the other representing a superimposed mineralization present in thin crushed zones. The latter may be a redistribution of the former (?).

Table 17. Gold contents of Krivoi Rog iron ores, U.S.S.R.

| Description | Range in gold content |
|---|---|
| | (ppm) |
| Magnetite-martite ores | 0–0.00*n*–0.*n* |
| Ferruginous quartzites | 0–0.0*n*–0.*n* |
| Shales | 0.0*n*–0.*n* |
| Mineralized zones in ferruginous quartzites | 0–0.0*n*–0.*n*–*n* |

Source: Rozhkov *et al.* (1971*a*).

The various data on iron-formations are interesting in the light of the common occurrence of commercial gold deposits in or near these formations in a number of places in the Canadian Shield and elsewhere in Precambrian rocks. The oxidate sediments together with sulphidic slates and schists that commonly accompany iron-formations may be the source of the gold that was later concentrated by secretion processes into deposits. These and other speculations are considered further in Chapter III.

Enrichment of gold in certain red (oxidized) sediments is also notable mainly as a result of adsorption and/or coprecipitation by ferric oxide hydrate. Thus, certain red sandstones and conglomerates may contain higher than normal amounts of gold than equivalent grey (reduced) rocks of the same type. Polikarpochkin *et al.* (1969) refer to this situation in the Baleisky, Onokhovsky and Lukinsky grabens where they find maximum contents of gold in red conglomerates up to 0.5 ppm. I have found higher than normal gold contents in some Carboniferous, Tertiary and Recent conglomerates containing abundant iron oxides in various parts of Canada. These are discussed in the section on placers.

There are apparently no systematic analyses for gold in the bedded sedimentary manganese deposits of the world. The results reported for deep sea manganese nodules generally show the gold content to be <0.001 ppm; some wads, however, are richer in gold (Table 12) with values up to 0.7 ppm Au or more.

Gold is frequently concentrated under unusual conditions in some types of sediments. Laur (1906) describes remarkable concentrations of gold and silver in Triassic sediments in the Meurthe-et-Moselle region of France. Up to 29 ppm Au (and 245 ppm Ag) are recorded for samples of sandy dolomite. The nature of the gold is not specified. Palmer (1935) has described an interesting occurrence of gold and silver in petrified logs in the Aspen district of Nevada. One log assayed 18.26 oz of gold and 10.8 oz of silver to the ton, and native gold was readily observed under the microscope. Palmer thought that the carbonized wood produced the reducing environment that precipitated the gold and silver from circulating solutions that came into contact with the logs. The writer has seen similar occurrences of gold in petrified Sequoia trees in samples from Alaska (G.B. Robbe collection, Michigan Technological College, Houghton, Michigan).

An interesting occurrence of traces of gold (and silver) is that in the salt-dome calcitic and gypsiferous cap rocks of Texas and Louisiana mentioned by Hanna and Wolf (1941). In these rocks the noble metals appear to be associated with sulphides, including pyrite, hauerite ($MnS_2$), galena and sphalerite and in some places with barite, celestite and native sulphur. The origin of the sulphides and their contained gold and silver seems to be best explained by the hypothesis that as $H_2S$ rose from underlying petroliferous layers it came into contact with groundwaters (or connate waters in some cases) carrying lead, zinc, iron, manganese, silver, gold, etc. in the region of the cap rocks and deposited the sulphides in the available porous zones.

Occurrences of auriferous sandstones and conglomerates are widespread throughout the world, the most famous and productive being those of the Witwatersrand, South Africa, Tarkwa, Ghana and Jacobina, Argentina. The Witwatersrand ores average 8 ppm Au and 0.8 ppm Ag; those at Tarkwa contain 10 ppm Au and 0.5 Ag, and those at Jacobina 15 ppm Au and about 1 ppm Ag. Other less well known occurrences occur in many parts of the world throughout the geological column. Only a few can be mentioned as examples. For details and descriptions of other similar auriferous rocks consult Chapter III, especially the section on placers.

In the United States Devereux (1882) describes the occurrence of gold in the Potsdam conglomerate-breccia-sandstone of the Black Hills near the famous Homestake deposit. Some streaks near the bedrock are said to run 85 ppm (2.5 oz/ton), but the overall grade of the conglomerate is low, probably of the order of 1 ppm or less. Devereux recognized two types of gold in the fossil placers – mechanically concentrated gold and chemically precipitated gold. The fineness of the placer gold was greater than that of the quartz veins from which it was said to have been derived, a feature that is normal in practically all placers.

Hastings (1908) described fossil placers near Antelope Springs, Park County, Colorado. These placers occur in a large area of unconsolidated lake beds that average about 0.01 oz/ton (0.3 ppm). The nature of the gold could not be determined. Dumble (1913) described somewhat similar deposits from the Eocene of Texas. The gold-bearing beds are clays and sands with interbedded lignite. The grade is low, but some samples ran as high as 1 oz/ton (34.2 ppm) and upward. In Oregon and California, Diller (1914) describes Cretaceous fossil marine placers formed about an old island. The gold-bearing rocks are conglomerates derived from an underlying auriferous slate bedrock series. They contained from 1 to 5 ppm Au on the average. More recently Antweiler and Love (1967) have described gold-bearing Cretaceous and Tertiary quartzite conglomerate in northwest Wyoming. The gold values run from 0.035 to 0.222 ppm. The gold is largely confined to sandstone layers and the sandy matrix of the conglomerates. Much of it is the particulate native variety, but some evidently occurs in an absorbed state or in the structure of a variety of minerals. In the Rocky Mountain region of the conterminous United States certain fossil black sandstones of Late Cretaceous age contain up to 1.3 ppm Au in Wyoming and Colorado according to R.S. Houston (U.S. Geol. Circ. 622, 1969, p. 8). In Wyoming the younger deposits contain the higher gold contents.

In Canada there are also numerous occurrences of gold-bearing conglomerates, sandstones and quartzites. The uraniferous conglomerates and quartzites of the Blind River–Elliot Lake area carry small noncommercial amounts of gold in some beds. The Edmonton Formation in Alberta is gold-bearing in places. It probably supplied most of the gold to the placers worked many years ago along the North Saskatchewan River (Tyrrell, 1915). Another example of gold-bearing conglomerate and sandstone is found in the basal Carboniferous of Nova Scotia in the Gays River area (Malcolm and Faribault, 1929). The gold content of the richer streaks was said to average 5.4 ppm (0.158 oz/ton); our analyses show much lower values, around 0.03 ppm. Yet another example of gold-bearing limonitic-cemented conglomerate is found in the Beauceville area of Quebec. This has been mined extensively in the past. The rocks may be early Pleistocene in age although some investigators have considered them to be of Tertiary age (*see also* the section on placers in Chapter III).

Throughout other parts of the world gold-bearing conglomerates, sandstones and quartzites are widespread, and many have been mined or washed for gold. The Witwatersrand, Tarkwa and Jacobina deposits have been mentioned previously. These are the most famous of all of the fossil gold placers. In U.S.S.R. there are numerous occurrences of gold-bearing sandstones and conglomerates. One of these in Cambrian sandstones is described by Pokrovskii (1968); others are mentioned by a number of other Russian investigators, the principal publication on their occurrence being that by Ivenson *et al.* (1969). In Switzerland, Hofmann (1965) describes quartzite-rich conglomerates of the Upper Marine Molasse (Miocene) and coarse Triassic sandstones that carry gold contents of the order of 1 to 2 colours per 100 kg of rocks. In South Island, New Zealand, conglomerates and quartzites ranging in age from Cretaceous to Recent have been washed for gold for many years. These conglomerates are of fluvial and glaciofluvial origin. They are discussed in greater detail in Chapter III.

The fossil gold-bearing placers typified by conglomerates, sandstones and quartzites are of two types. These are only briefly described here since more details are given in the section on placers in Chapter III. The ancient Precambrian types (Witwatersrand, etc.) are characterized by relatively high gold contents and an abundance of pyrite. The gold is mainly free, but some is contained in pyrite and other minerals. Uraniferous minerals are common, and in some there are also thorium and rare-earth minerals. Iron oxides are rare except in the Tarkwa deposits. The more recent types are often characterized by limonite or iron oxide cemented conglomerates in which the gold is mainly free with only small amounts in adsorbed or other forms. Uranium, thorium and rare-earth minerals are rare or present in only small amounts; pyrite tends to be rare, but in some deposits, it is present in small amounts in the basal parts of the sequences. While both types may represent similar sedimentary conditions of formation it is obvious that their subsequent history has been much different.

The writer has extensively investigated the nature of gold in sedimentary rocks, and while it is often difficult to determine precisely the location of parts per billion gold in some samples, concludes the following from his research:

1. In conglomerates, sandstones, quartzites and similar rocks most of the gold is present in particulate form as the native metal. The size of the particles ranges all the way from less than 1 μ to nuggets the size of peas. Much of this gold is of detrital or detrital-chemical origin. Some gold is also present in forms, the nature of which we have not been able to ascertain with certainty. Where pyrite is present there are small amounts of the element in this mineral as shown by the results from Elliot Lake (Table 11). Other minerals such as limonite, magnetite, pyrrhotite, etc. may also contain traces of gold, the form of which is unknown.

2. In pyritiferous black shales and schists most of the gold is present in pyrite and/or pyrrhotite as shown by the analyses in Table 11. It is of interest to note that in rocks containing coexisting sedimentary pyrite and arsenopyrite gold prefers the arsenopyrite whereas silver is concentrated mainly in the pyrite. This feature is particularly clear in samples from the Meguma slates in Nova Scotia (Ovens, N.S., Table 11). In some black shales, oil shales, etc. the gold is largely associated with the carbonaceous substance, probably in an adsorbed form or as some type of organometallic compound. Where fine-grained pyrite and/or pyrrhotite are present, however, the gold tends to be partitioned into these mineral phases. The same is true if other sulphides such as chalcopyrite and galena are present. From this it seems to follow that the degree of diagenesis and metamorphism of the black shales and schists more or less determines the location of gold (and silver). In black shales that have undergone little metamorphism the gold appears to be associated with both the carbonaceous substance and fine-grained nearly colloidal sulphides. With increase of metamorphism and migration of the sulphides into knots or crystals, the bulk of the gold (and silver) tends to collect either in the iron sulphides or in chalcopyrite and other sulphides that occur in blebs or in small fractures in the pyrite and/or pyrrhotite. It is of interest to note that Kucha (1973) observed that much of the gold in the copper-bearing shale of the Fore-Sudetic monocline in Poland is present in minerals containing native silver but also in organic compounds of the thioaurate and chelate types. Legedza (1967) has examined the problem of the accumulation of gold in sulphides in the sediments of the Russian Platform during diagenesis. He thinks that thiosulphates in groundwaters act as collectors and carriers of both sulphur and gold, and that during diagenesis the metal is largely precipitated in pyrite (apparently in the metallic state) according to the reactions:

$$\mathrm{FeO} + \mathrm{H_2S} + n\mathrm{H_2O} \rightarrow \mathrm{FeS}\cdot n\mathrm{H_2O}$$

$$2\mathrm{FeS}\cdot n\mathrm{H_2O} + [\mathrm{Au(S_2O_3)_2}]^{3-} \rightarrow 2\mathrm{FeS_2} + \mathrm{Au} + 2\mathrm{SO_3} + n\mathrm{H_2O}$$

In lithified sulphide-free sediments, gold apparently remains in its finely dispersed state.

3. I have not been able to determine the nature of gold in normal shales, carbonate rocks, evaporites, etc. with any degree of certainty. The amounts of gold are so low that the mineral separation and analytical problems are in many cases insuperable. My results suggest that the gold, in some fine-grained sediments such as shales, is present in particulate form (flour gold) or in the small amounts of pyrite, magnetite, limonite and other heavy minerals that are frequently present in such rocks. In carbonates and evaporites the gold is probably largely present in carbonaceous matter or in colloidal pyrite. In all fine-grained sedimentary rocks there is probably some gold present as an adsorbed element.

The average gold content of the sediments of the Russian Platform is given by Nikitin and Yasyrev (1974) as 0.005 ppm. In the minerals of these sediments the average gold content ranges from 0.0008 ppm in chlorites to 0.0137 in the iron oxides; the organic constituents contain an average of 0.0089 ppm Au.

## Gold in metamorphic rocks

The available data on the gold content of metamorphic rocks are given in Table 18. The number of analyses in some of the categories are too few to draw sound conclusions, but the following indications are noted.

In metamorphic rocks gold appears to occur in the same minerals as those noted for igneous and sedimentary rocks. My research shows that much of the gold occurs in pyrite, pyrrhotite, etc. and in the ferromagnesian minerals, principally magnetite, biotite, pyroxenes and amphiboles. Where pyrite and pyrrhotite are present in the same rocks, gold generally prefers the pyrite. If arsenopyrite is present, this mineral is enriched compared with pyrite and pyrrhotite. In certain quartzites and metaconglomerates the element may be present as the native metal. These types of metasediments are discussed in greater detail in the section on auriferous quartz-pebble conglomerates and placers in Chapter III.

Regionally metamorphosed rocks appear to have gold contents in the same range as those of the igneous and sedimentary rocks from which they were derived. Certain skarns and other contact rocks, on the other hand, are often enriched in gold (and silver). This appears to be normal since such rocks often contain copper deposits and a few gold-silver deposits. These are discussed in further detail in Chapter III.

Certain metamorphic rocks seem to be exceptionally high in gold over large areas, an example being those in the Sob River basin in the Ukraine (Latysh *et al.*, 1974). Certain shales, containing high contents of magnetite, report up to 0.3 ppm Au in this area. Other rocks contain from a trace to 0.02 Au. It is not clear whether these are fresh rocks, or whether there is a superimposed mineralization present. Relatively enriched quantities of gold are also recorded by Usenko *et al.* (1973) in the garnetiferous quartzites, crystalline schists, skarns and magnetite ores from the Sea of Azov region, U.S.S.R. They report gold contents ranging from 0.3 to 1.0 ppm in the ferruginous quartzites. Other rocks contain from traces to 0.2 ppm Au. Certain of the Grenville marbles in the Adirondacks of New York appear to be enriched in gold in places. Seeland (1973 *a,b*) found that 24 per cent of the samples he analyzed ranged in gold content from 0.020 to 0.20 and averaged 0.053 ppm.

The migration trend of gold during metamorphism is indicated in a number of investigations:

Brammall and Dowie (1936) noted low gold contents (0.07 ppm) in basic igneous rocks, grey granites, gneisses and schists of the Malvern Hills, England. Higher values (up to

Table 18. Gold content of metamorphic rocks

| Rock type | Number of samples | Range | $\bar{X}$ (ppm) | S | G | $\bar{X}$g | Sg | Ag* $\bar{X}$ (ppm) | Au/Ag ratio |
|---|---|---|---|---|---|---|---|---|---|
| Quartzites and indurated sandstones | 289 | 0.0002–1.1500 | 0.0317 | 0.0836 | 0.0047 | –2.3325 | 0.9282 | – | – |
| Slates, phyllites, meta-argillites | 225 | 0.0009–0.0150 | 0.0022 | 0.0022 | 0.0016 | –2.7959 | 0.3126 | 0.2 | 0.0110 |
| Gneisses, granulites | 1929 | 0.0002–0.3000 | 0.0031 | 0.0071 | 0.0027 | –2.5682 | 0.1806 | – | – |
| Amphibolites, greenstones | 425 | 0.0001–0.1000 | 0.0071 | 0.0110 | 0.0041 | –2.3837 | 0.4399 | 0.25 | 0.0284 |
| Schists | 1969 | 0.0001–3.7000 | 0.0186 | 0.1545 | 0.0037 | –2.4351 | 0.5388 | 0.2 | 0.0930 |
| Marble and crystalline limestones | 40 | 0.0002–0.1000 | 0.0132 | 0.0224 | 0.0036 | –2.4385 | 0.7243 | 0.05 | 0.2640 |
| Hornfels and meta-pelites | 368 | 0.0003–0.3000 | 0.0064 | 0.0262 | 0.0018 | –2.7341 | 0.5037 | – | – |
| Eclogites | 103 | 0.0008–0.0400 | 0.0036 | 0.0045 | 0.0024 | –2.6132 | 0.3626 | 0.10 | 0.0360 |
| Skarns | 44 | 0.0076–0.0220 | 0.0086 | 0.0028 | 0.0083 | –2.0789 | 0.0887 | – | – |
| Undifferentiated metamorphic rocks (porphyroids, chloritized and epidotized tuffs, etc.) | 12 | 0.0004–0.0084 | 0.0038 | 0.0022 | 0.0029 | –2.5308 | 0.3812 | – | – |
| All metamorphic rocks | 5404 | 0.0001–3.7000 | 0.0109 | 0.0960 | 0.0031 | –2.5092 | 0.4703 | 0.15 | 0.0727 |

*The arithmetic mean for silver is taken from a previous compilation by Boyle (1968*b*). It does not refer to the samples quoted in the column – number of samples.

2.06 ppm) were recorded in red granites, red granite pegmatites and mixed rocks affected by the reddened granites. They attributed the increased amounts of gold to disseminations of hematite attributable to pneumatolytic processes associated with the latest phase of granitic intrusion.

Boyle (1961*a*) observed decreases in the gold contents of chloritized zones and marked increases in carbonatized zones associated with the formation of quartz in the Yellowknife Greenstone Belt, Northwest Territories, Canada.

Buryak (1964) noted that the gold mineralization of the Lena goldfields, U.S.S.R. is closely related in time, space and possibly genetically to regional metamorphism.

In the Altai and Transbaikalian massifs Anoshin and Potap'yev (1966) found a two- to threefold increase of gold in an early stage of altered granites compared with the unaltered varieties. The gold content, thereafter, decreased with increased hydrothermal alteration. In other words gold was lost from rocks that have undergone metamorphism according to their data.

Shilin (1968) found that low temperature carbonatization processes reduced the content of gold in primary gold-enriched magmatic rocks in central Kamchatka.

Voskresenskaya and Zvereva (1968) noted a direct correlation between gold mineralization and the degree of metasomatism in northern Kazakhstan. In weakly propylitized rocks they recorded an average of 0.006 ppm Au whereas in highly propylitized varieties the values were as high as 0.06 ppm. Roslyakov (1969) noted that gold was concentrated in rocks formed at the terminal stages of metamorphism in the Darasun ore field.

Chaika and Nezhdanova (1969) examined the problem of the migration of gold during the metamorphism of the sulphide-bearing graphitic kyanite shales of the Keyv Series of the Kola Peninsula, U.S.S.R. They noted that pyrite contained the most gold (0.006–0.008 ppm), followed by graphite (0.004–0.006 ppm), pyrrhotite (0.003 ppm) and muscovite (0.003–0.004 ppm). During the metamorphism of the shales gold migrated together with silica (quartz) from the shales into nearby cavities. These contained gold in quantities up to 2.86 ppm. In the kyanite schists of the Vitim-Patom Highland, U.S.S.R. Kepezinskas *et al.* (1970) state that a complete redistribution of gold results from metamorphism. Petrov *et al.* (1972) noted a similar tendency during the metamorphism of the sedimentary rocks of the Patom Highlands, U.S.S.R. Gold was lost from the rocks of the amphibolite facies and accumulated in the epidote-amphibolite and greenschist facies. Uranium and thorium were relatively inert. Buryak *et al.* (1972) also found that the granitization of the Upper Proterozoic Patom Series of shales, schists, etc. resulted in significant losses of gold. This gold is evidently slightly concentrated in the youngest pegmatites.

During the autometasomatic amphibolitization of ultrabasic rocks gold is practically inert according to Shcheka and Moiseenko (1970). However, during serpentinization processes much gold is lost from these rocks; granitization and migmatization of ultrabasic rocks also results in significant losses of gold. Li and Kornev (1972) also noted appreciable losses of gold during serpentinization of dunites. In another paper Moiseenko *et al.* (1970) state that the main sources of gold in the earth's crust are basic and ultrabasic rocks. During the metamorphism of these rocks the gold is freed, transferred to melts and solutions and after migration is deposited in local faults and fractures. The same theme, greatly amplified and illustrated, is discussed by Moiseenko *et al.* (1971) and Moiseenko and Fat'yanov (1972).

In their study of the Rice Lake Gold Belt of Manitoba, Stephenson (1971), Stephenson and Ehmann (1971) and Weber and Stephenson (1973) concluded that the low gold values recorded for high-grade gneisses was the result of gold depletion during high-grade metamorphism of the belt.

Finally, Pchelintseva and Fel'dman (1973) examined the gold content of the metamorphic rocks in the Koktchetav uplift and concluded that the gold distribution in these rocks is determined by the composition of the initial rocks (sediments and volcanics), not by the grade of the metamorphism which ranges from greenschist to amphibolite facies.

A number of more recent studies suggest that gold is relatively mobile during metamorphic processes. Li and Shokhina (1974*a*) found that during regional metamorphism no substantial change took place in the Precambrain rocks of the Yenisei Mountain Ridge. However, they observed that the deep reformation of the mineral composition of some of the rocks under conditions of high temperature was attended by an internal redistribution and dispersion of gold. Palandzhyan and Razin (1974) working in the ultrabasic and basic massifs of the Sevan Ridge, U.S.S.R. observed that metamorphic transformation of rocks of the ophiolite association is accompanied by a decrease in their gold content, and Mushkin *et al.* (1974) found that eclogitization of granulite facies gneisses leads to upward movement of gold, together with Si, Na and K, into quartz veins. Gavrilenko *et al.* (1974) observed that the regional metamorphism of Lower Proterozoic rocks in the Kolmozero-Voron'ya complex (Kola Peninsula) was essentially isochemical, the overall concentrations of petrogenic and ore-forming elements, including gold, being the same as the concentrations in the parent rocks. The great dispersion of gold observed and the anomalous concentrations of the metal in hydrothermally altered rocks in fissured zones, at contacts between mafic and ultramafic intrusives, and in mineralized pegmatites and their enclosing rocks were considered to be due to redistribution of gold to some degree during metamorphism. During the formation of contact-metasomatic zones associated with granitic intrusions in the Altai-Sayan Korobeinikov (1976) observed that most of the gold in the original rocks was redistributed and concentrated in the hornfels and marbles, particularly in magnetite, epidote, amphibole and chlorite.

Despite all these indications there are still insufficient data to establish unequivocally the migration trend of gold (and silver) during metamorphic processes. Nevertheless, certain trends seem to be indicated from my research and that of others. During high grade metamorphic processes and granitization gold (and silver) appears to be liberated from the rocks but is not concentrated in pegmatities despite the fact that the migration of much silica is involved in the process. The element is, however, markedly enriched in some skarn zones, in various types of veins and in a variety of other deposits that appear to form during the late stages of the metamorphic and granitization history of a mineralized belt.

Gold is not a chalcophile element but has certain tendencies in this direction since it appears to follow sulphur, arsenic and antimony during regional and contact metamorphic processes. There is also considerable evidence to suggest that the migration characteristics and diffusion rates of gold are about the same as those of K, Na, Mo, W, Cu, Ag, Zn, Cd, Hg, Pb, As, Sb, Se and Te since these elements are commonly associated in deposits. The tendency of gold to follow copper and silver is common in some skarn deposits (Table 44); in others it follows arsenic and/or antimony. There is also a marked coherence in the migration tendencies of silica and gold, the two constituents being nearly always associated in auriferous deposits. An explanation of these and other features is reserved for the discussion on the origin of gold deposits in Chapter III.

> As a land surface is worn away in regions where conditions are unfavourable for solution, gold tends gradually to become concentrated at the surface.
> –W.H. Emmons, 1937

## Gold in soils and other products of weathering

The average gold content of most soils is low, but the element is enriched in certain types of soils and in a variety of glacial and weathered products in the vicinity of gold-bearing rocks or auriferous deposits. Some of these weathered products constitute valuable deposits of the element; they are discussed in the section on placers in Chapter III.

Relatively little precise knowledge on the migration and concentration of gold during weathering is available despite the importance of the subject. Both physical and chemical processes are involved; the importance of each in the migrational history of the element depends on numerous factors discussed below.

### *Soils*

Data on the gold content of soils are limited, and the calculation of an average value seems unwarranted at the present time. Swaine (1955) does not list an average value, and Vinogradov (1959) states that the data on gold in soils were insufficient at the time of his compilation to give values for the contents of normal soils.

Nemec *et al.* (1936) found an average gold content of 0.1 ppm in some Czechoslovakian soils formed from andesite and rhyolite, and Nemec *et al.* (1937) recorded gold values from 0.185 to 0.350 ppm in other soils of Czechoslovakia. Babicka (1943) records values from 0.2 to 6 ppm Au in some Czechoslovakian soils. Goldschmidt and Peters (1933) found 0.1 ppm Au in the humus of a birch forest in Germany.

Relatively few data on the gold content of soils well removed from gold deposits are extant in the literature. One particular study, however, carried out in Greece gives considerable information on the content and nature of gold in Grecian residual and alluvial soils, including one loessial soil from Illinois (Yassoglou and Nobeli, 1968). The values recorded range from 0.005 to 0.150 ppm Au. The results indicated that the silt clay fractions contain much higher amounts of gold than does sand. Parent materials, which have undergone one cycle of soil formation, appear to contain gold in the silt in the resistant metallic form. In other cases, the element was found to be associated with easily weatherable minerals and appeared to be progressively lost from the silt fraction during processes of soil genesis. The authors thought that gold could be used as an index of soil weathering, either as a resistant or as a removable constituent of the silt, depending on the composition and the origin of the parent material of the soil. They also felt that gold can be used as an index of the lithological continuity of soil profiles.

Crocket *et al.* (1973) record gold values for some Arctic Island soils: the Prince Patrick grey soils contain 0.001 ppm Au and the Melville Island grey-brown and red-brown soils 0.0003 and 0.0018 ppm Au respectively. The average for the Arctic soils is given as 0.001 ppm Au. The analyses were done by neutron activation methods.

The writer has carried out investigations of the gold content of soils far removed from gold deposits in a number of Canadian areas, with the results noted in Table 19. Summarizing we can say that the general background range of the soils in most parts of Canada is from <0.0005 to 0.005 ppm. There is a slight enrichment of gold in the A (humic) horizons compared with other horizons in some soil profiles.

Numerous investigations of the gold content of soils in the vicinity of gold-bearing deposits are extant in the literature. These, together with some of my data, are summarized in Table 20. Enrichment of the element in the A (humic) horizons of soils is again apparent in numerous places, although in some profiles there is a considerable concentration

Table 19. Gold content of Canadian soils well removed from gold-bearing rocks and deposits

| Description | Range in gold content (ppm) |
|---|---|
| Southwestern Ontario, Port Lambton–Wallaceburg area | |
| Soils developed on glacial lake clay | |
| A horizon (virgin) | <0.005–0.01 |
| B horizon (virgin) | <0.005–0.01 |
| C horizon (virgin glacial clay) | <0.005 (av.) |
| A horizon (cultivated area) | <0.005–0.01 |
| B horizon (cultivated area) | <0.005–0.01 |
| C horizon (virgin glacial clay) (cultivated area) | <0.005 (av.) |
| Soils developed on glacial sand | |
| A horizon (virgin) | <0.005 |
| C horizon (virgin) | <0.005 |
| A horizon (cultivated) | <0.005 |
| C horizon (cultivated) | <0.005 |
| Central Ontario, Minden-Bobcaygeon area | |
| C horizon (till) | <0.005 |
| Eastern Ontario, Carleton Place–Ottawa area | |
| C horizon (till) | 0.01 –0.035 |
| C horizon (Leda clay) | <0.005 |
| Eastern Ontario, Lavant Township, Lanark County | |
| Soils developed on glacial till | |
| B horizon below pine needle mat | <0.005–0.01 |
| Northern Ontario, Cobalt area | |
| A horizon (humic) | <0.005 |
| $A_2$ horizon (sand) | <0.005 |
| B horizon (sand) | <0.005 |
| C horizon (sand) | <0.005 |
| A horizon (humic) | <0.005 |
| C horizon (glacial clay) | <0.005 |
| C horizon (till) | <0.005 |
| New Brunswick, Bathurst area | |
| Soils developed on glacial till, sand and gravel | |
| $A_{00}+A_0$ horizon (humic) | <0.005–0.03 |
| $A_1$ horizon (reddish loam) | <0.005–0.017 |
| $A_2$ horizon (leached layer) | <0.005–0.017 |
| $B_2$ horizon (abundant iron oxides) | <0.005–0.017 |
| C horizon (sand, till) | <0.005–0.017 |
| Manitoba, Falcon Lake area | |
| Soils developed on sandy glacial till | |
| A horizon | <0.005–0.015 |
| B + C horizon | <0.005 |
| Northwest Territories, Yellowknife area | |
| Soils developed on glacial till, sand and gravel | |
| A horizon (humic) | 0.005–0.10 |
| B horizon | 0.008 (av.) |
| C horizon (sandy till; glacial sand and gravel; clay locally) | 0.009 (av.) |
| Northwest Territories, Regan Lake area | |
| Regosoils* | <0.005–0.005 |

*Data from Cameron, E.M. and Durham, C.C. (1974), Geol. Surv. Can. Pap. 74-1, Pt. A, p. 53–60.

of gold in the B and C horizons directly over deposits (viz., Crestaurum profiles). As a generalization one can say that gold is enriched in one or more of the soil profiles in the vicinity of auriferous deposits.

A number of studies have been carried out by the writer to determine the mode of binding of gold in soils. The results of these studies suggest that gold is bound in the following ways in most soils:

1. As a constituent of flour gold and small flakes and nuggets of native gold. These occur almost universally in the weathered products of gold deposits, auriferous sulphide deposits, etc. and in nearby soils, especially those of a residual nature. Similar flakes and nuggets have been noticed in glacial till, sand and gravel overlying, or in the vicinity of, gold-bearing deposits. This gold is readily extracted by aqua regia, KCN, and other gold solvents. Frequently, the gold is of much greater fineness than that in the underlying deposits. This feature is discussed in greater detail in Chapters III and IV.

2. As a minor constituent of a number of partly oxidized residuals of primary vein minerals, particularly pyrite, arsenopyrite, chalcopyrite, sphalerite, magnetite, etc. These minerals have been noticed in soils overlying all types of gold deposits throughout Canada.

3. As a minor constituent of a number of discrete secondary (supergene) minerals, particularly limonite, wad, beudantite, bindheimite, anglesite, jarosite, copper carbonates, etc. These minerals generally occur in soils quite close to the underlying deposits. Most occur in the C horizons; only a few have been noted in the A and B horizons, and their presence in these horizons is generally due to solifluction and other disturbances of the soil.

4. As a minor constituent of manganese oxide coatings on sand and silt; also in similar material cementing sand, silt, etc. in the B and C horizons of the soil. It has been noted that some soils enriched in manganese oxides are also enriched in gold (and silver). The enrichment of gold is presumably due to the presence of foreign colloids such as positively charged hydrous iron oxides, alumina, etc., which impart a net positive charge to the initially negative hydrous manganese oxide gels. These in turn attract and coprecipitate the negatively charged gold complexes and colloids. (*See also* the section on gold in oxides in the first part of this chapter.) The gold in manganese oxides is evidently present mainly as an adsorbed phase or in a very finely divided native form. Some wads in oxidized auriferous deposits contain wiry and powdery forms of native gold.

5. As a minor constituent of various hydrous iron oxide coatings in sand and silt; also in similar material cementing sand, silt, etc. in the B and C horizons of the soil. Hydrous iron oxides in soils in the vicinity of gold-bearing deposits are invariably enriched in gold, the probable cause being that negatively charged gold complexes and hydrosols are strongly adsorbed and precipitated by positively charged hydrous iron oxide sols and gels. The gold in hydrous iron oxides is evidently present mainly as an adsorbed phase or in a very finely divided native form. Some limonites in oxidized auriferous deposits contain wiry and powdery forms of native gold.

6. As a minor constituent of organic matter (humus) in soils. We have found an enrichment of gold in some of the A (humic) horizons of soils in the vicinity of gold-bearing deposits and also in normal soils. The nature of the gold in this material is difficult to ascertain. Some is evidently a constituent of the undecayed plant and animal matter (*see* below under gold in plants and animals.) The remainder is probably present as a chelate or some other organometallic gold compound. Only small amounts of gold (and silver) are

Table 20. Gold content of soils in the vicinity of auriferous deposits

| Locality | Material | Range or average (ppm) | Reference | Remarks |
|---|---|---|---|---|
| Région de l'Afema en Côte d'Ivoire | Argillaceous lateritic soils | 0.02–5.4 | 1 | |
| Minerai Banora en Guinée | Argillaceous lateritic soils | 0.5–30 | 1 | |
| Aldan Shield, U.S.S.R. | Soils | 0.1–5.7 | 2 | Kuranakh-type (karst) gold deposits |
| | $A_0$ horizon | 0.1–5.5 | 2 | |
| Mont Flotouo (Ity, Côte d'Ivoire) | Argillaceous lateritic soil | 0–>8 | 3 | |
| Northwest Wyoming | Soil on/or derived from Harebell and Pinyon conglomerate-sandstone formations | 0.036–0.048 | 4 | Rock underlying soil contains 0.0–0.43 ppm Au |
| Silver Reef, Utah | Soil | <0.05–0.35 | 5 | Underlying rocks are sandstones, shales, etc. |
| Southeastern, U.S.A. | Near surface soil | 0.02–0.52 | 6 | 0–5.5 ft deep |
| | Soil from a pit | 0.03–0.23 | | 0–12 ft deep |
| Ity, Ivory Coast | Lateritic ores | up to 18.3 | 7 | |
| British Guiana | Laterites and ironstones | 0–>17 | 8 | Precipitated ironstones (limonite) are often rich in gold |
| Mill Canyon area, Nevada | Mull (forest humus) | 0.8 (av.) | 9 | Composite of 2 samples |
| Empire district, Clear Creek County, Colorado | Mull (forest humus) | 1.4 (av.) | 9 | Composite of 8 samples |
| Empire district, Clear Creek County, Colorado | Mull (forest humus) | 0.6 (av.) | 9 | Composite of 9 samples |
| Empire district, Colorado | Mull layer | <0.04–>0.60 | 10 | About 70% of values cluster in the range <0.04–0.59 and 30% in range >0.60 |
| | Soil (6–12 in. depth) | <0.04–>0.60 | 10 | About 90% of values cluster in the range <0.04–0.59 and about 10% in range >0.60 |
| Auriferous areas in Colorado, Utah, Nevada and Arizona | Mull layer | <0.04–5.1 | 11 | |
| | Other soil horizons | <0.04–29 | 11 | High concentrations of gold commonly found near the bottoms of the profiles |
| Cros Gallet, Guyane française | Soil | 0.053–1.10 | 12 | |
| Rhodesia; near Leopardess Mine | Topsoils and subsoils | 0.042–0.049 | 13 | Kalahari sand |
| Lavant, Ont. (Joe Lake Mine) | B horizon below pine needle mat | 0.01–0.05 | 14 | Podsol developed on till |
| Falcon Lake, Man. (Falcon Lake Mine) | A horizon | <0.01–0.025 | 14 | |
| | B + C horizon (till) | <0.01 | 14 | |
| Yellowknife, N.W.T. | | | | |
| Profile 1 (Crestaurum Mine area) | A (humic) horizon | 0.85 | 14 | Arctic brown soils developed on till. Permanently frozen in places |
| | B + C (rusty till) | 24 | | |
| Profile 2 (Crestaurum Mine area) | A (humic) horizon | 1.1 | 14 | |
| | B + C (clay) | 0.04 | | |
| Profile 3 (Lynx area) | A (humic) horizon | 0.04 | 14 | |
| | B horizon (clay ) | 0.02 | | |
| | C horizon (reddish till and clay) | 9.0 | | |
| Near and over gossan zone, Regan Lake area, N.W.T. | Soils and disintegrated gossanous material | <0.005–0.810 | 15 | Regosoils |
| Bathurst area, N.B.<br>Profile 1 (Nigadoo vein) (For geological description *see* Davies *et al.* (1969), Geol. Surv. Can. Pap. 67-49) | $A_1$ (humic layer) | <0.01 | 14 | Podsols developed on glacial till |
| | $A_2$ (leached zone) | <0.01 | | |
| | $B_2$ (rich in iron oxides) | <0.01 | | |
| | C (till | 0.01 | | |
| | C (till and disintegrated gossan) | 0.045 | | |
| | Gossan | 0.41 | | |
| | Sulphide ore | 0.01–0.20 | | |
| Profile 2 (Bathurst No. 6 deposit) (For geological description *see* Boyle and Davies (1964), Geol. Surv. Can. Pap. 63-24) | $A_0$ (humic layer) | 0.025 | 14 | |
| | $A_2$ (leached layer) | 0.015 | | |
| | $B_1$ (reddish loam) | 0.120 | | |
| | $B_2$ (yellowish-brown loam-till) | 0.220 | | |
| | $B_3$ (reddish loam-till) | 0.465 | | |
| | Gossan-limonite cemented conglomerate | 0.017–0.684 | | |
| | Sulphide ore at interface of gossan and orebody | 2.8 | | |
| | Sulphide ore | 0.30 | | |

References:
1. Martinet and Cuper (1961).
2. Razin and Rozhkov (1963).
3. Granier *et al.* (1963).
4. Antweiler and Love (1967).
5. Cornwall *et al.* (1967).
6. Kinkel and Lesure (1968).
7. Jones (1969).
8. Harrison (1908).
9. Curtin *et al.* (1970).
10. Curtin *et. al.* (1968).
11. Lakin *et al.* (1974).
12. Machairas (1970*a*).
13. Watson (1972).
14. Boyle (unpublished).
15. Cameron, E. M. and Durham, C. C. (1974) Geol. Surv. Can., Pap. 74-1, pt. A, p. 53–60.

removed by cyanide leaches of humic material. Ashing is necessary to effectively liberate the gold (and silver).

Zhukova (1974) found that up to 50 per cent of the gold in the organic horizons of soils over auriferous deposits in eastern Transbaikal, U.S.S.R. was water soluble. The remainder was bonded to organic substances, such as resins, waxes, fats, etc., extractable with an alcohol-benzene-chloroform mixture. Only small amounts of gold were bonded to humic and fulvic acids according to the data presented.

7. As a minor constituent of the clay fraction. The precise mode of binding of the gold in this fraction is uncertain. Small amounts are liberated by aqua regia and cyanide leaches indicating that some of the gold is present in an adsorbed state. The remainder of the gold appears to be tightly bound in the clay complex or clay-humate complexes. Roslyakov *et al.* (1971*a*) have noted that gold is relatively immobile where kaolin-type weathering predominates; on the other hand the metal is highly mobile in regions of lateritic weathering.

In addition to the above mechanisms, one can postulate that there is probably a minor amount of gold in the soil solutions of all soils. Roslyakov *et al.* (1971) found mobile gold in the form of ionic complexes – $[AuCl_2]^-$, $[Au(OH)_2]^-$ and $[Au(OH)_4]^-$ – in the pore solutions of soils and weathered debris in the vicinity of gold deposits. There are probably also small amounts of gold in bacteria and other organisms in the soil. These occurrences would seem to complete the possible modes of binding of gold in most soils.

Our investigations indicate that the mobility and fixation of gold in soils is influenced by the following factors:

1. Topography: in the mountainous parts of the Yukon and British Columbia, the soils tend to be consistently disturbed by solifluction and downhill migration. This results in poor profile development and mixing of material from different horizons. Both these features make systematic work difficult with respect to the migration and concentration tendencies of gold and other elements within the soil horizons. It is necessary to carry out the work on a local basis, and I have found that broad generalizations do not apply. On the other hand in the Canadian Shield and eastern Canada, where elevations are subdued and where profile development is fair to good, certain generalizations on the geochemistry of gold in the soils are permissible.

2. Climate: my investigations were too restricted to draw adequate conclusions about the effect that climate may have on the chemistry of gold in the soil. In the far northern regions where permafrost prevails, the soils are greatly disturbed by frost-boiling, solifluction, etc. This tends to disrupt the profiles and brings particles of unweathered material to the surface. This is a favourable feature for geochemical prospecting, since particles of gold and gold-bearing secondary oxidation products occur near the surface in the vicinity of deposits, a circumstance that permits relatively shallow sampling. In the more temperate regions where podzols and other types of soils predominate, normal chemical conditions prevail, and the chemistry of gold in the soils can be traced with more assurance. Under conditions of tropical weathering gold appears to be relatively mobile in lateritic terranes according to the recent investigations of Roslyakov *et al.* (1971*a*). This feature has been noted by others earlier (*see* the next section on gold in natural waters). Despite the asserted high mobility of gold under tropical weathering conditions much of the metal remains behind in the weathered mantle as can be seen by perusing Table 20. (*See also* the section on placers in Chapter III and the pertinent discussion in Chapter IV.)

3. Parent materials: no major differences have been noted in the gold content of soils developed from different rock types in Yukon. In the Canadian Shield and in eastern Canada, where the soils are developed on glacial tills or mixtures of tills and residual soils, I have noted no radical variations in the gold content of the normal soils. There may be slight enrichments of gold (up to 0.01 ppm or more) in residual soils and weathered residuum developed on pyritic graphitic schists, phyllites, quartzites, etc. containing an abundance of quartz blows and boudins. Evidently, the gold derives from the quartz bodies and oxidized pyrite. Some tills record slightly higher than average contents of gold (0.005–0.010 ppm) for reasons that are obscure.

In all of my investigations I have found that the presence of auriferous deposits normally influences the gold content of the soils. In Yukon, Canadian Shield areas, New Brunswick and Nova Scotia the gold content of shallow soils is generally increased over or near these deposits. Where deep glacial deposits overlie gold-bearing veins, as in some parts of the Yukon, Canadian Shield and eastern Canada, this generalization does not hold. In such situations, however, the basal members of the glacial materials normally report high contents of gold near auriferous deposits.

4. Drainage conditions: well-drained soils tend to have lower contents of gold (and silver) compared with poorly-drained soils in the same area. This is probably due to the fact that all gold (and silver) compounds are highly soluble and are gradually removed in time from the various soil horizons.

5. Presence of complexing agents: the free ions, $Au^+$ and $Au^{3+}$, are unknown in aqueous media. Both are highly complexed or hydroloysed, and the mobility of gold is hence largely dependent on suitable available complexing agents. Complexing agents such as $(S_2O_3)^{2-}$ or $(CN)^-$ or an excess of $Cl^-$ give soluble complexes of the type $[Au(S_2O_3)]^-$, $[Au(CN)_2]^-$ and $[AuCl_2]^-$ which render gold highly mobile. Some organic (humic) complexes evidently have the same facility. Anions, cations and complexes which inhibit the mobility of gold are numerous. Cations and anions such as $OH^-$, $Fe^{3+}$, $Mn^{2+}$, etc. precipate insoluble compounds that coprecipitate or adsorb soluble gold thus decreasing the mobility of the element. The presence of $H^+$ in solution causes the dissociation of many gold complexes stable only in alkaline environments; $OH^-$ has the same effect on the acid complexes. The presence of $H_2S$ or $S^{2-}$, due to the bacterial reduction of protein complexes in organic environments, may precipitate the sulphide or the free metal, thus greatly reducing the mobility of gold.

6. Eh of soils: soluble forms of gold are easily reduced, generally to the metal, by practically all substances as shown in the next section on natural waters. The migration of gold in soluble forms in soils is, therefore, temporal and generally not extensive. Complexing, however, may increase the mobility of the element in some environments. Indirectly, the Eh is also of major importance in the migration of gold in soils since it

plays a part in the hydrolysis of iron and manganese, the precipitation of hydrous iron and manganese oxides, the oxidation of organic complexes, etc., and these exert a major influence on the mobility of gold as described below.

7. pH of soils: the pH of soils affects the mobility of gold in many ways, some of them directly and some indirectly. These are discussed below. Normally, gold is more soluble under acidic conditions such as where pyrite, pyrrhotite, and other sulphides are undergoing oxidation. However, in alkaline environments where suitable complexing agents are present gold is highly mobile.

The chloride complex $[AuCl_4]^-$ and other acid complexes are stable only under acidic conditions. On neutralization these complexes dissociate and the oxide, hydroxide or metal are precipitated. Similarly the alkaline complexes of gold viz. $[Au(CN)_2]^-$ and $[Au(S_2O_3)]^-$ are stable only under alkaline conditions, the oxide, hydroxide or metal being precipitated on neutralization. Changes in pH are, therefore, important, in the mobility of gold in soluble complex forms in soils. However, the chemistry of gold in soils is rarely dependent alone on the effect of pH on gold ions and complexes since the presence of iron, manganese, alumina and organic matter modify the course of events in a number of ways.

In an environment where decreasing acidity and a relatively high Eh prevail, iron if present in the ferrous state, is oxidized to the ferric state, undergoes hydrolysis and may be precipitated as a basic salt or as the oxide hydrate, $FeO(OH){\cdot}nH_2O$. In some profiles where the pH ranges from 3 to 5, jarosite, $KFe_3(SO_4)_2(OH)_6$, and beudantite, $PbFe_3(AsO_4)(SO_4)(OH)_6$, two complex basic sulphates of ferric iron, may be present, and these tend to scavenge much gold, rendering the element immobile. In other profiles it is evident that much of the gold is tied up in the hydrous iron oxides. Normally ferric oxide hydrate is a good carrier of gold, since its colloid bears a positive charge, which tends to coprecipitate the negative gold complexes and the negatively charged gold colloids. Where $PO_4^{3-}$, $AsO_4^{3-}$, hydrated $MnO_2$, silica, humic colloids, etc. are present these are attracted to the ferric oxide hydrate and may give the combined colloidal complex a negative charge, a feature which permits the adsorption or coprecipitation of cationic gold as well as numerous other cations.

Decreasing acidity, likewise, causes the precipitation of hydrated manganese oxides and since these carry a negative charge they adsorb and coprecipitate any available hydrous iron oxides, alumina, etc., which impart a net positive charge to the gels. These in turn adsorb and coprecipitate the negatively charged gold complexes and hydrosols. Clay minerals have a similar effect. (*See also* the discussion on adsorption and coprecipitation of gold complexes and colloids in the section on gold in natural waters and their precipitates.)

These features serve to emphasize the fact that gold is relatively immobile in soils where the pH lies between 4 and 8. The mobility of the element is restricted in part by the dissociation of alkaline gold complexes in an acid medium, the dissociation of acidic gold complexes in an alkaline medium, but mainly by the hydrolytic and colloidal reactions that characterize the chemistry of iron, manganese and alumina in the soils.

8. Presence of organic compounds: organic matter, particularly the humic substances, adsorb gold strongly and apparently build the element into their structures, perhaps forming chelated complexes with the metal. Whatever the mode of binding, it is evident that much gold is immobilized where abundant organic matter is present in the soil. This is shown by the marked enrichments of gold in the $A_0$ (humic) horizons of many soils, and its presence in relatively increased amounts in some peat and half bog soils and in decomposed organic debris in marshes. Soils containing charcoal layers (from ancient forest and peat fires) may exhibit marked enrichments of gold (and silver) in these layers.

The pH seems to have little effect on the mobility of gold in the organic horizons of soils or in peats, etc. The pH may be as low as 3.0 with no particular decrease in the content of gold in the humic components.

Another point of interest is the fact that as the humification processes proceed the large co-ordinated humic groups dissociate and pass into a soluble (colloidal) form in the soil solutions and are ultimately removed by the ground waters. As the soluble groups appear to retain much of their gold during the disintegration process, the mobility of gold is increased in the soils. (*See also* the section on gold in natural waters in this chapter.)

Finally, under a high oxidation potential the humic complexes may be oxidized yielding $CO_2$, $H_2O$, etc. and liberating any bound gold. This gold is then in an extremely mobile state, although in most cases it is generally seized quickly by the remaining humic complexes. This process repeated *ad infinitum* leads to the enrichment of gold (and silver) noted in some of the organic layers of soils, in peats, etc.

9. $Fe^{2+}$ — $Fe^{3+}$ content of soil solutions: the acid reactions[20,21]

$$Fe^{2+} + Au^+ \leftrightarrows Au + Fe^{3+}$$
$$3Fe^{2+} + Au^{3+} \leftrightarrows Au + 3Fe^{3+}$$

are reversible, the direction depending on the $Fe^{2+}/Fe^{3+}$ ratio in solution. Where a high $Fe^{2+}$ concentration prevails, gold is precipitated, and the mobility of the element is reduced. Where a high $Fe^{3+}$ concentration is present gold is retained in the soluble and hence mobile state. It should be particularly noted that the reactions apply only to iron in solution; once hydrated oxides of hydroxides are precipitated these no longer play a part in the oxidation-reduction reactions. Soluble manganous salts probably also play a role similar to those of ferrous salts in slightly acid, neutral, and mildly alkaline soils.

$$2Au^+ + Mn^{2+} + 4H^+ + 2O_2 \leftrightarrows 2Au + MnO_2 + 2H_2O$$
$$2Au^{3+} + 6H_2O + 3Mn^{2+} \rightleftarrows 2Au + 3MnO_2 + 12H^+$$

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[20] These reactions are some of the most important as regards the geochemistry of gold (and silver) in near surface processes. The first has been discussed in detail by Tananaeff (1925) as regards silver.

[21] The oxidation-reduction couples for ferrous, manganous, aurous and auric ions and their potentials as given by Latimer (1952) are as follows:

$Fe^{2+} = Fe^{3+} + e^-$ $\quad E^0 = -0.771$
$2H_2O = O_2 + 4H^+ + 4e^-$ $\quad E^0 = -1.229$
$Mn^{2+} + 2H_2O = MnO_2 + 4H^+ + 2e^-$ $\quad E^0 = -1.23$
$Au = Au^{3+} + 3e^-$ $\quad E^0 = -1.50$
$Au = Au^+ + e^-$ $\quad E^0 = -1.68$

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Note: Both ferrous and manganous ion can reduce gold from its ionic state to the metal.

10. Formation of colloids: practically nothing is known about natural gold colloids in soils. Gold colloids carrying a negative charge are easily prepared in the laboratory, and if these occur in nature they would be expected to increase the mobility of the element in soils. Because the gold hydrosols carry a negative charge the precipitation of these colloids would take place readily where positively charged colloids and electrolytes are present in the soil solutions. *(See also* the discussion on colloids in the section on natural waters.)

11. Influence of organisms: there are no direct data on the part that organisms such as bacteria and fungi play in the mobility of gold in the soil. Indirectly, one can assume with some confidence that the effects are important in two ways—some bacteria and fungi solubilize and hence mobilize gold, whereas others precipitate the element. Williams (1918) noted that *Penicillium glaucum* and *Oidium lactis* develop in colloidal gold solutions containing tannin and that they remove the metal from solution, but no explanation of the process could be suggested at that time. Parès and Martinet (1964) noted that *Bacillus subtilis, Serratia marcescens* and *Pseudomonas fluorescens* were capable of solubilizing gold to a marked degree, the effect diminishing and precipitation increasing with the age of the cultures. Lyalikova and Mokeicheva (1969) have also found that many heterotrophic bacteria have the ability to dissolve gold, and that sulphur compounds (thiosulphates and polythionates) which accumulate during the oxidation of sulphides by sulphur bacteria contribute to the solution of gold. A culture isolated from a gold deposit, similar to *Bacillus alvei,* was found to dissolve 500 to 600 ppb Au in 3 weeks. In an extended study on the solubilization of gold by micro-organisms, Doxtader (*in* Lakin *et al.,* 1974) found that the microbial strains utilized showed various abilities to solubilize the noble metal. *(See also* the section on gold in plants and animals.)

Bacteria and other micro-organisms also break down and decompose the various organic complexes and hence would liberate any complexed gold in a reactive and relatively soluble form. The production of $H_2S$ by bacteria on the other hand would reduce the solubility of gold as mentioned above.

Finally, burrowing animals such as gophers, groundhogs and ants may physically transport gold particles from depth to the surface profiles of soils. An interesting case of the action of termites in Kalahari sand, Rhodesia is described by Watson (1972). The termites in excavating galleries to the water table have evidently brought some particles of gold to the surface from gold-bearing fissures and deposited them in their mounds. *(See also* the section on biogeochemical methods in geochemical prospecting in Chapter V.)

The above reminds one of the wonderful tale of the gold digging ants that has been passed from antiquity down through the generations to modern times. Herodotus had one version, Strabo another, Pliny yet another. In his *Historia naturalis* (Book II, Chapter 31) Pliny records:

> "In the countrey of the Northerne Indians, named Dardae, the Ants do cast up gold above ground from out of the holes and mines within the earth: these are in colour like to cats, and as big as the wolves of Aegypt. This gold beforesaid, which they worke up in the winter time, the Indians do steale from them in the extreme heate of Summer, waiting their opportunitie when the Pismires (ants) lie close within their caves under the ground, from the parching sun. Yet not without great danger: for if they happen to wind them and catch their sent, out they go, and follow after them in great hast, and with such fury they fly upon them, that oftentimes they teare them in pieces; let them make away as fast as they can upon their most swift camels, yet they are not able to save them. So fleet of pace, so fierce of courage are they, to recover gold that they love so well."

As can be imagined various interpretations have been placed on this quaint tale which we cannot pursue here. Evidently the site of these gold-digging ants was the Gobi Desert, but there have been various other theories (Adams, 1938).

### *Other products of weathering*

There are few data on the occurrence and content of gold (and silver) in weathered products such as bauxites, laterites, bog-iron ores, bog manganese deposits, etc.

Some laterites tend to be enriched in gold especially in the vicinity of underlying gold deposits. Some values for these laterites are shown in Table 20. Normally laterites contain only small amounts of gold, generally less than 0.01 ppm. There appear to be only limited investigations of the gold content of typical bauxites.

Tenyakov *et al.* (1970) determined the gold content of bauxites from various localities in U.S.S.R. and Hungary. They concluded from their results that:

1. Gold appears to be always present in bauxite since the element was detected in all samples analyzed from all deposits.
2. The gold concentration in bauxite exhibits an extremely wide range from 0.0004 ppm to 0.0290 ppm, a variation of two orders of magnitude. The average (arithmetic mean) gold content of bauxite is 0.0045 ppm.
3. There is some difference in the average content of gold in geosynclinal bauxite and platform bauxite; the latter is somewhat richer in gold (0.0049 ppm compared with 0.0036 ppm).
4. The gold content of bauxites is clearly related to their parent rock type; the metal is generally enriched in bauxite presumably formed from igneous or eruptive rocks but is much lower in that formed from clay and shale.

Tenyakov *et al.* (1970) thought that the gold in bauxites is probably mainly present in a mechanical form (as native gold).

The gold content of bog iron and manganese deposits is not well known. My analyses of most of the bog iron and maganese deposits of Ontario and Quebec show that such deposits contain only low amounts of gold (<0.005 ppm). A bog iron-manganese deposit in Canoe Lake, New Brunswick was found to contain 0.015 ppm Au and 2.2 ppm Ag; another in Bass Brook, near Walton, Nova Scotia had 0.34 ppm Au and 0.68 ppm Ag; and a third near Long Lake, New Brunswick had up to 1.4 ppm Au and 0.8 ppm Ag. The last bog is near stringers of quartz that carry a little gold.

During the weathering of gold- and silver-bearing rocks and deposits the two metals tend to concentrate in particles of native gold in the weathered detritus. Such auriferous blankets or eluvial deposits are common in Brazil, the Guianas, Mexico, Africa, Asia and elsewhere. They are composed principally of laterite—a mixture of ferric oxides, hydrated ferric oxides, clay and sand. Some contain essentially gravel, sand and clay and may be partly cemented by caliche and iron oxides. The origin of the gold-silver particles in these materials has been a long-standing problem. It is certain that some of the particles are of residual origin and represent the flakes and nuggets weathered from gold-quartz veins. Some of the gold and silver is probably also of chemical origin; that is, the particles are either enlarged or individually accreted by additions of gold and silver from solutions that derived the metals both from the weathered constituents of the rocks and from various gold- and silver-bearing sulphides in veins and other types of deposits.

As the weathering cycle proceeds the material in deposits may be further decomposed, eroded, transported and redeposited. This can be effected by wind, streams, rivers or by the surf of the sea, resulting in aeolian, stream, river, delta and beach placers. During these movements the gold-silver particles may be comminuted and reduced to a flour or, as is more often the case, especially in an aqueous environment, the small particles may be recrystallized, partly dissolved and the gold reprecipitated on the larger particles. Since silver is more mobile (more soluble) than gold the chemical processes of solution and reprecipitation generally lead to an increase in the fineness of the gold flakes and nuggets with increasing distance from the source. Furthermore, the outside parts of nuggets often have a significantly greater fineness than the inner parts, a feature that adds convincing support to the theory of accretion of gold from solutions as the particles are moved along by mechanical processes. Other evidence of the solution and precipitation of gold and silver in placers is witnessed by the occurrence of gold crystals in places, wire gold, sprigs of gold, replacement of deer horns by film gold, agatelike structures of certain nuggets and the fact that some investigators have found increased amounts of gold and silver in stream waters in the vicinity of gold veins and polymetallic deposits. (*See* the section on gold in natural waters.) Further details on the interesting problems of the geochemistry of the origin of gold in oxidized zones and placers is given in Chapters III and IV.

The most frequent associates of gold-silver particles in placers, in addition to the common silicates, are magnetite, ilmenite, rutile, monazite, garnet, zircon, tourmaline, pyrite, native bismuth, cassiterite and cinnabar. Nuggets of native silver are rare, although they do occur in some of the placers in Alaska and in those of Burwash and Arch creeks (Kluane and Donjek rivers district), Yukon. Arquerite, the silver-gold-mercury amalgam, occurs in the placers of Silver, Vital, Kenny and Kwanika creeks in the Fort St. James area, British Columbia and in Burwash Creek in the Kluane Lake district, Yukon.

Certain types of eluvial and alluvial fans and similar deposits, in addition to gold and silver, also contain galena, anglesite, bindheimite, mimetite and other oxidation products of lead-zinc-silver and gold veins. Such deposits are known in many parts of the world, particularly in the unglaciated regions. Those associated with a mineralized porphyritic granite stock near Guadalcázar in Mexico have received detailed attention (Foshag and Fries, 1942; Fries and Schmitter, 1948). Few of these deposits contain in excess of 0.10 ppm Au. In general the average gold content is about 0.025 ppm. Other types associated with sink-holes in limestone are known in Burma and China (Rundall, 1927–1928; Searls, 1952) and have been worked in the past. Somewhat similar deposits developed in karsts are mined in the Yakutia region of the U.S.S.R. There the deep oxidation of auriferous metasomatic rocks developed in limestones has led to concentrations of gold in karsts in the limestones. These deposits are called 'Kuranakh type' by the U.S.S.R. geologists; they are described in more detail in Chapter III.

Undoubted fossil gold-silver placers have been described from several countries. They occur in conglomerates, sandstones, and arkoses of various ages. Examples are known in the Black Hills, South Dakota; Gays River, Nova Scotia; Indian River, Yukon (Maclean, 1914); and elsewhere. (*See also* the section on placers in Chapter III.) The auriferous Witwatersrand quartz-pebble conglomerates, the greatest of all gold deposits, are considered to be modified fossil placers. These deposits, and others in the same category, are discussed at length in Chapter III.

> Mountains big with mines, whence
> many a bursting stream auriferous plays
> —Thomson, *Summer*

## Gold in natural waters and their precipitates

Gold is widely diffused in ground, spring, stream, river and lake waters, but generally only in small amounts. The average for all fresh waters is about 0.00003 ppm (0.03ppb) Au. Marked variations above and below this average have been reported for a number of regions.

Most of the gold in natural fresh waters is derived from gold present in rocks, mineral deposits and their weathered products. Infinitesimally small amounts of gold (and silver) in some fresh waters may arise from industrial and domestic usage.

Several investigations of the gold content of hot spring, ground, stream, river and lake waters have been carried out in a number of countries. Data from these investigations and from my own limited studies are recorded in Table 21.

Only a few detailed investigations of the gold content of hot springs and thermal waters are extant in the literature. Some of the more comprehensive studies are summarized below.

Koga (1960, 1961) carried out an extensive investigation of the gold, silver and numerous other trace elements in 27 hot springs in the Beppu area of Japan. The range in the gold contents was 0.0 to 2.2 ppb, and the average for all hot springs was 0.53 ppb Au and 10.7 ppb Ag, giving an average Au/Ag ratio of 0.05. Ninety per cent of the springs had less than 1 ppb Au. Hot springs with low pH values (2.0–3.8) contained the highest amounts of gold, especially those enriched in sodium sulphate and sodium chloride. The silver content was low in NaCl springs and high in sodium bicarbonate ones. Gold showed no particular relationship to sodium bicarbonate. The temperature of the springs influenced the gold content; in general the higher the temperature the higher the gold content. Most spring precipitates were found to contain gold, the highest value being 56.5 ppb (0.056 ppm). No

Table 21. Gold content of natural waters

| Description | No. of samples | Au (range) (ppb) | pH (range) | Remarks |
|---|---|---|---|---|
| Hot springs | 35 | 0.004–2.2 | <1–14 | 65% of the values lie in the range 0.04–0.7 ppb |
| Groundwaters and cold springs | 8 | <0.005–0.2 | 6.3–7.3 | $H_2S$ carbonate springs at Matzesta (Sochi) U.S.S.R. are enriched in gold; up to 35 ppb according to Zverev *et al.*, (1947) |
| Groundwaters, cold spring waters and mine waters in vicinity of gold deposits | 84 | <0.0008–80 | 2–8 | 84% of the values lie in the range 0.001–1.0 ppb |
| Stream and river waters | 24 | 0.002–4.7 | 6.5–7.7 | 73% of the values lie in the range 0.002–0.1 ppb |
| Stream and river waters in vicinity of gold deposits | 24 | 0.0048–35 | 6.5–7.6 | 91% of the values lie in the range 0.0048–0.150 |
| Lake waters | | | | |
| Fresh | 21 | 0.12–7.7 | | Lake Baikal (Jones, 1970) and Greek lakes (Grimanis *et al.*, 1965) |
| Saline | 4 | <0.1–32 | | Great Salt Lake, Utah and Owens Lake, California |
| Oceans and seas | 73 | 0.001–46 | | 71% of the values lie within the range 0.001–0.50 ppb |

Compiled from data by: Albul and Miller (1959)
Baur (1942)
Borovitskii *et al.* (1966)
Brooks (1960)
Browne (1969)
Chernyayev *et al.* (1969)
Cushing and Rancitelli (1972)
Fischer (1966)
Gebler and Stramkovskaya (1957)
Goldberg (1957)
Goleva (1970)
Goleva *et al.* (1970*a,b*)
Gosling *et al.* (1971)
Gottfried *et al.* (1972)
Grange (1937)
Grimanis *et al.* (1965)
Haber (1927, 1928)
Hummel (1957)
Ikeda (1955*a,b*)
Jenne *et al.* (1968)
Jones (1970)
Kaspar *et al.* (1972)
Koga (1960, 1961)
Kropachev (1935)
Lincoln (1911*b*)
Lombardi (1964)
Noddack and Noddack (1939)
Oka *et al.* (1964)
Popova (1971)
Putnam (1953)
Razin and Rozhkov (1963)
Rosenbaum *et al.* (1969)
Schiller *et al.* (1971*a,b*)
Sharma (1972)
Stark (1943)
Talipov *et al.* (1972)
Vorotnikov *et al.* (1973)
Weiss and Lai (1963)
Weissberg (1969, 1970)
White *et al.* (1963*a,b*)
Yasuda (1927)
Zverev *et al.* (1947)
Zvyagintsev (1941)

detailed correlation between gold and silver was found in the spring water, but there was a positive correlation between the two elements in the spring precipitates. The average Au/Ag ratio in the spring precipitates was about 0.05, much the same as the average ratio for the water. Positive correlations of gold with chromium and manganese and a negative correlation with titanium were found in the spring waters, and a positive correlation with silver and arsenic and a negative correlation with manganese obtained in the spring precipitates. The positive correlation of gold with chromium is of interest considering the common occurrence of chromium-rich alteration minerals (fuchsite) in certain types of gold deposits.

Weissberg (1969, 1970) described red-orange amorphous sulphides with opaline silica, precipitating from thermal waters along the eastern margin of the Taupo volcanic belt in New Zealand; these contained a number of ore elements up to the following concentrations:

| | | | |
|---|---|---|---|
| As | 2% | Tl | 1000 ppm |
| Sb | 10% | Pb | 50 ppm |
| Au | 85 ppm | Zn | 200 ppm |
| Ag | 500 ppm | W | 3% |
| Hg | 2000 ppm | Au/Ag ratio 0.17 | |

The transporting waters carry these elements in the following maximum values:

| | | | |
|---|---|---|---|
| As | 8 ppm | Tl | 0.007 ppm (7 ppb) |
| Sb | 0.3 ppm | S (as sulphide) | 120 ppm |
| Au | 0.00004 ppm (0.04 ppb) | Au/Ag ratio 0.06 | |
| Ag | 0.0006 ppm (0.6 ppb) | | |

These thermal waters are essentially alkaline (pH 6–7) Na-K-Cl-$HCO_3$-$CO_3$-$SO_4$-$SiO_2$ waters, with temperatures ranging from 200 to 290°C at a depth of 1 km.

Browne (1969) records 0.0001 to 0.001 ppm Au and 0.002 Ag in water separated at atmospheric pressure from the Broadlands geothermal drillhole, Taupo Volcanic Zone, New Zealand. The pH of the water was 8.55 and the type – Na-K-Cl-$HCO_3$-$CO_3$ – carrying small amounts of As (9 ppm), Sb (1.5 ppm), W (0.03 ppm), Zn (0.015 ppm), Cu (0.012 ppm), Tl (0.01 ppm) and a number of other elements. This water has deposited base metal sulphides (pyrite, galena and sphalerite with silver telluride, cobaltite and Ni-glaucodot) in tuffs, tuffaceous sediments and rhyolites, which it penetrates.

Goleva *et al.* (1970*a,b*) found 0.8 to 1.6 ppb Au in strongly acid (pH <1, Eh >0.8 V) HCl fumaroles of the Ebeko volcano on Paranushir Island, Kamchatka, U.S.S.R. They concluded that the gold was present mainly as halide complexes.

Gottfried *et al.* (1972) report that the gold content of the thermal waters in Yellowstone National Park, U.S.A. is very low, generally 0.004–0.040 ppb, with a maximum of 0.1 ppb. The sinters on the other hand, are relatively enriched in gold, 5 to 50 ppb with maximum values up to 5000 ppb. Sinters having high gold concentrations also contain correspondingly higher amounts of arsenic, antimony and mercury. The pH of the waters ranges from 2 to 9, but most have a neutral to slightly alkaline reaction.

Summarizing the available data on hot springs one can say that the pH of the water seems to have little effect on the transfer of gold. All springs, including those with acid, neutral and alkaline reactions may carry the element, although there is a tendency for it to be enriched in neutral and alkaline waters. Temperature evidently has an effect, the hotter the water the higher the gold content in some spring systems. Correlations with other elements are difficult to establish with certainty mainly because of insufficient data. Gold is generally accompanied by silver, and in nearly all auriferous springs there is a relatively high content of As, Sb and $SiO_2$. Nearly all hot springs carry sufficient Cl, $S^{2-}$, As and Sb to complex and render mobile the small amounts of gold present.

There are insufficient data on the gold content of normal groundwaters and cold springs to draw satisfactory conclusions about the transport of the element in these waters. From my experience I conclude that the average gold content of most normal groundwaters and cold springs is about 0.005 ppb. My compilation of the gold content of normal stream and river waters shows that the values range from 0.002 to 4.7 ppb with some 73 per cent of the values in the range from 0.002 to 0.1 ppb. In my experience most streams and river waters have $<0.005$ ppb total gold including that dissolved and associated with particulate matter. In a recent study Cushing and Rancitelli (1972) found that the gold and silver contents of the Columbia River water, as determined by neutron activation analyses, varied from time to time as shown below.

|  | Date |  |  |  |  |
|---|---|---|---|---|---|
| Element | 11-4-68 | 2-12-69 | 4-24-69 | 6-11-69 | 8-14-69 |
|  |  |  | (ppb) |  |  |
| Au | 0.030 | <0.005 | <0.005 | <0.005 | <0.005 |
| Ag | 0.50 | <0.01 | <0.01 | 3.03 | <0.01 |

There are insufficient data on the gold content of freshwater lakes to draw any conclusions. Grimanis *et al.* (1965), using activation analysis methods, reported gold contents in 11 Greek lakes to range from 0.2 to 7.7 ppb (av. 1.5 ppb). The corresponding silver contents were less than 10 ppb.

In salt lakes Lincoln (1911*b*) reported up to 32 ppb Au in Great Salt Lake, Utah; in the Nevada salt marshes the same author reported no gold present. Carpenter (1941) found no gold in the salts and other materials of the dry lakes in Nevada. In the summer brine of Owens Lake, California Lombardi (1964) reports the presence of gold in the 10 to 100 ppb range.

Most of the work on the gold content in cold springs, groundwaters and stream and river waters has been done in the vicinity of gold-bearing deposits. As shown in Table 21, the values tend to be higher than in similar bodies of water remote from gold deposits. A number of detailed investigations are extant in the literature, some of which merit brief reviews.

Kropachev (1935) seems to have been the first to examine the gold content of normal fresh waters as well as those in gold belts. He found from 40 to 60 ppb Au in the rivers of nonauriferous regions and some five times as much gold in the river water of auriferous regions. Still higher quantities of gold were found in the drainage waters of gold mines (500–1300 ppb). While his analytical methods were crude they did show that the waters in auriferous regions are commonly enriched in gold.

Borovitskii *et al.* (1966) examined the gold content in the waters of the Kuranakh gold-bearing area of the Aldan massif, U.S.S.R. The gold ores are mainly oxidized disseminated pyritic ores with pyrite, magnetite, hydrogeothite, hematite and gold. (*See also* Chapter III.) Associated elements are Ag, Cu, Pb, Zn, As, V and Ga. Three types of groundwaters are distinguished in the area – those in unconsolidated recent materials above the permafrost (mainly organic and calcium bicarbonate and sodium bicarbonate waters); those above- and inter-permafrost in the Lower Cambrian rocks (mainly calcium bicarbonate waters); and those below the permafrost in Lower Cambrian and Archean rocks. The results of the investigation showed that: the most common companions of gold in the groundwaters were As, Sb and Tl (and to a lesser extent Ag, Ti, Sn and Te); the inter-permafrost waters contained the highest gold contents; the gold contents in groundwaters near the gold deposits fluctuated from 0.03 to 10.0 ppb; the maximum gold concentrations occur in groundwaters with a high content of dissolved iron (up to 300 ppb) and manganese (up to 100 ppb); and that the gold contents in stream waters near the gold deposits were generally less than 0.05 ppb. An earlier investigation of the waters associated with the Kuranakh deposits by Razin and Rozhkov (1963) indicated that the more acid the waters the higher the gold content. Gold appears to be much more mobile than silver in the area since the ratio Au/Ag in the groundwaters as calculated from the data of Borovitskii *et al.* (1966) is generally high, in some cases up to 450.

Chernyayev *et al.* (1969) reviewed the literature on gold in natural water and carried out work on the natural waters of northern Kazakhstan and southern Urals. In the near-surface groundwaters of the Kokchetav uplift gold was found in 40 per cent of the analyzed samples (altogether 180 samples were analyzed). Its content varied from 0.1 to 4 ppb. The distribution of gold in the groundwaters was lognormal. Its average content in the samples for which positive results were obtained is 0.4 ppb, or if all analyzed samples are considered (including those in which gold was not detected), 0.15 ppb. Little difference was found in the gold content of waters circulating through different rock types (e.g., gabbro, 0.58 ppb; granodiorite, 0.5 ppb; shales and sandstones, 0.522 ppb). In the Shalkarsk area the mode was 0.2 ppb and the mean content (all samples) 0.154 ppb. Analyses of groundwaters from one of the Kokchetav gold deposits showed gold contents ranging from 0.4 to 1 ppb. These waters always contain As, Mo, La, Y, Yb, Li, Cu and a number of other elements. The content of silver in these waters is low. There was no well defined correlation between the content of gold in the waters and any of the trace elements nor between such constituents as carbonate, sulphate, chloride and hydrogen ion (pH). The hydrogeochemical profiles plotted across the gold deposits, however, show that directly over the orebodies there are peak concentrations of Au, Ag, As and Bi. The peaks for Ag and As are sharp; those for Bi are broad.

Goleva *et al.* (1970*a,b*) examined both ground and surface waters in the vicinity of a number of gold deposits in various geological and geographical settings in U.S.S.R., mainly in East Transbaikal, Central Asia, Southern Urals and Kamchatka. The contents they found ranged from 0.05 to 10 ppb Au. From their studies they concluded that:

1. The commoner types of natural water (pH 5–8 and Eh 0.1–0.5 V) most probably contain gold as uncharged particles and organic complexes. Gold in the presence of thiosulphate ions forms the very stable $[Au(S_2O_3)_2]^{3-}$ ion.

2. The halide complexes, $[AuCl_2]^-$, $[AuCl_4]^-$ and $[AuBr_4]^-$, can be formed only in media with Eh $>0.9$ V and pH $<1$ at appropriately elevated concentrations of chloride and bromide ions ($Cl^- \geq 2$ mM, $Br^- > 0.6$ $\mu$M). Such waters are exotic

under natural conditions and occur only in the HCl fumaroles of active volcanoes (Ebeko, etc.).

3. Waters containing $H_2SO_4$ are unfavorable for the migration of gold. Thus, waters in rapidly oxidizing zones of gold-sulphide deposits have only 0.1–0.5 $\mu$g/L.

4. The commonest coprecipitants of gold in natural waters are: iron hydroxides, calcium carbonate, disulphides and colloidal silica.

5. The gold content of groundwaters can be used as a specific means of prospecting for gold-bearing deposits.

In the Balei gold district of eastern Transbaikal, U.S.S.R., Goleva (1970) found background contents of $<0.07$ ppb Au and anomalous contents $>0.15$ ppb in the groundwaters. In alluvial and surface waters the background and anomalous contents were respectively $<0.05$ and $>0.1$ ppb Au. Most of the waters are weakly mineralized calcium, magnesium and sodium bicarbonate types with small amounts of sulphate. The main indicators of gold deposits in the hydrologic system were found to be Au, Ag, As and Zn and in some areas Bi and Sb.

Gosling *et al.* (1971) used neutron activation methods to investigate the gold content of stream, spring and mine water in both gold-bearing and barren areas underlain by sedimentary, igneous and metamorphic rocks of the Colorado Front Range. The total gold content ranged from nondetectible ($<0.001$ ppb) to 0.150 ppb. The 'solute' (dissolved) gold concentrations were generally higher by a factor of 2 to 6 than the gold held on or in particulates, and no relationship was found between both these values (solute and particulate) and rock or water types. Their data indicated a spring flush-out of dissolved gold in groundwater during the snow-melt recharge period. They concluded that direct hydrogeochemical prospecting using gold as an indicator of its deposits is unpromising.

Talipov *et al.* (1972) determined the Au, Ag and As content of the surface waters of the central Kyzylkum gold belt and found the gold content to range from 0.01 to 0.95 ppb; the corresponding arsenic contents were 10 to 378 ppb. The gold content was not related to the chemical composition of the water.

Kasper *et al.* (1972) found from 0.09 to 0.20 ppb in waters flowing from old gold mine tunnels in Austria (Imhoff and Bockhart) and Czechoslovakia (Jilové). They noted a general development of inhomogeneity in the waters after 21 days of storage.

Volkov and Shakhbazova (1973) determined the gold content of the surface and groundwaters of the Beskes auriferous copper ore field. The gold content was found to range from 0.0 to 5.2 ppb. The distribution of gold in the waters obeyed the lognormal law with a mean gold content of 0.09 ppb and a dispersion factor of 0.474. Within these parameters the minimum anomalous content was 0.3 and the maximum 2.5 ppb, the last value being a positive indication of the presence of gold in the ores. No relation was observed between the chemical composition and the distribution of gold in the waters although the highest concentration of the precious metal was noticed in $Ca(HCO_3)_2$ waters.

In the west Siberian artesian basin of U.S.S.R. Shvartsev (1974) found gold in all saline groundwater samples from the petroleum fields in the northern Tomsk region, the contents ranging from 0.02 to 0.49 $\mu$g/L. Shvartsev concluded that all the gold in the saline groundwaters was of lithological origin.

The available data on the gold content of ocean water is given in Table 21. The average gold content of the oceans appears to be about 0.0117 ppb and the average silver content about 0.3 ppb giving an Au/Ag ratio of 0.04.

The French chemist, J.L. Proust (1754–1826) was the first to report the presence of gold in seawater, and the English chemist S. Sonstadt (1872) carried out the first quantitative analysis finding less than a grain of gold per ton (about 65 ppb). Many years later Fritz Haber carried out over a period of some 7 years an extensive investigation of the gold content of seawater. Reviews of these and other investigations are given by Mellor (1923), Jaenicke (1935), Gmelin (1950), Purkayastha and Das (1965), Jones (1970) and Wood (1971).

The gold content of the oceans appears to be variable as will be readily apparent from the following short review of some of the significant investigations. This variation appears to be real, although some variations reported in the literature may be due to different methods of analysis.

Haber (1927, 1928) found that seawater did not contain nearly as high contents of gold as had been earlier reported. His values ranged from 0.003 to 4.8 ppb. He noted large variations in the sea both on an areal and local basis and attributed them to a variety of causes mainly to the presence of gold in various forms – as the chloroauric ion, in colloidal form and adsorbed by both organic and inorganic matter.

Yasuda (1927) found relatively large amounts of gold (3–20 ppb) in the water of bays in various parts of Japan. The equivalent silver content was 20 to 70 ppb.

Putnam (1953) gives an interesting account of the investigation of gold in seawater from Sonstadt and Haber up to the 1950's. He, himself, carried out a number of investigations of the gold content of seawater and concluded from these and analyses in the literature that the concentrations could vary through the range of 0.003 to 44 ppb Au.

Hummel (1957) found by radioactivation analysis that the gold content of the oceans depended on the distance from the shore. He recorded 0.40 ppb Au for English coastal waters and 0.015 ppb Au for water from the northwestern limit of the Bay of Biscay.

Brooks (1960) using an ion exchange enrichment technique obtained 0.009 ppb Au in seawater at Sea Point, Cape Town, South Africa. Weiss and Lai (1963) used cocrystallization methods to determine the gold content of seawater 40 mi due west of San Francisco. Their average was $0.068 \pm 0.003$ ppb. Oka *et al.* (1964) found from 0.006 to 0.429 ppb Au in surface ocean samples and samples taken at a depth of 100 to 200 m off the Japanese coast. Schutz and Turekian (1965) found the gold content of seawater from the Atlantic and Indian oceans to range from 0.004 to 0.027 ppb with an average of 0.011 ppb. The silver content in all oceans ranged from 0.055 to 1.5 ppb and the average was 0.29 ppb. The average Au/Ag ratio in the sea as calculated from their data is, therefore, 0.04.

Wood (1971) carried out an extensive investigation of the geochemistry of gold in the marine environment to determine possible natural concentrating processes which may be used to extract gold. Radioactive gold tracers $^{195}$Au and $^{198}$Au were used in the investigations. The solubility of gold in seawater was determined to be of the order of 4μg Au/L (4 ppb) about the same order of magnitude as previously predicted by Sillén.

Differences in the ion change properties of Au (I) and Au (III) were determined by experiments with electrolytically produced mixed solutions of aurous and auric chloride which were passed through strong anion exchange columns. Approximately 10 per cent of the soluble gold in equilibrated seawater solutions was found to be nonionic. The soluble character of the gold in these solutions was unchanged when mixed with sulphide waters. This indicated to Wood (1971) that gold would not be concentrated in anoxic basins. The character of the soluble gold was also studied using dialysis and electrophoresis.

Soluble gold was rapidly adsorbed on several clays followed by a release of gold within about 24 h of the mixing time. This is about the time for the equilibrium shift of auric to aurous gold to be established.

$$AuCl_4^- + 2\,Au + 2\,Cl^- \rightleftharpoons 3\,AuCl_2^- \quad K_{eq} = 1.8 \times 10^{-8}$$

Gold was found to be easily reduced and to be adsorbed on many different materials. Most materials used in sampling and analysis for gold in aqueous media adsorbed gold least from acidified solutions. Rubber and cellulose ester fiber filters were notable exceptions.

Neutron activation methods were devised by Wood (1971) to analyze marine samples for gold. Analyses of samples from southeast Alaska indicated that gold in seawater is predominantly in a soluble nonionic form, with ionic and particulate forms making up only about 20 per cent of the total. The average gold content in these waters was found to be 3 ng Au/L (0.003 ppb) with a range of 1 to 11 ng Au/L. Analyses of sediment in Gold Creek and Gastineau Channel at Juneau, Alaska indicate that the transport of gold is mainly by physical means with the majority of the gold appearing in the $4\phi$ size range in and near Gold Creek.

Cationic forms of gold were found by Wood (1971) to be absent in seawater, and gold was not associated to any great extent with dissolved organic matter which is extractable in either chloroform or ethyl acetate.

The gold concentrations in samples from the east Pacific found by Wood (1971) showed a heterogeneous distribution. The average concentration was 0.004 ppb with a range of 0.001 to 0.025 ppb Au.

Wood (1971) estimates that approximately 10 per cent of the gold in seawater is ionic, probably Au(I)chlorohydroxy anions, e.g., $[AuClOH]^-$. Another 10 per cent is associated with particulate matter, and the remaining 80 per cent is less than 0.45 μ, nonionic, not extractable in ethyl acetate nor chloroform and probably colloidal.

Ryabinin *et al.* (1974) determined the gold content in 89 water samples collected with bathometers from different levels of the Atlantic Ocean tropical zone at some 19 sites. The concentrations ranged from 0.004 to 3.4 ppb. The average concentration for all samples was 0.202 ppb, a value considerably higher than that found by other investigators for ocean water. The distributions were very irregular, and no particular pattern was discernible.

Polyakov (1959) observed that the amount of gold and silver in foam and slime of Kara-Bogas-Gol Bay (Caspian Sea) U.S.S.R. was considerably greater than that in the seawater. Dudey *et al.* (1969) found $7.3 \times 10^{-7}$ μg/m$^3$ Au in marine aerosols over the Atlantic Ocean.

The investigations of the gold content in ocean water indicate that there are major areal variations. The data are not extensive enough to draw any conclusions about the variations with depth. Most studies seem to indicate that nearshore samples are higher in gold than those in the open oceans, a feature that is probably due to the greater amount of inorganic and organic particulate matter, and hence more adsorbed and particulate gold, in nearshore waters compared with those at a great distance from the shore. Major local variations in the gold content of seawater are probably due to the presence of variable amounts of particulate matter. Future research on the gold content of the oceans should be directed to determining precisely the quantity of 'solute', adsorbed, and particulate gold in the samples.

The source of the gold in ocean water is speculative and problematical. Presumably most of the precious metal is the result of terrestrial weathering, and there may be a small contribution from the weathering of marine sediments. Along the ridges and rises of the oceans some of the gold in oceanic water may be of volcanic exhalative origin.

The oceans are an enormous reservoir of gold (and silver). A calculation using the average gold content of seawater (0.02 ppb) and the total mass of the oceans ($143 \times 10^{16}$ metric tons) indicates some $28.6 \times 10^6$ metric tons of the metal in the oceanic system. Other estimates in the literature of the total gold content of the oceans range from $5 \times 10^6$ to $6 \times 10^{10}$ metric tons. The presence of so much gold in the oceans has whetted the scientific interest of many men, especially as regards commercial recovery of the metal. Fritz Haber (1927, 1928), as mentioned previously, had this in mind and spent some 7 years dealing with the problem, finally abandoning any hope during his lifetime of developing a feasible commercial recovery process. Others have taken up the problem with the hope of alleviating the economic ills of their nations (Purkayastha and Das, 1965). Perhaps in the future a highly specific resin for gold such as that described by Koster and Schmuckler (1967) will form the basis for commercially extracting the metal from the vast reservoir of the oceans. Lancaster (1973), however, considers that the extraction of gold from seawater by any known method is an unrealisable dream.

Many of the natural precipitates from hot springs, cold springs and groundwaters contain small amounts of gold (and silver) as shown in Table 22. Some precipitates are greatly enriched in the element, especially those near gold deposits. Others, such as those probably from submarine hot springs as in the Red Sea, contain up to 5.6 ppm Au (Table 14).

Manganese oxides (wad) frequently concentrate gold and certain varieties of limonite, especially if they are admixed with or contain manganese oxides, phosphate, arsenate, etc., tend to carry considerable amounts of the element. Organic compounds (humic complexes) also seem to be major concentrators of gold in some areas. Sulphate efflorescences and stalactites in the drifts and workings of gold-silver mines of the Tintic district, Utah and Empire district, Colorado were found by Morris and Lovering (1952) and Lakin (1969*a*) to be

Table 22. Gold content of natural precipitates (dry matter)

| Location | Description of precipitate | Au | Ag | Au/Ag ratio | Reference |
|---|---|---|---|---|---|
| | | (ppm) | | | |
| New Guinea | Wad and other manganese oxides; mangenese content 7.15% | 35.9 | 4801.7 | 0.007 | 1 |
| | Wad and other manganese oxides; manganese content 12.15% | 28.7 | 147.0 | 0.2 | 1 |
| New Guinea | Dark brown to greenish, pin point organic (iron humate) compound along seepages | 27 920 | 15 660 | 1.8 | 1 |
| Guiana (British Guiana) | Precipitated ironstones (limonite) on sides of hills near gold-bearing rocks and deposits | 0–>17 | | | 24 |
| U.S.A.; Tintic Standard Mine, Tintic district, Utah | Various sulphates such as chalcanthite, epsomite, pisanite, etc. Value given is maximum value in chalcanthite. Minerals on shale walls were highest in gold | 2.7 | 1162 | 0.002 | 2 |
| U.S.A.; Southeastern states | Transported limonite | 0.14–2.9 | – | – | 17 |
| U.S.A.; (various areas) | Iron oxides and hydroxides (crusts and stains) | 0.5–1.7 | – | – | 16 |
| U.S.A.; Empire district, Colorado | Supergene sulphates of copper and iron | 11.7 | – | – | 27 |
| U.S.A.; Arkansas | Manganese ore leached from country rock | 0.7 | 23 | 0.03 | 4 |
| U.S.S.R.; Kuznetski-Alatau gold deposits | Ocherous and nodular transported limonite | <10–100 | <10–100 | – | 15 |
| U.S.S.R.; Chatkal-Kurama region | Iron hydroxide precipitates from mine drainage | 0.06 | 20 | 0.003 | 26 |
| Canada; Holman Mine, N.S. | Limonite | 1.1 | – | – | 3 |
| Canada; Keno Hill, Y.T. | Limonite, residual | 0.08 | 500 | 0.0001 | 5 |
| | Limonite and cerussite (transported) | 0.7 | 500 | 0.001 | 5 |
| | Wad and minor limonite (transported) | 0.08 | 50 | 0.002 | 5 |
| | Limonite, scorodite and other oxidation products | 0.5 | 500 | 0.001 | 5 |
| | Scorodite and limonite (residual in part) | 10.26 | – | – | 5 |
| | Anglesite (transported) | 0.5 | >1000 | <0.0005 | 5 |
| | Bindheimite (residual in part) | 0.7 | 500 | 0.001 | 5 |
| | Pyromorphite and cerussite (residual in part) | 0.17 | 500 | 0.0003 | 5 |
| | Various sulphates of iron and zinc | 0.08 | – | – | 5 |
| Canada; Walton, N.S. | Manganese oxides; wad; precipitate from springs | 0.3 | 0.7 | 0.4 | 6 |
| | Iron oxide precipitates (limonite) | <0.08 | 18.5 | <0.004 | 6 |
| Canada; Yellowknife, N.W.T. | Limonite, Lynx area (transported) | 0.17 | | | 7 |
| Canada; Ross Mine, Holtyre, Ont. | Limonite precipitate, 450 ft level | 0.06 | 2.0 | 0.03 | 7 |
| | Hydrous manganese oxide precipitate, 150 ft level | 3.04 | 7.8 | 0.39 | 7 |
| Canada; Annapolis Royal, N.S. | Bog manganese oxides (wad) | <0.01 | 1.4 | <0.007 | 7 |
| Canada; Bathurst area, N.B. | Bog iron and manganese, Canoe L. | 0.01 | 2 | 0.005 | 7 |
| | Transported limonite and other Fe-Mn-Si precipitates associated with massive sulphide deposits | <0.01–0.77 | <0.8–26.6 | <0.05 | 7 |
| Canada; Long Lake area, N.B. | Bog manganese in peat | 1.4 | 0.8 | 1.75 | 7 |
| U.S.A.; Ojo Caliente, N. Mex. | Calcareous tufa (calcite and limonite) | 0.047 | 2.73 | 0.017 | 22 |
| U.S.A.; Anaconda Hot Springs, Mont. | Limonite and travertine | 1.7 | – | – | 8 |
| U.S.A.; Steamboat Springs, Nev. | Sinters, muds, carbonates, sulphides, etc. | 0.2–12 | 39–42 | 0.15 | 11 |
| | Metal-bearing siliceous muds | up to 200 | – | – | 19 |
| | Siliceous sinters | 0.11 | – | – | 19 |
| U.S.A.; Casa-Diablo hot spring area, Mono County, Calif. | Hot spring sinter | trace | up to 17 | – | 12 |
| U.S.A.; Niland, Calif. | Residue from high temperature steam well | 3.7 | 13 030 | 0.0003 | 13 |
| U.S.A.; Yellowstone National Park, Wy. | Siliceous sinters | 0.005–0.05<br>(up to 5.5) | – | | 18, 19 |
| New Zealand; Rotorua | Siliceous sinter | 0.855 | 25.8 | 0.331 | 9 |
| | Sulphurous sinter | 1.99 | 138.1 | 0.014 | 9 |
| New Zealand; Whakarewarewa and other areas | Siliceous sinter deposited mainly from alkaline springs; maximum values | 5.3 | 138 | 0.04 | 10 |

Table 22. (cont'd.)

| Location | Description of precipitate | Au | Ag | Au/Ag ratio | Reference |
|---|---|---|---|---|---|
| | | (ppm) | | | |
| New Zealand; Taupo volcanic zones | Siliceous and sulphide precipitates associated with hot springs | 85 | 500 | 0.17 | 14, 23 |
| New Zealand; Puhipuhi, North Island | Hot spring sinter (opal). Sinter also enriched in Hg. *See* paper by Hoggins and Brooks (1973). | 0.03–1.30 | 1.6–3.0 | 0.02–0.43 | 7 |
| Japan; Motoyu spring, Nasu | Yellow precipitate | 1–10 | | | 21 |
| Columbia, South America; La Sufral volcano | Native sulfur | 0.42–1.71 | – | – | 25 |

Compiled from data by:
1. Blanchard (1933)
2. Morris and Lovering (1952)
3. Knight (1911)
4. Foley (1960)
5. Boyle (1965*a*)
6. Boyle (1972)
7. Boyle (unpublished)
8. Weed (1905)
9. Maclaren (1906)
10. Grange (1937)
11. Brannock *et al.* (1948)
12. White (1955)
13. White *et al.* (1963*a,b*)
14. Weissberg (1970)
15. Mikov (1970)
16. U.S. Geol. Surv. (1968), Prof. Pap. 600-A, p. 7
17. Kinkel and Lesure (1968)
18. Gottfried *et al.* (1972)
19. U.S. Geol. Surv. (1969*c*), Prof. Pap. 650-A, p. 121
20. Lincoln (1911*b*)
21. Ikeda (1955*a,b*)
22. Lindgren (1910)
23. Browne (1969)
24. Harrison (1908)
25. Goodchild (1918)
26. Skryabin (1968)
27. H. Lakin (1969*a*), U.S. Geol. Surv., Circ. 622, p. 4.

gold-bearing. Of the precipitates associated with hot springs, the siliceous sinters (usually with some sulphides) deposited from alkaline waters tend to concentrate more gold (and silver) than the carbonate and limonitic sinters.

In the natural precipitates gold is most frequently accompanied by enrichments of $SiO_2$, As, Sb, Cu, Ag, Zn, Cd, Hg, Ti, Zr, Mn, Fe, B, Al, P, Te and S and less frequently by Li, K, Ca, Mo, W, Co, Ni, Tl, Bi, Se, V, Cr, Sn, Th and U. These are also the common associates of gold in natural waters. Judging from the data in the literature (Table 22) the Au/Ag ratio of hot spring deposits such as siliceous sinter, travertine, etc. is generally less than 1. There is considerable variability in the Au/Ag ratios of cold spring deposits, precipitates from groundwaters, organic precipitates, etc., but they are commonly much less than 1. The highest contents of gold and silver generally occur in the siliceous sinters precipitated from hot alkaline saline waters. This circumstance is particularly marked at Whakarewarewa and other thermal areas in New Zealand (Grange, 1937; Browne, 1969; Weissberg, 1970). Such natural data suggest that some gold-silver-quartz deposits were probably precipitated from alkaline, saline siliceous waters or from diffusion currents in an alkaline environment.

Numerous other occurrences of gold in spring precipitates are recorded in the literature. Many of these are associated with pyrite, which partly replaces rotting wood and other organic debris in the spring waters. References as far back as Sterry Hunt (1879) and Liversidge (1893*c*) draw attention to this mode of occurrence of gold and other metals. There are a number of references in the old literature attesting to the solubility of gold in mine waters and its precipitation (or plating) on iron particles such as rails, shovels, mine cars, etc.

The mode of occurrence of gold in natural precipitates is exceedingly variable. In manganese oxides and limonite much of the gold is probably present in an adsorbed form or as an integral part of the oxide complexes. Some varieties of auriferous limonites, particularly those associated with sulphide and gold-quartz deposits, contain the element in a number of ways: in minute specks, wire and sprigs of native gold; in a great variety of secondary minerals such as jarosite (plumbojarosite and argentojarosite), bindheimite, beudantite, anglesite, pyromorphite, malachite, azurite, etc.; and in an adsorbed or bound form in the hydrous iron, manganese, aluminum and silicon oxides. Limonite and wad, intimately mixed with organic substances, probably hold the element partly as some form of gold humate or other gold-organic compound. In precipitates containing secondary sulphides such as pyrite, melnikovite and marcasite, most of the gold is present in these sulphides in an unknown form. More details on the form of gold in natural precipitates and secondary oxides, sulphates, carbonates, etc. are given in a previous section on gold in other minerals in this chapter.

There are only scattered references to the possible presence of gold in the various products of volcanoes and fumaroles. Recent quantitative data appear to be lacking, but the element is probably present in the precipitates and sublimates associated with these high temperature phenomena since Goleva *et al.* (1970*a,b*) detected up to 1.6 ppb Au in the waters of the HCl fumaroles of the volcano, Ebeko, in the Kuril Islands, U.S.S.R., Goodchild (1918) mentions the presence of up to 1.7 ppm Au in the sublimated sulphur of La Sufral volcano in Columbia. Gold has also been detected in traces in the pyrite associated with the sulphur "blowers" in the Sulphur Bank at Borax Lake, California (Liversidge, 1893*c*).

The extremely small amounts of gold in natural waters (circa 0.03 ppb) make the problem of the determination of the state of the element most difficult. There has been much theorizing on the state of gold in waters, but as yet we have no satisfactory data on which to base solid conclusions, nor have we yet available any experimental techniques to decide exactly how gold exists in natural waters. About all that we can truthfully say is that gold migrates in waters by some process of natural alchemy as yet undiscovered. This statement notwithstanding we can suggest from the known chemistry of gold that the element may be present in natural waters in one or all of the following forms:

1. As finely divided particles of native gold: gold is slightly 'soluble' in water, especially in a very finely divided state. The form of this 'dissolved' gold is, however, unknown. In some cases the particles are probably colloidal in size and the solution is, therefore, in the nature of a colloid (*see* 13 below). In other cases the finely divided particles may be hydrated, coated with a variety of natural substances which

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stabilize the particles in 'solution' or adsorbed to fine silt, organic compounds or a variety of colloids such as the hydrous iron oxides. In some surface waters much gold is transported as fine particles that appear to float or are carried along as silt. This gold is the familiar 'flour gold' or 'float gold' frequently referred to in the literature. Goni *et al.* (1967) have shown by experimental methods that gold can be made to form a stable suspension of very fine (colloidal) particles by prolonged abrasion by quartz grains. This suspension is stabilized by the presence of carbonate in small amounts (up to 1 per cent). Above this concentration the carbonate acts as a flocculent. The colloidal silica also formed by abrasion, assists in maintaining the gold in suspension, probably acting as a protective colloid. Machairas (1967, 1970*a*) refers to particles of gold in iron oxide stalactites in the Cros Gallet Tunnel in France which he thinks have been transported in suspension in groundwaters. These particles have a maximum size of 20$\mu$. Chernyayev *et al.* (1969) have also concluded that gold migrates in the supergene zone of gold and sulphide deposits partly as very fine particles in suspension in the oxidizing solutions.

In a recent paper Goleva *et al.* (1970*b*) claim that gold in the common types of natural waters (pH 5–8 and Eh 0.1–0.5 V) is present mainly in the form of Au(0) (uncharged particles) and as organic complexes.

At high temperatures and pressures metallic film gold precipitated on quartz and porcelain is relatively soluble in water according to the experiments carried out by Vilor and Sarapulova (1971). At 100°C they noted a solubility of 6.6 ppb of the film gold; at 300°C, 67.5 ppb; and at 350°C a decrease in solubility to 34–45 ppb. Lower values were recorded when film gold precipitated on porcelain was used. They concluded that gold dispersed in sedimentary rocks during sedimentation may be leached out by dilute aqueous solutions in the course of progressive metamorphism, transported and then precipitated on encountering a change in pressure and temperature in the rocks through which filtration of the solutions took place.

2. As the ions $Au^+$ and $Au^{3+}$: these states have been suggested by some early investigators, but their presence as ions in any normal natural water appears unlikely. Gold has an extremely high affinity for electrons, hence its character as the most noble of metals. The ionization potentials for both ions are ($Au^+$–9.2 eV; $Au^{3+}$– $\sim$30 eV) and hence their interaction with water is marked. Aurous ion decomposes to form metallic gold and auric ions in aqueous solutions. It can, however, be stabilized by ligands such as $(CN)^-$. Auric ion is stable in very acid waters (pH $<$2) (Fig. 1); at higher pH it is strongly hydrated or is stabilized in water as the numerous complexes noted in 3 and 4 below. As a rule gold is highly inert in nature, and strong oxidizing agents such as $MnO_2$, $Fe^{3+}$, $As^{5+}$, $Sb^{5+}$, $Cu^{2+}$, $O_3$ or $O_2$ are necessary to oxidize the metal to the (I) and (III) states. Only when complexing agents such as $(S_2O_3)^{2-}$, $(CN)^-$ and $Cl^-$ are present can gold be maintained in a mobile (soluble) state in the presence of these oxidizing substances.

3. As gold hydroxide, $Au(OH)_3$: gold hydroxide is slightly soluble in water (Lenher 1918; Johnston and Leland, 1938), the quantity being about $3.1 \times 10^{-6}$ mole/L or approximately 600 ppb. Being amphoteric the hydroxide exhibits increased solubility in acid solutions especially those containing the halogens or halogen acids – $4HCl + Au(OH)_3 = HAuCl_4 + 3H_2O$ – and in alkaline solutions in which it forms the complex ions $[AuO_2]^-$, $[AuO_3]^{3-}$ and their hydrated equivalents, e.g., $[H_2AuO_3]^-$ and $[HAuO_2]^{2-}$. Tyurin and Kakovskii (1960), from thermodynamic calculations, consider that gold may be present as the hydroxide or its complexes in some supergene waters. Vorotnikov *et al.* (1973) also consider that some of the gold in these waters is present as $[Au(OH)_2]^-$.

Lenher (1918) carried out a number of experiments on the hydrothermal transport of gold as the hydroxide. At relatively low temperatures and pressures (110°C, 1.5 atm) the hydroxide is relatively stable in solution; at higher temperatures and pressures decomposition to the metal takes place to a variable degree. Vilor and Shkarupa (1971) investigated the system $Au–SiO_2–H_2O$ within the temperature interval 100 to 400°C and at $H_2O$ pressures of up to 1000 atm. Below 200°C concentrations of Au and $SiO_2$ are equal and independent of pressure. Above 200°C they increase with temperature and pressure. The gold is said to be present as $[AuO_2]^-$ and colloidal particles. The colloidal gold system is stabilized by dissolved and polymerized $SiO_2$. Narseev (*in* Petrovskaya, 1974), likewise, advocates the transport of gold in hydrothermal solutions in the form of hydroxy complexes and chloroaurates stabilized by polymeric silica compounds when high concentrations of silica are present in the solutions.

4. As soluble halogen salts and halogen complexes: when salts such as $AuCl_3$, $AuBr_3$ and $AuI_3$ dissolve in water they do so with the formation of complex ions of the type $[AuCl_4]^-$, $[AuCl_3(OH)]^-$, $[AuCl_2(OH)_2]^-$, $[AuCl(OH)_3]^-$ and so on. There are analogous bromine and iodine complexes whose stability increases in the order I $>$Br $>$Cl. Actually the formation of these complexes is a very intricate matter, but it is apparent that the auric ion can probably form every state of the fourfold complex from $[Au(OH)_4]^-$ to $[AuCl_4]^-$ depending on the pH of the solution and the concentration of chloride ions. This is evidently because an aqueous solution of auric chloride is in reality a solution of the acid $H[AuCl_3OH]$. There is also an unusual series of addition products of auric chloride with the halides of P, Se, Si, Sb, etc. These evidently give soluble complex ions but relatively little is known about their chemistry. Some, such as those with silicon and antimony, may have geochemical significance in the migration of gold since the three elements are invariably found together.

Further discussion of the various aspects of the halide complexes of gold is beyond the scope of this book, but four recent papers dealing with traces of gold in chloride solution are of interest. Beneš (1967) concluded from dialysis and electomigration experiments that traces of gold ($10^{-7}$–$10^{-8}$M) (2–20 ppb) in chloride solutions between the pH range 6 to 13 exist predominantly as complex anions or molecules, probably of the hydroxoaurate type, $[Au(OH)_xCl_y]^{(x+y-3)-}$ with ($x + y \leq 4$). In the pH range 0 to 4 Beneš and Riedel (1967) and Beneš and Singer (1968) concluded from adsorption experiments that the trace amounts of gold in chloride solutions were present predominantly as undissociated molecules of $HAuCl_4$ at low pH and positively charged hydrolytic products of this acid at higher pH. With increasing pH ($>$4) the negatively charged hydroxo complexes noted above are dominant. On the mechanism of the dissolution of gold in chlorine water Svistunov (1970) concluded from thermodynamic data that the gold is present mainly as $HAuCl_4$ and that the metal reacts with atomic rather than molecular chlorine as is generally considered to be the case.

Complex aurous halides, bromides and iodides of the type $[AuCl_2]^-$ are known, but they are relatively unstable, the aqueous solutions rapidly decomposing with separation of metallic gold and the formation of auric complexes.

Numerous investigations have considered that gold in surface waters leaching gold-bearing deposits is largely present as a complex halide. Lenher (1909, 1912) was one of the first to deal with this form of transport in detail, and he summarized the earlier literature on the subject. Brokaw (1910) and Emmons (1917) pointed out that gold could be dissolved in acid supergene solutions as the soluble auric chloride complex when a strong oxidizing agent such as manganese dioxide was present to oxidize the gold to the Au(III) state. This view is supported experimentally by Miller and Fisher (1974). Chukhrov (1947) considered that the solution of gold in the oxidation zone of mineral deposits was due to the formation of soluble alkali gold bromides and iodides. Shcherbina (1956*b*), Krauskopf (1951), Kelly and Cloke (1961) and Shabynin (1966) have postulated that the auric chloride complex, $[AuCl_4]^-$, is one of the important forms in which gold is transported in supergene waters. Kelly and Cloke (1961) concluded that if an activity of $10^{-5}$ moles/L (2ppm) is chosen as the lower limit of the geological solubility of gold, the element is soluble in acid chloride solutions ($pH < 5.5$), oxidation potentials greater than 0.9 V, and chloride ion activities greater than $10^{-3.2}$ moles/L. In the waters of the southern Enisei region, U.S.S.R. Vorotnikov *et al.* (1973) concluded from dialysis studies that gold migrated in an ion-dispersed state in the form of negatively charged anion complexes, principally as $[AuOH_2]^-$ and $[AuCl_3OH]^-$. Roslyakov *et al.* (1972) found that the $[AuCl_2]^-$ complex prevailed in the pore solutions of oxidized ores, eluvial layers and soils overlying gold deposits. It was commonly accompanied by gold in the form of the $[Au(OH)_2]^-$ complex.

The views that supergene waters transport gold mainly as $[AuCl_4]^-$ and as other halide complexes has been questioned by a number of investigators particularly Boydell (1924), Tyurin and Kakovskii (1960), Goni *et al.* (1967), Goleva (1968) and Goleva *et al.* (1970*a,b*). They point to the relative instability of the auric chloride complex at a pH greater than 4 (the normal range of most supergene waters), the relatively easy reduction of the complexes by metallic minerals, organic compounds etc., the paucity of chloride, bromide and iodide in most supergene waters, and the general absence or late stage appearance of oxidants such as $MnO_2$ in many deposits.

Boydell (1924) and Goni *et al.* (1967) consider colloidal transport more probable, and Tyurin and Kakovskii think that the effective soluble complex is a thiosulphate one (*see* 5 below). Lakin *et al.* (1974) stress the relative immobility of gold chloride in geologic environments because of the easy reduction of the various complexes to the metal by most common geological materials. They also note that while bromide and iodide form stronger complexes with gold they are rarely if ever in sufficient natural concentrations to be of importance as a supergene agent of transfer of the precious metal. The writer's observations on the halide content of supergene waters leaching gold-bearing deposits in temperate climates confirms the low content of these elements. Only in rare cases do the supergene waters contain more than a few, a few tenths or a few hundredths parts per million respectively of Cl, Br or I. Higher concentrations can be expected in arid regions where some supergene transport of gold may take place as halide complexes.

Transport of gold in hypogene waters (hydrothermal solutions) as chloride complexes has also appealed to a number of investigators, particularly Ogryzlo (1935), Krauskopf (1951), Helgeson and Garrels (1968) and Rabenau and Rau (1968). Krauskopf stated that gold may be transported at high temperatures and pressures as the ion $[AuCl_4]^-$ in acid solutions provided that reducing agents are absent. He thought that at the temperature and pressure of most hydrothermal solutions that the hydrogen ion of the acid was a sufficient oxidizing agent to keep the gold in the oxidized state. Helgeson and Garrels concluded from thermodynamic considerations that gold is carried in acid hydrothermal solutions primarily in the aurous state as chloride complexes. The writer (Boyle 1969*c*) has criticized this proposed acid-chloride transport mechanism from a number of angles, pointing to the general low content of chloride now present in gold veins and their wall-rock alteration zones, the alkaline character of the wall-rock alteration associated with gold deposition, the low transfer percentages of alumina in alteration zones associated with gold deposits, the general presence in gold deposits of carbonates which are difficult to precipitate from highly acid solutions and so on. Because of these and other features of gold deposits it seems probable that near neutral to alkaline sulphide solutions also carrying As, Sb and Ag are the most likely gold-transporting media. Recently Weissberg (1970) has shown experimentally and by examination of thermal waters precipitating gold in the Broadlands, Ohaki and Waiotapu areas, New Zealand that the $[AuS]^-$ complex is more than adequate to account for the transport of gold in these near-neutral low salinity hydrothermal solutions (*see* 12 below).

More recent views on the transport of gold as chlorides are found in a number of papers. Vilor and Shkarupa (1971) examined the system $Au\text{-}SiO_2\text{-}NaCl\text{-}H_2O$ between the range 100 to 400°C and at $H_2O$ pressures up to 1000 atm. They found that the gold and silica contents increase with temperature, pressure and acidity as compared to neutral solutions. At NaCl concentrations higher than 50 g/L the disperse Au phase was found to be stable within the whole temperature range. They concluded that their data confirmed the possibility of the formation of gold deposits by the leaching of gold from various rocks by metamorphogenic hydrothermal solutions. In a further study of the system $Au\text{-}SiO_2\text{-}H_2O\text{-}NaCl\text{-}HCl\text{-}NaOH$ in the range 200 to 400°C, Vilor and Kazmin (1973) concluded that the basic gold complex in chloride solutions is $[AuCl_2]^-$ supporting the view of Helgeson and Garrels (1968) that the oxidation state of gold is low at high temperatures and pressures.

Kolonin and Aksenova (1971) studied the effects of temperature on complex formation of gold in chloride solutions by spectrophotometric methods. They observed that for $[AuCl_4]^-$, hydrolysis was greatly increased with increase in temperature in the interval 21 to 90°C.

Henley (1973) determined the solubility of gold in chloride solutions in the range 300 to 500°C. The solutions were buffered with respect to HCl by a K-feldspar–muscovite–quartz assemblage and to oxygen by the assemblage hematite-magnetite. Solubilities were found to increase rapidly with temperature from about 10 ppm at 300°C to 500 and 1000 ppm at 500°C at 1 and 2 kbar respectively. Based on this evidence Fyfe and Henley (1973) have concluded that water of dehydration (metamorphic water) in which chlorides are present could move gold from piles of rocks into available shear zones and faults where it precipitates at lower temperatures and pressures.

Rytuba and Dickson (1977) investigated the reaction of pyrite + pyrrhotite + quartz + gold with NaCl-$H_2O$ solutions within a temperature range 300 to 500°C and pressure range from 500 to 1500 bars. Contrary to previous investigations they found no evidence of gold-chloride complexing under the near-neutral and reducing conditions of the experiments. They concluded that the appreciable solubility of gold in their experiments was due to the pyrite-pyrrhotite equilibrium, which sets the $S^0$, $Fe^{2+}$ and $S^{2-}$ activities; the hydrolysis of $S^0$, which forms $HS^-$, required for complexing; hydrolysis of $Cl^-$, which buffers the acidity; oxidation of gold by $S^0$ and $H^+$; and the formation of $[Au(HS)_2]^-$. Genetically, processes capable of depositing gold and gangue minerals from NaCl solutions initially saturated at 500°C and 1500 bars, were postulated to be: decreased temperature, decreased pressure, dilution to lower NaCl concentrations or combination of the three processes.

Gold chloride is volatile as $Au_2Cl_6$ (Landsberg and Hoatson, 1970; Visnapuu *et al.* 1971), and this form has appealed to some as a mode of transport during endogenic processes. Thus, Anoshin and Potap'yev (1966) have concluded that gold moves in the gaseous phases $Au_2Cl_6$ and $Au_2Cl_2$ said to be stable over a wide temperature interval (300–800°C). There are also a number of other volatile species of gold, e.g., $AuFeCl_6$ and $AuAlCl_6$, that could conceivably occur in nature. These have considerable volatility in the range 200 to 500°C (Heinen and Eisele, 1974).

A number of early investigators have concluded that the dissolved (solute) gold in seawater is present mainly as the $[AuCl_4]^-$ and $[AuO_2]^-$ complexes, the latter according to Krauskopf (1951) being about 100 times the concentration of the former. Peshchevitskii *et al.* (1965, 1970) have investigated the problem of gold in seawater carefully from the viewpoint of the thermodynamic stabilities of various complex forms of gold having regard to the composition of seawater, the redox potentials of the possible gold complexes and the redox potentials of seawater. They concluded that gold was present mainly as the aurous complex $[AuCl_2]^-$ and a few per cent as $[Au(Cl,Br)]^-$. The other relative contents of the complex forms of gold such as $[AuCl_4]^-$, $[AuBr_4]^-$, $[AuBr_2]^-$, $[AuI_2]^-$, $[AuS]^-$, $[AuCl_2OH]^-$, $[AuCl_2(OH)_2]^-$, $[AuCl(OH)_3]^-$, $[Au(OH)_4]^-$, $[AuOHCl]^-$, and $[Au(OH)_2]^-$ are small.

In summary we are probably justified in saying that the transport of gold as chloride complexes in hydrothermal and supergene oxidizing waters is minimal compared with other modes of migration. Certain acid chloride thermal springs may transport some gold, but in general these do not seem to be related to gold deposits. In arid regions oxidation of gold deposits may be attended by transport of gold in the form of halogen complexes. In the sea the soluble gold appears to be present mainly as the aurous chloride complex, $[AuCl_2]^-$, but at the concentration present (0.02 ppb) it will remain difficult to prove that this is in fact so.

5. As thiosulphate complexes of the type $[Au(S_2O_3)_2]^{3-}$: both gold and silver are soluble in thiosulphate solutions containing oxidants, gold forming the complex noted above and silver the complex $[Ag(S_2O_3)_2]^{3-}$. Both complexes are relatively stable in weakly acid, neutral and alkaline solutions (pH 4–9) but decompose in acid solutions. The silver complex yields S, $Ag_2S$ and some $Ag_2SO_4$; the gold complex yields a variety of indefinite products according to my investigations. Depending on the concentration of thiosulphate these appear to be S, native gold and probably $Au_2S$. The presence of any reducing substance gives free gold and some sulphur in the precipitate. The general stability of the two metal complexes is also considerably different in my experience. Silver thiosulphate solutions are relatively stable to natural agents of oxidation and reduction, and silver is relatively difficult to precipitate from the solutions in any form. Gold on the other hand is relatively easily precipitated as the metal both by oxidation and reduction of the complex by a variety of agents. In a more general sense thiosulphate complexes of both gold and silver are relatively stable in the presence of ferrous sulphate (in gossans, etc.) and are not readily reduced by this compound. This is especially so for silver and less so for gold. The varied habit of the decomposition of the thiosulphate complexes of silver and gold are important in the oxidation of gold-silver deposits containing sulphides since with respect to silver, a soluble sulphate is formed whereas with the gold complex the metal is precipitated. These circumstances permit a ready separation of the two metals, and a natural refining, therefore, takes place – gold is concentrated mainly as the native metal whereas silver is leached out, a phenomenon consistently found in eluvial and alluvial placers (*see* Chapter III).

Other oxidized sulphur species can arise as intermediate products between sulphide and sulphate during the oxidation of sulphides according to the scheme: $S^{2-} \rightarrow [S_2O_3]^{2-} \rightarrow [SO_3]^{2-} \rightarrow [S_{2-5}O_6]^{2-} \rightarrow [SO_4]^{2-}$. Sulphite and polythionate form soluble complexes with gold. These can be characterized as $[Au(SO_3)_2]^{3-}$ and $[Au(S_{2-5}O_6)_2]^{3-}$. These complexes and other soluble species of the oxygenated sulphur compounds are fairly stable in alkaline solutions. They are not readily reduced by pyrite and other sulphides, and hence if formed endow gold with considerable mobility. On long contact with sulphides however, alkali species are ultimately reduced to native gold. In acid solutions the sulphite and polythionate complexes of gold and silver are decomposed to give the metals, sulphur, the metal sulphides or the metal sulphates (silver only) depending on the Eh and pH of the decomposition process.

Summarizing the above we see that all of the thio complexes can form only where the solutions are only slightly acid, neutral or alkaline, a condition that may obtain where oxidizing auriferous sulphide deposits have carbonate wallrocks or gangue.

Information on the presence of thiosulphates and other thio species in waters leaching gold deposits is limited. My observations indicate that these constituents are present in neutral and alkaline environments but only in small amount (up to 5 ppm), most of the sulphur being present as sulphate. Thiosulphates are, however, formed in some quantity in various metallurgical practices involving oxidation of sulphides (Forward and Mackiw, 1955) and various thiosalts are produced during the alkaline oxidation of a variety of sulphides (Schmidt and Conn, 1971). It can be concluded, therefore, that thio complexes of both gold and silver may be instrumental in the transport of gold where the supergene solutions acting on sulphide-bearing gold deposits are only slightly acid, neutral or alkaline.

Tyurin and Kakovskii (1960) have postulated that gold (and silver) migrates in the supergene environment mainly as thiosulphate complexes. They find these complexes to be relatively stable and that the dissolution of gold and silver as thiosulphate complexes is greatly accelerated by the presence of cupric ion, which catalyzes the various reactions. Listova *et al.* (1966) showed experimentally, using natural Fe, Pb and Zn sulphides, that the oxidation of these minerals in the presence of carbonates yielded Ca thiosulphate and polythionate. They observed an increased solubility of gold when these sulphur compounds were present, and postulated that they were the main solvents of gold during oxidation processes in gold deposits. They concluded that gold could have a marked migration capacity in the supergene environment when thio salts were present. Cherepnin *et al.* (1973) have also suggested that the enrichment of gold in the oxidized zones of the sulphide-quartz veins of the Kuznetsk Alatau is the result of the deposition of gold from solutions of its thiosulphate salts. Lakin *et al.* (1974) concluded that thiosulphate ion may be present in enviroments high in sulphur but generally in very low concentrations. Above pH 5 gold may be transported as the thiosulphate complexes in these environments.

Lenher (1912) considered that gold could be transported as soluble thiosalts in hydrothermal solutions, and Tyurin (1963,1965*b*) set out to prove that thiosulphates transport gold in hydrothermal solutions. Shcherbina (1964), however, disagrees with this view pointing out that no thiosulphate minerals are known, that thiosulphate has not been detected in hot springs, and that liquid inclusions do not contain the compound. He also notes that at high temperatures ($>100°C$) the thiosulphate complexes are unstable and break down. Kim (1972) essentially agreed with this view, stating that the migration of gold in hydrothermal solutions in the form of the thiosulphate complex $[Au(S_2O_3)_2]^{3-}$ is insignificant. Tyurich (*in* Petrovskaya, 1974), on the other hand, maintains that the formation of complex compounds of gold in sulphide solutions such as the oxygenated species $Au_2S_2O_3$ and $[AuS_2O_3]^-$ must be taken into account during hydrothermal processes. Ellis (1967) states that thiosulphate and polythionate ions do not persist in natural waters at temperatures of 200 to 300°C but break down according to the reaction types:

$$S_2O_3^{2-} + H_2O \rightarrow H_2S + SO_4^{2-}$$
$$2S_5O_6^{2-} + 8H_2O \rightarrow 5SO_4^{2-} + 6H^+ + 5H_2S$$

A search of the literature revealed relatively little information on the abundance of thiosulphate in hot springs. In the great memoir on the hot springs of Yellowstone by Allen and Day (1935) values for $(S_2O_3)^{2-}$ in the waters range from 0 to 21 ppm. A similar range is found in a few other hot springs in various parts of the world according to scattered data in the literature and personal communications; values up to 37 ppm are recorded from hot springs according to the summary given by Lakin *et al* (1974). If these values are actually the contents in the thermal waters and not due to oxidation of the waters near the surface, it would appear that some low temperature hydrothermal solutions may carry enough thiosulphate to complex and transport the small amounts of gold that give rise to deposits.

6. As the soluble sulphate: gold is said to be soluble in $H_2SO_4$ solutions as the sulphate in the presence of an oxidizing agent such as $O_2$, $MnO_2$, etc. Gold (III) hydroxide is also said to be soluble in $H_2SO_4$ probably with the formation of the complex sulphate $[Au(SO_4)_2]^-$. These views are reiterated many times in the old literature (Lenher, 1904) and sometimes appear in the newer literature on gold compounds. Mellor (1923) characterized aurosoauric, $AuSO_4$, and auric, $Au_2(SO_4)_3$, sulphates and mentions complex alkali gold sulphates of the type $K[Au(SO_4)_2]$. These on solution may give rise to the complex ion $[Au(SO_4)_2]^-$. Relatively little is known about the solubilities or the stabilities of these various sulphates and complexes. They would appear to be relatively unstable, especially in the presence of reducing agents. In water, gold sulphates are extensively hydrolyzed, another feature that makes them relatively unstable. On thermodynamic grounds Roslyakov *et al.* (1972) consider that the solubility of gold as the sulphate in oxidizing waters is infinitesimal, the standard electrode potential for the $[Au(SO_4)_2]^-$ complex being unfavourable.

It has long been noted that gold exhibits some mobility where sulphides are undergoing oxidation, and it has frequently been postulated that the agent aiding its solution in such environments is ferric sulphate, $Fe_2(SO_4)_3$. One also notes that in some places the content of gold in oxidizing waters of sulphide deposits is greatest when the waters are acidic and charged with iron, manganese, arsenic and sulphate.

Ferric sulphate as an aid in the solution of gold in oxidizing waters has been questioned by a number of investigators in the past, particularly Stokes (1906) and Emmons (1917) who stated that the solvent action of ferric sulphate alone is negligible. Kreiter *et al.* (1959), on the other hand, found by experiment that solutions of ferric sulphate and sulphuric acid are good solvents of gold.

To resolve this problem I have carried out a number of experiments using atomic absorption methods to detect gold in solution. The results (Boyle *et al.*, 1975) indicate that amorphous gold is weakly soluble in ferric sulphate solutions alone, and more so when free $H_2SO_4$ is present. The presence of NaCl in the solutions appears in some cases to slightly reduce the solubility of the precious metal for reasons that are not clear.

7. As soluble gold arsenate or gold arsenate complexes: gold is soluble in arsenic acid, $H_3AsO_4$ or $As_2O_5 \cdot H_2O$, in the presence of $MnO_2$ and other strong oxidants. The nature of the solute is unknown, but presumably it is gold arsenate, a complex molecule of the type $[AuAsO_4]$, or a complex ion of the type $[Au(AsO_4)_2]^{3-}$ analogous to the sulphate.

The common occurrence of arsenic in gold deposits ensures a supply of dissolved arsenic in oxidizing supergene waters since the oxidation of arsenic minerals such as arsenopyrite yields arsenic acid or some derivative of this acid in solution as shown by the following simplified reaction:

$$4FeAsS + 13O_2 + 6H_2O \rightarrow 4FeSO_4 + 4H_3AsO_4$$

There are no detailed investigations to determine the extent of migration of gold as arsenate or arsenate complexes from oxidizing sulphide-arsenide deposits, but we have noted that some waters rich in soluble arsenic are, likewise, enriched in gold.

8. As soluble gold antimonite or antimonate complexes: relatively little is known about these. By analogy with arsenic it appears probable that gold will form complex antimonites of the form $[Au(SbO_2)_4]^-$ and possibly also complex antimonates. There are also a number of double complexes of antimony and chloride which may have geochemical significance in the migration of gold. The common occurrence of antimony in gold deposits ensures a supply of dissolved antimony since the oxidation of antimony minerals such as stibnite or tetrahedrite yields soluble antimonites and/or antimonates depending on the redox potential. We have noted increased amounts of gold migrating in waters enriched in antimony.

9. As soluble nitrates, nitrites and other soluble inorganic species: auric nitrate and a variety of complex nitrates and nitrites are known, but these appear to hydrolyze so extensively that they are not stable in water. In natural settings, however, some of these complexes may be stabilized by the organic constituents of humus, and gold may migrate in the form of combined organic nitrate, nitrite or ammine complexes, especially where a source of nitrates, nitrites or ammonium ion is available as in decaying vegetation, humus, etc.

Gold is soluble in phosphoric acid, $H_3PO_4$, presumably with the formation of gold phosphate. The stability of this compound in water is unknown, and nothing is known about its occurrence in natural situations. It may occur in some natural waters where phosphate is abundant.

Gold is said to be soluble in hot selenic acid, $H_2SeO_4$, at high temperatures (300°C) and in hot solutions of telluric acid containing $H_2SO_4$ or $H_3PO_4$. The transport of gold presumably as selenates and tellurates at high temperatures could conceivably take place, but there are no data by which to judge the efficiency of the mechanism. Transport of gold during low temperature supergene processes as selenates, etc. would not appear to be important, but again no data are available for judgement.

Colloidal gold is said to be soluble in dilute alkalis apparently with the formation of the hydroxide, hydroxide complexes or oxide complexes (*see* 3 above). Colloidal gold and very finely divided gold is said to exhibit some solubility in alkali carbonate solutions, although Ogryzlo (1935) found that sodium carbonate has no solvent effect on gold at high temperatures and pressures. The reported solubility of gold in carbonate solutions may be due to the formation of very slightly soluble alkali aurate species such as $KAuO_2$ (*see also* 3 above). The reaction may first involve the formation of the hydroxide or some hydrous complex followed by formation of the aurate.

$$2Au(OH)_3 + K_2CO_3 = 2KAuO_2 + CO_2 + 3H_2O$$

The writer has experimented with gold and various carbonate solutions and finds that the normal carbonates are poor solvents of gold. Solutions of alkali bicarbonates on the other hand dissolve small amounts of amorphous gold (Boyle *et al.*, 1975).

Two other mechanisms involving the solution of gold in potassium or sodium carbonate solutions concern the presence of $H_2S$ in these solutions. The alkali sulphide or bisulphide formed are well known solvents of gold (*see also* 12 below).

$$Na_2CO_3 + H_2S = Na_2S + H_2O + CO_2$$
$$NaHCO_3 + H_2S = NaHS + H_2O + CO_2$$

These mechanisms may be important in the transfer of gold during both hypogene and supergene processes as shown by our experiments (Boyle *et al.*, 1975).

Liversidge (1893*c*) reported that gold is dissolved in a solution of potassium or sodium silicate at a pressure of 90 psi. The form in which the dissolved gold was present is not mentioned. It may have been as a colloid or as some complex, perhaps an aurate. Cumenge and Robellaz (1898) also refer to alkali auro-silicates and think that they play an important part in the formation of auriferous quartz deposits. The experiments by Von Veimarn (1913), the result of which led him to suggest the presence of an unstable gold silicate when $NaAuCl_2$ and $Na_2SiO_3$ are mixed, are also of interest in the formation of gold quartz veins. These experiments should be repeated since they have a direct bearing on the transfer of gold and silica during hypogene processes (*see also* the reference to Frondel and others in 13 below).

The writer has experimented with the solubility of gold in various solutions of sodium and potassium silicate (saturated – 10 per cent saturated, pH 10–12). The nature of the gold used in the experiments was the same as that described in Boyle *et al.* (1975). In saturated solutions of sodium metasilicate gold solubilities up to 40 μg/mL were noted, but in similar solutions of potassium silicate the solubility was much lower (up to 1.2 μg/mL). When $H_2S$ was bubbled through the various alkali silicate solutions considerable amounts of gold were taken into solution (>100 μg/mL). On completion of the $H_2S$ treatment the solutions gelled but still retained the gold in the gel. It can be assumed that $AsH_3$ and $SbH_3$ would have a similar effect on the solubility of gold judging from my previous work noted above.

Stokes (1906) found that gold is dissolved by cupric chloride and HCl, the reaction being as follows:

$$Au + 3CuCl_2 = AuCl_3 + 3CuCl$$

He remarks that addition of a chloride to cupric sulphate would probably also have the same solvent effect on gold. The same author found that ferric sulphate has no solvent effect on gold. Addition of sodium chloride to the ferric sulphate solutions, however, led to the solution of some gold. This is the oxidation and complexing effect on gold referred to in 4 above. Stokes (1906) also found that gold is soluble in a solution of ferric chloride and HCl. Again this is due to the oxidation and complexing effect. Experimentally, Miller and Fisher (1974) found that gold exhibits some solubility in $FeCl_3$ solutions in a dynamic system when $(Fe^{2+})$ is continuously removed. The reason for this is obvious, $Fe^{2+}$ being a strong reductant of gold in solution. The gold dissolved in the ferric chloride solutions was completely sorbed by pyrite. The presence of bromide in the solution aided the dissolution of gold and impeded its reduction and precipitation on pyrite. All of these experiments are of interest in understanding the transport of gold during supergene processes as noted in

Chapter IV. Their significance in the hypogene transfer of gold is problematical.

Lenher (1909) found that boiling HCl under pressure dissolves gold readily, and that hot solutions of sodium chloride and HCl under pressure have a similar effect. High temperature sodium chloride and other alkali chloride solutions under high pressure, even in the absence of HCl, also have a solvent effect on gold. These mechanisms for the solution of gold may be significant in hypogene environments.

Babička (1943) mentions work by J. Barvir and C. Doelter that indicated that sodium chloride is a weak solvent for gold, but in my experiments I have not been able to confirm this (Boyle *et al.,* 1975). Babička (1943) also mentions that Egleston found that magnesium sulphate also dissolves the metal, but this seems improbable. Vilor and Shkarupa (1971) experimented with the Au-$SiO_2$-NaCl-$H_2O$ system at temperatures between 100 and 400°C and $H_2O$ pressures up to 1000 atm. They found that the gold and silica contents increase with temperature, pressure and acidity as compared to neutral solutions. At NaCl concentrations higher than 50 g/L the disperse gold phase decreased while the ionic form increased. The chloride complexes were found to be stable within the whole temperature range. The $Au^{3+}/Au^{+}$ ratio increased with increase in temperature in the range from 200 to 400°C. They considered that silicon-chloride complexes play a major role in the transfer of $SiO_2$.

Morris and Lovering (1952) noticed an affinity of gold for cupric sulphate solutions as indicated by the presence of the precious metal in chalcanthite and pisanite efflorescences in the Tintic District, Utah (Table 22). They also found gold in copiapite, which suggested to them an affinity of gold for ferric sulphate solutions with iron just commencing to hydrolyze. Along the same line Lakin (1969*b*) mentions the fact that gold is relatively soluble in solutions leaching dumps of porphyry copper deposits (ferric and cupric sulphate solutions at pH 1.5) when sodium chloride and $MnO_2$ are added and air is bubbled through the solutions. Two aliquots of 200 mL each, one containing NaCl and $MnO_2$ and the other free of these constituents, contained 400 and 4 μg of gold respectively.

10. As a soluble cyanide or thiocyanate complex: gold forms very soluble cyanide and thiocyanate complexes in an oxidizing environment. The cyanide complexes are $[Au(CN)_2]^-$ and $[Au(CN)_4]^-$, and there are also a number of multiple complexes of the type $[Au(CN)_2Cl_2]^-$. The thiocyanate complex can be characterized as $[Au(CNS)_4]^-$. The dissolution of gold in cyanide and thiocyanate solution is usually written as:

$$4Au + 8CN^- + O_2 + 2H_2O = 4[Au(CN)_2]^- + 4OH^-$$
$$Au + 4[CNS]^- = [Au(CNS)_4]^-$$

The various gold cyanide and thiocyanate complexes are stable, but only in mildly acid, neutral and alkaline solutions.

Numerous plants and seed kernels, some fungi and certain insects contain cyanide in the form of cyanogenic glycosides, which are composed of one or more types of sugar with CN and other groups bonded through hydroxyl (OH) (Armstrong and Armstrong, 1931; McIlroy, 1951; Kingsbury, 1964; Conn, 1969). A familiar cyanogenic glycoside is amygdalin, the bitter essence in almonds. *In vitro,* cyanogenetic glycosides are hydrolyzed in acidic aqueous solutions and split out HCN, thiocyanates, sugars and other products generally aldehydes or ketones. *In vivo,* enzymatic reactions produce similar products. Plants, fungi and insects on their death undergo decomposition during which HCN may be split out of the organic complexes as a result of hydrolysis or bacterial action. Interactions of HCN with alkalis in soils, humus, etc. in neutral and alkaline environments may produce alkali cyanides and thiocyanates which, as noted above, solubilize gold (and silver). From what has been said it is evident that gold may be transported in the exogene cycle as cyanide or thiocyanate complexes in an environment where humification processes are proceeding. Such complexes would, however, seem to be transitory since their stability during humification processes is relatively low as a result of oxidation and bacterial activity which break them down to simpler compounds such as $CO_2$, $H_2S$, $SO_4^{2-}$ and nitrates.

The presence of available cyanides and thiocyanates in or about oxidizing gold deposits where humification processes are progressing is uncertain. Biochemically they should exist. My research on this matter has failed, however, to definitely establish their presence, but work is continuing on the problem. Certain identification of traces of cyanide is difficult in natural waters as shown by Goulden *et al.* (1972).

Lungwitz (1900*a,b*) thought that cyanide derived from the decomposition of plants could be a solvent of gold but dismissed the idea because he thought this active agent could only be formed at high temperatures. He also noted that CN had not yet been found in the decay products of vegetation. Shcherbina (1956*b*) postulated that gold forms soluble complexes with humic acids, one of the complexes being $(Au(CNS)_4)^-$. Curtin *et al.* (1970) leached three gold-bearing samples of mull (forest humus layer) from Nevada and Colorado with demineralized water, obtaining gold in solution in the range 27 to 120 parts per trillion ($1 \times 10^{-12}$). They suggested that most of the gold in the leachates was probably present as extremely small colloidal particles (<0.05 μ diameter), with much smaller amounts in the form of gold cyanide and thiocyanate ions.

In later papers Lakin *et al.* (1971; 1974) explained that at a pH of 5 to 8, $(CNS)^-$ and $(CN)^-$ may be expected to dissolve gold. They found that thiocyanates were relatively sparse in soils, but that cyanides could be abundant as a result of the hydrolysis of cyanogenetic glycosides. More than 1000 species of plants yield HCN on hydrolysis; many arthropods produce HCN; and some animals and fungi also yield appreciable amounts of the compound. Macerated aqueous suspensions of 16 species of native plants collected in Colorado, Utah, Nevada and Arizona were found to dissolve leaf gold. Lakin *et al.* (1974) consider that gold cyanide offers the most feasible form of soluble gold in soils.

Cyanide- and cyanate-bearing minerals exist in places. A number of cyanide minerals are recorded by Povarennykh and Rusakova (1973) and Rusakova and Povarennykh (1973) in various gold belts of U.S.S.R. One mineral kafehydrocyanite, $K_4[Fe(CN)_6]\cdot 3H_2O$, has been characterized. Cyanides were found in the waters from which these minerals were precipitated. According to the investigators, cyanides and thiocyanates are significant in the migration and redistribution of gold in the supergene zone of gold deposits. The source of the cyanides is considered to be decaying organic matter. A thiocyanate mineral, julienite, $Na_2Co(SCN)_4\cdot 8H_2O$ occurs in small amounts at Chamibumba, Katanga, Zaire (Belgian Congo).

It is usually considered that cyanides and thiocyanates play no role in the primary endogenic migration of gold. Our views in this respect may require reassessment. Recently, Mukhin (1974) has authenticated the presence of thiocyanates and hydrogen sulphide in the thermal springs in the caldera of the Golovnin volcano (Kunashir Island, Kuriles). From these and other data the author concludes that hydrocyanic acid (HCN) is present in volcanic gases. If so, a ready solvent for gold is available in deep-seated processes. Similarly, gold may have migrated as a soluble complex thiocyanate in endogenic processes.

11. As soluble organic complexes: gold forms a great variety of organic compounds. Gold (I) alkyls, isonitriles, carbenes and mercaptides have long been known and are quite stable, and there are also a great number of gold (III) alkyls and chelated diarsine, phosphine and other complexes. In addition there are the various cyanide and thiocyanate complexes noted in 10 above. The facility with which gold binds with organic molecules is, therefore, well established.

In natural environments organic compounds are extremely complex especially those occurring as plant and animal residues and in humus. The latter substance is a most complicated material with no well established composition. In addition to humic acid and fulvic acid components it apparently consists of a great variety of relatively unknown constituents derived from the breakdown of dead vegetable and animal matter. Furthermore, these constituents are exceedingly variable depending upon the degree of humification. Various types of humus appear to react differently toward the metals, and no one component can be effectively tagged as being responsible for the strong binding action on metals displayed by some varieties of humus; thus, the subject can only be discussed in general terms.

When available the metals of Group IB are generally strongly bound by humus. Copper forms a strong bond with humus, a feature that has been discussed at great length by numerous investigators and summarized by Manskaya and Drozdova (1968), Ong *et al.* (1970) and Boyle (1977). The nature of the copper bond to humus is uncertain, but the experimental evidence suggests some kind of internal or chelated complex. Silver, likewise, is strongly bound by humus probably as a chelate or some other such organometallic complex (Boyle, 1968*b*). Gold is no exception. The writer's observations and those of others (*see* the section on soils) show that gold is markedly enriched in the humic horizons of some soils, and that much of this gold is bound in the humic component. An important question in the transport of gold is not whether gold can be bound by humic materials – this much seems proved – but whether it can migrate in natural solutions in this manner. The latter has given rise to considerable controversy.

Lungwitz (1900*a,b*) working in Guyana, postulated that gold chloride may be formed during the oxidation of gold deposits by supergene waters containing chloride ion and nitric and sulphuric acids derived from the decomposition of organic matter. The gold chloride, he thought, could form double salts with water-soluble organic compounds such as those in the brown colouring matter (humus) in streams. This feature would give gold considerable mobility in the hydrologic regime and may account for the high contents of gold found in trees and other plants. Harrison (1908) concurred in the view that much of the secondary gold in Guyana was transported in organic-rich waters. Freise (1931) experimented with the solution of gold by humic acids extracted from lignite and black river water generated in virgin forests in Brazil that was rich in dissolved organic compounds. He reported relatively rapid dissolution of gold as a humate by these compounds when oxygen was excluded. Blanchard (1933) found certain humic materials near gold deposits in New Guinea (*see* Table 22) greatly enriched in gold. He thought that at least some of the gold was dissolved by and migrated in organic solutions but that the conditions were complicated by the presence of much dissolved manganese. Shcherbina (1956*b*) suggested that gold may possibly form soluble compounds with humic acids in organic environments, and Steelink (1963) thought it probable that gold may react with humic acids, in the presence of oxygen, to form soluble compounds. He considered the solution and precipitation reactions to be as follows:

$$\text{Solution: Au} + \text{H}^+ + \text{humic acid} + \text{O}_2 = [\text{Au humate}]^{3+} + \text{H}_2\text{O}$$

$$\text{Precipitation: } [\text{Au humate}]^{3+} + \text{R} = \text{Au} + \text{humic acid} + \text{R}^+$$

(R = a reducing agent such as $Fe^{2+}$ or organic compounds)

Goleva (1968) mentions the fact that up to 70 per cent of the gold in certain natural waters is extracted by chloroform, a feature which suggests considerable organo-metallic binding of gold in these waters. Finally, Udodov *et al.* (*in* Petrovskaya, 1974) find that gold exhibits some solubility in humic and fulvic acids.

Investigations by Garces (1942) and Fetzer (1934, 1946) oppose the concept that humic acids dissolve gold. Both have found experimentally that gold (and silver) are not dissolved by humic acids extracted from peat and lignite.

Recent studies have tended to confirm the transport of gold as natural organic complexes, often colloidal in nature. Ong and Swanson (1969) have shown that gold is neither dissolved, complexed nor oxidized by organic (humic) acids, but rather that the element in solution as gold chloride is reduced by the acids to a negative colloid of metallic gold. This colloid is then stabilized by a protective layer of organic molecules around the gold thus permitting a relatively high mobility of the element in soil and other natural waters. Curtin *et al.* (1970) and Lakin *et al.* (1971) in the papers summarized in 10 above noted that gold is mobile in an organic environment mainly as a colloid and in minor amounts as gold cyanide and gold thiocyanate ions.

A recent study of the interaction of natural organic acids with gold by Fisher *et al.* (1974) indicates that humic acids alone do not dissolve gold, but if the gold occurs in a colloidally dispersed state, containing adsorbed oxygen, the humic and fulvic acids solubilize the element. Furthermore, these acids interact with dissolved $[AuCl_4]^-$ forming stable auriferous humate and fulvate complexes. Experimentally a gold-fulvate complex was shown to be very stable under most natural supergene conditions.

We have carried out a number of investigations involving the 'solubility' of gold in humic-rich solutions (Boyle *et al.*, 1975). These show that gold is slowly 'dissolved' in these solutions; the metal is intimately associated with the humic matter being either chelated, organometallically bonded or adsorbed. When the humic matter is removed by ultra filtration the solutions are essentially free of gold.

There seems to be little doubt that gold is 'solubilized' in one form or another by a variety of organic compounds. In some cases the compounds or complexes actually assist in the dissolution of gold; in other cases they act as protective agents (colloids) for gold colloids. Such mechanisms are undoubtedly important in the migration of gold under supergene conditions in organic-rich terranes.

Under hypogene conditions there is some evidence to support the contention that gold is often transported as an organometallic complex. The common occurrence of gold in thucholite (an indefinite C-H-O-N-S-U-Th compound) as in the Rand and at the Richardson deposit in southeastern Ontario suggests that gold may migrate in natural waters combined with bitumen or other petroliferous substances, perhaps specifically as a porphyrin which can be synthesized. (*See also* the section on biogeochemistry.) Further details on the association of gold and hydrocarbon substances are given in the section on gold and its associated minerals in Chapter III.

12. As complex sulphide, polysulphide, telluride and sulphide-arsenic-antimony complexes: it has long been known that gold is soluble in alkali hydrogen sulphide (e.g., NaHS) solutions at low temperatures and that gold sulphide is soluble in solutions of alkali sulphide and polysulphide in excess at low temperatures. At high temperatures gold is also soluble in concentrated alkali sulphide solutions. Egleston (1881), Liversidge (1893*c*), Becker (1887), Lenher (1904, 1912, 1918), Mellor (1923), Gruner (1933), Ogryzlo (1935), Zviagincev and Paulsen (1940), Smith (1943), Krauskopf (1951), Kim (1972) and Seward (1973) have dealt in one way or another with the various aspects of the experimental and thermodynamic problems in the various aqueous systems involving gold, gold sulphide and alkaline sulphides. There is some agreement that the principal complex ion is $[AuS]^-$, although some $[AuS_2]^-$ may also be present in the systems. In a recent paper Seward (1973), determined the solubility of gold in aqueous sulphide solutions from pH 4 to 9.5 in the presence of a pyrite-pyrrhotite redox buffer at temperatures from 160 to 300°C and 1 kbar. Maximum solubilities were obtained in the neutral region of pH. It was concluded that three gold complexes contributed to the solubility: $[Au_2(HS)_2S]^{2-}$ predominated in alkaline solution, $[Au(HS)_2]^-$ in the near neutral pH region and $[Au(HS)]^0$ with less certainty in the acid pH region. The stabilities of the first two complexes are much greater than chloroaurate (I) species, a feature which suggests that the chloride complexes play only a subsidiary part in the transport of gold in neutral and alkaline hydrothermal solutions.

The sulphide and polysulphide complexes of gold are stable in aqueous solutions between a pH of 6 up to at least 10. The $[AuS]^-$ complex is also relatively stable to metallic sulphides and a number of other reductants. Since many hot spring waters are alkaline, and other effects such as certain types of wall-rock alteration suggest alkaline solutions, transport of gold as soluble alkaline sulphide complexes has appealed to a number of investigators as a transport mechanism for gold during the formation of hypogene deposits.

Smith (1943) carried out an extensive series of experiments involving the solution and transport of gold, silver and tellurium in alkali sulphide solutions. He was able to show experimentally that gold is soluble in, and can be crystallized from, such solutions, and that two other common gold minerals, electrum (Au,Ag) and calaverite ($AuTe_2$), can be similarly synthesized. His conclusions on the transport and deposition of gold, silver and tellurium merit quotation in full because of their probable importance in the formation of hypogene gold ores:

> Gold is much more soluble than most of the common metals in alkali sulphide solutions. It is included in the group of metals whose sulphides are very soluble in dilute aqueous solutions of alkali sulphide at ordinary temperature. This group also contains mercury, bismuth, antimony, arsenic, and tellurium. In the group of metals whose sulphides are soluble in aqueous solutions of alkali sulphide only at elevated temperature, the most soluble metal appears to be silver. Thus the natural association of minerals containing gold which are deposited late in the ore sequence with minerals containing silver, bismuth, and tellurium is explained. When the soluble double sulphides of gold and alkali are broken down by a lowering of the sulphide concentration, gold deposits as the metal, since its sulphides are very unstable above 40°C. In solutions containing both silver and gold, if the sulphide concentration is reduced to the point where metallic gold separates, it does so along with considerable silver in solid solution, forming argentiferous gold or electrum.
>
> If tellurium is present along with gold in natural alkali sulphide solutions, gold tellurides may or may not precipitate as the sulphide concentration is reduced, depending on the state of the tellurium in the solutions. If the free sulphur concentration in the polysulphide form is high, then the tellurium is present as alkali thiotellurites, and when in this form metallic gold precipitates first and much later the thiotellurite complex is broken down and metallic tellurium is precipitated. If the free sulphur concentration is low, then the tellurium is present in part as polytelluride ion and gold tellurides are first precipitated, followed later by the excess of metallic gold. These reactions have been duplicated by experiment, the order of solubility in alkali sulphide solutions being found to be, starting with the most insoluble – gold telluride, gold, tellurium. This explains the natural paragenesis of gold tellurides, gold, and tellurium, which apparently deposit in the same order.

In recent years Weissberg (1970) has reinvestigated the solubility of gold in alkaline sulphide solutions and finds that the solubility of gold experimentally determined at elevated temperatures in alkaline $Na_2S$ solutions ranges from 1 to 6 ppm Au in solutions containing from 0.25 to 0.9 moles $Na_2S$/kg solution at temperatures between 150 and 290°C. In less alkaline solutions, where the $HS^-$ ion predominates, the experimentally determined solubility of gold ranges from 100 to 200 ppm Au in solutions containing from 0.2 to 0.3 moles NaHS/kg solution at temperatures between 150 and 250°C, in good agreement with earlier workers. Having done the necessary calculations he concluded that gold solubility due to the formation of a gold sulphide complex tentatively formulated as $[AuS]^-$ is more than adequate to account for the transport of gold in some natural near-neutral low salinity hydrothermal solutions, such as in the Broadlands, Ohaki and Waiotapu areas, New Zealand, where currently forming surface precipitates contain up to 85 ppm Au (*see* Table 22). This makes a postulated near-neutral gold sulphide transport mechanism a particularly effective means for the formation of epithermal gold deposits.

One of the problems with the alkali sulphide theory of gold transport is that pyrite, one of the ubiquitous sulphide minerals in gold deposits, is insoluble or only sparingly soluble in alkali sulphide solutions. There are a number of other sulphides that also show this phenomenon to some degree, some of them relatively abundant in gold deposits, viz. molybdenite, argentite, pyrrhotite, sphalerite, etc. To circumvent these difficulties it is usually said that gold is deposited later than pyrite in deposits. This is true in many deposits, but late pyrite accompanied by gold is common in most deposits. Early pyrite, with gold as a lattice constituent or in a very finely divided submicroscopic form, is also common. Perhaps we are not dealing with pyrite as such in alkali sulphide solutions but with stable species of iron sulphide complexes, which are ultimately partitioned out of the solutions or diffusion currents as the solid phases pyrite and/or pyrrhotite. The same may be true for the other metals such as Mo, Ag, Zn, etc. With respect to pyrite we may also not be dealing with the transport of iron at all, this element being largely derived from the nearby host rocks as McKinstry (1957) has observed. The derivation of the other metals is more difficult to explain by this secretion hypothesis; they appear to have been transported some distance according to my investigations.

Gruner (1933) has referred to the problem of the low solubility of gold in hydrosulphide hydrothermal solutions charged with silica. Zvyagintsev and Paulsen (1940), however, doubt the earlier data and maintain that silica in fact promotes the solution of gold in hydrosulphide solutions. They also state that sulphides and quartz are not precipitants of gold from hydrosulphide solutions as some investigators have suggested. On the contrary, hydrosulphide solutions may pass through a sulphide zone without depositing gold and may in fact dissolve gold, which is contained in the sulphides. To precipitate the gold they call on decreased solubility as a result of falling temperature. Gold in the sulphides of gold deposits results from coagulation processes involving gold sols and the surface properties of sulphides.

Gold may also be dissolved in the oxidized zone of auriferous deposits principally as $[AuS]^-$. The formation of the $H_2S$ necessary to form this complex is most probably provided by the action of sulphate-reducing bacteria active in the oxidized zones. In most oxidized zones the amount of $H_2S$ is minimal but is invariably present. In their study of a number of oxidized zones, eluvial layers and soils overlying gold deposits in eastern Transbaikal and the Kuznetskii Alatau, Roslyakov *et al.* (1972) found that the sulphide complex of gold, $[AuS]^-$, prevailed over all other forms (chloride, hydroxy, etc.) in the aqueous extracts of the materials in and associated with the oxidized auriferous zones. From this data they reasoned that when $H_2S$ is present in oxidized zones most of the gold migrates as a sulphide complex.

Arsenic and antimony are nearly universal associates of gold in its deposits, as discussed at length in the section on associated elements. These two elements as sulphides are also readily soluble in aqueous alkali sulphide solutions. These facts have led the writer (Boyle, 1969*c*) and others (Seward, 1973; Sorokin, 1973) to postulate that arsenic and antimony complexes are probably important agents in the hypogene transport of gold. The solution of the various arsenic and antimony sulphides in sodium sulphide gives the arsenites, thioarsenates, thioantimonites and thioantimonates as follows:

$$As_2S_3 + 3\,Na_2S = 2\,Na_3AsS_3 \text{ (thioarsenite)}$$
$$As_2S_5 + 3\,Na_2S = 2\,Na_3AsS_4 \text{ (thioarsenate)}$$
$$Sb_2S_3 + 3\,Na_2S = 2\,Na_3SbS_3 \text{ (thioantimonite)}$$
$$Sb_2S_5 + 3\,Na_2S = 2\,Na_3SbS_4 \text{ (thioantimonate)}$$

The complexes formed in these solutions are of the type $[AsS_3]^{3-}$. Complexing of these with gold could yield double complexes of the type $[Au(AsS_3)]^{2-}$ and $[Au(SbS_3)]^{2-}$ and others such as $[Au(AsS_2)]^0$, $[Au(Sb_2S_4)]^-$, etc. depending on the pH and other factors. These complexes may be responsible for the transport of gold (and silver) in typical hypogene environments. Experimentation with carbonate solutions containing various combinations of $H_2S$, $AsH_3$ and $SbH_3$ has shown that amorphous gold is relatively soluble under these conditions (Boyle *et al.,* 1975). The soluble species formed in the solutions are evidently $[AuS]^-$, $[Au(AsS_3)]^{2-}$, $[Au(SbS_3)]^{2-}$, $[AuAs]^{2-}$, $[AuSb]^{2-}$ or more complicated polymerized and hydrolyzed species.

In the supergene environment transport of gold as the $[AuS]^-$ complex or as the complexes of arsenic and antimony mentioned above may be a feature of the lower parts of oxidized zones where the solutions are neutral or alkaline and carry sulphide ion, $H_2S$, or dissolved arsenide and stibnide complexes. The enrichment of gold in the secondary (supergene) sulphide zones of some deposits suggests this mode of transport.

The complex $[AuS]^-$ is stable in seawater, but the general absence of $S^{2-}$ and $HS^-$ ions makes its presence in this environment practically negligible (Peshchevitskii *et al.* 1965, 1970).

Relatively little is known about complex telluride species and the migration of gold as tellurides. A sodium thiotellurate (IV), $Na_2TeS_3$, is reported to be formed by dissolution of Te in solutions of $Na_2S_2$ and $Na_2S_3$ but not $Na_2S$. The corresponding complex is probably $[TeS_3]^{2-}$ from which the double complex $[AuTeS_3]^-$ may be derived. In addition there may be a variety of other complexes such as $[Au(Te_2)]^-$, $[Au_2(Te_2)]^0$ and $[Au(Te_2)_2]^{3-}$ derived from the stable reduced ditelluride ion $(Te_2)^{2-}$ as suggested by Seward (1973). The attempts by Smith (1943) to synthesize gold tellurides from alkali sulphide solutions suggest that the systems are complex. He concluded that in alkali sulphide solutions, gold telluride is less soluble than gold sulphide, which in turn is less soluble than tellurium sulphide, and also that gold telluride appears in alkali sulphide systems only when the free sulphur concentration is low. For the extension of these data to natural systems see the quotation from Smith above.

13. As various colloids or sols: metallic gold readily forms a colloid, the 'Purple of Cassius' being known for centuries, and the red gold sol, obtained by reduction of a dilute gold solution with tannin and other organic compounds, was extensively investigated by Faraday. The metallic gold colloid carries a negative charge in the pH range 4 to 8. The charge can be reversed by the addition of ferric chloride and other salts (Weiser, 1933). Gold sols are, therefore, similar in most respects to the metallic silver colloids. Other gold compounds can apparently also form stable colloids. Beneš (1967) mentions positively charged hydrolytic products formed as the result of the hydrolysis of gold solutions in the pH range 1 to 3.

These products are apparently hydroxides, e.g. $Au(OH)_3$. Hydrous auric oxide, $Au_2O_3{\cdot}xH_2O$, and aurous oxide, $Au_2O{\cdot}xH_2O$, also have colloidal tendencies.

Gold colloids may arise in nature in a number of ways, some of which are: by comminution of gold particles by repeated abrasion; by reduction of a dissolved (ionic) gold compound or complex by numerous inorganic and organic substances, e.g., $Fe^{2+}$; by hydrolysis of dissolved gold compounds or complexes; as a result of the dissociation of a variety of dissolved gold complexes; and by release of gold held in the lattices of gold minerals such as tellurides and in solid solution in various sulphides and arsenides, particularly pyrite and arsenopyrite, as a result of oxidation processes. The gold (mustard gold) so released is extremely finely divided and reactive. Stabilization or peptization of gold colloids is accomplished by numerous organic and inorganic compounds, especially humic compounds, colloidal silica, hydrous iron oxides, etc. Gold colloids are stable at least up to temperatures of 100°C or more; at higher temperatures their stability decreases, but in the presence of suitable peptizers such as silica they are stable up to relatively high temperatures (350°C) (Frondel, 1938). Sulphide sols probably have a similar stabilizing effect at elevated temperatures. Flocculation and precipitation of gold from colloidal solutions is accomplished by various electrolytes, positive colloids, organic compounds and many other substances, all of which are mentioned subsequently.

Most of the work on gold colloids in the past (Zsigmondy and Thiessen, 1925) has been done on relatively enriched solutions. More recently some work on traces of gold ($<10^{-8}$M; 2 ppb) in solution has been carried out by Schweitzer and Bishop (1953) who showed by centrifugation studies that the gold exhibited colloidal behaviour in the pH range 2 to 13. Beneš (1967) has found, however, that traces of gold ($10^{-8}$–$10^{-5}$M) form only colloids (pseudocolloids) between pH 1 to 3. Above pH 3 the gold species is present mainly as a complex hydroxo anion (*see* 4 above). The pseudocolloids are evidently positively charged hydrolytic products, $Au(OH)_3$(?).

The transport of gold as a colloid in surface waters and supergene oxidizing groundwaters has long been advocated. Maclaren (1908) and Boydell (1924) and others before them considered this mode of transport as probable, and Lindgren (1933) inclined to the view that gold was transported as a colloid in certain oxidized zones of gold deposits.

Bastin (1915) experimented with gold colloids and was able to produce the dull brown finely divided gold often found in the oxidized zones of gold deposits. He suggested the possibility of gold being transported in colloidal solution in the oxidized zones of gold deposits in the presence of protective colloids such as silica sol.

Mering *et al.* (1953) observed that negative gold sols were fixed by kaolinite as a result of surface cation exchange processes (Au for Na, Ca, H, etc.).

Goni *et al.* (1967) investigated experimentally the stability, transport and flocculation of gold colloids in the surficial cycle. They observed that ionic and metallic gold give stable colloidal suspensions that permit migration over great distances. Chemically the colloidal suspensions were formed by reduction of dissolved gold by both humic and fluvic acids in acid and alkaline solutions respectively. Mechanically the gold colloids were formed by prolonged abrasion of gold particles. In both cases the colloids were found to be stabilized by the presence of colloidal iron hydroxide and colloidal silica. A high content of carbonate (as $K_2CO_3$) depressed the stability of the gold colloid, but low amounts (up to 0.2%) had only a minor effect. The authors postulated that the gold colloids could be flocculated in a number of ways, including changes in pH and Eh, interaction with organic matter in swamps and bogs, intermingling of waters with different salinities, adsorption by clay minerals, etc. Goni *et al.* (1967) were also able to make small artificial gold nuggets morphologically similar to those found in nature by compaction of colloidal particles due to turbulence. (*See also* the section on placers in Chapter III.)

A number of other investigators have suggested colloidal transport of gold under a variety of supergene conditions. Chernyayev *et al.* (1969) considered that some of the gold in the natural waters of northern Kazakhstan, U.S.S.R. was present as a colloid. Curtin *et al.* (1970) reasoned from their experimental work on the leaching of gold-bearing mull (forest humus layer) by demineralized water that most of the mobile ('soluble') gold was present in the leachate as extremely small colloidal particles ($<0.05\mu$ diameter). Machairas (1970*a*) thinks that some of the gold in the exogene cycle travels in (colloidal) suspension and gives some natural examples of where he thinks this process has been active (*see* 1 above). Gosling *et al.* (1971) concluded that some of the gold in the natural waters in Colorado was present in a fine colloidal form with an organic acid protective coating, the complex particles being capable of passing the 0.1 $\mu$ membrane filter used in the determination of 'solute' and 'particulate' gold. During oxidation processes of gold-quartz deposits Kraft *et al.* (1974) consider that gold migrates mainly in colloidal forms (*see also* Chapter IV).

Ong and Swanson (1969) and Ong *et al.* (1970) carried out an extensive investigation of the effect of organic acids in stabilizing gold colloids in the surficial environment. To summarize their findings they stated that:

> Interactions of various forms of gold, as plates, coarse particles, colloids, and ions $[AuCl_4]^-$, with different types of natural organic acids show that gold is not oxidized and complexed by the organic molecules as reported by some investigators. To the contrary, organic concentrations in the range of 3 to 30 ppm have the capacity to reduce gold chloride solutions to negatively charged colloids of metallic gold. For the 30-ppm organic acid solutions, the reduction process is accomplished by the formation of a protective coating of hydrophilic organic molecules around the hyrophobic gold sol making the gold very stable for at least 8 months and not easily coagulated by cations. The gold sols so formed are less than 10 m$\mu$ in size. This protective layer is also formed when colloidal gold is mixed with organic acids. For the 3 ppm organic acid, the organic matter concentration is too low to form the protective coating and the colloidal gold precipitates.
>
> Two of the organic acids used in this study were extracted from peat and humate-cemented sand, and one was collected from a brown lake water. All three are similar in composition and in physical properties to organic acids isolated from soils and surface waters. These natural organic acids can be considered as hydrophilic colloids having a particle size in the 2.4–10 m$\mu$ range and having negative charges due to the dissociations of the carboxylic and phenolic groups.
>
> The significances of this study in geochemical processes involving the mobility of gold are: (1) in a very acidic solution, for example near an ore deposit, where gold is soluble as its chloride and organic acids are not soluble, the presence of solid organic

> matter causes the reduction of gold chloride, and metallic gold of colloidal size will be precipitated and intimately associated with the organic matter; (2) in slightly acidic to basic waters, for example in the general range of composition of natural waters, gold can only be transported as stable organic protected colloids; and (3) these organic-protected gold colloids are precipitated when they enter a different chemical environment, such as sea water or brackish water with their abundant ions or clay colloids, or when they enter an acid environment ($pH<3$).

The hydrothermal hypogene transport of gold in a colloidal form received some attention in the early years of the present century, but relatively little work has been done on the problem in recent years. Hatschek and Simon (1912) experimented with silica gels throughout which were uniformly dispersed soluble gold salts in an effort to produce some of the features common in gold-quartz veins. By using a number of reducing agents, viz. oxalic acid, ferrous sulphate, sodium sulphite, graphite, charcoal, bituminous shale and crude petroleum, they found that in a gel consisting of silicic acid in which a gold salt is uniformly distributed, a reducing or precipitating agent has the following effects:

(a) If the reducing agent is hypotonic (undersaturated) in relation to the salts in the gel the whole of the gold will leave the gel and will deposit in aggregates, probably of crystalline form, at the point or points of contact of the reducing agent with the gel. The gel, as a result of losing part of its soluble gold content, may cause the reducing agent to become hypertonic (supersaturated) and the gold still remaining in the gel would then be precipitated as below.

(b) If the reducing agent is hypertonic in relation to the salts in the gel the gold will be precipitated within the gel, not, however, necessarily uniformly throughout the gel, but often in distinct layers, the layers being parallel to the surface of the gel in contact with the precipitating agent, and the distance from one layer to the next one increasing with the distance from this surface.

From these experimental results they sought to explain the banding and ribbon structure so common in gold-quartz veins and to explain the distribution of gold in the quartz of the veins. They concluded that such phenomena could originate when a structure such as a fracture was filled with gelatinous silica into which or through which gold salts had diffused, precipitating native gold mainly as a result of reduction by a variety of common substances. Goni *et al.* (1967) repeated some of the diffusion experiments of gold chloride through silica gel and obtained gold films and some textures frequently present in gold deposits.

In a classic work on the role of colloidal solutions in the formation of mineral deposits Boydell (1924) referred to the occurrence of much fine-grained quartz, chalcedony and opal in gold deposits and to the presence of sulphides and gold in many deposits in an extremely fine state of division. He thought that these phenomena indicated colloidal transport of gold and silica, flocculation of the colloids to form gels, and finally recrystallization of the constituents of the gels to form the quartz and gold as it is now found. Lindgren (1933) advocated a somewhat similar origin for certain types of gold-quartz deposits. More recently Zhirnov (1972) has described spherical brownish-coloured colloidal-sized particles of gold (0.1 $\mu$ and smaller) in colloform bands in the Kaul'da gold deposit of the Almalyk ore field U.S.S.R. The fineness of these particles was 794. Zhirnov concluded that these particles initially represented colloidal gold protected by silica sols, and that they were deposited from solutions by a rapid drop of temperature at the margins of the veins where pyrite assisted in the coagulation of the gold colloids. Wright (1969) figures numerous textures of ore and gangue minerals in the auriferous Tennant Creek (Australia) deposits, which he thinks proves that the minerals were at one time in the colloidal state. Subsequent to deposition they have crystallized, and some have been partly mobilized. He suggests that the mobilization process took place by thixotropic reliquefaction of the gelatinous parent materials of the minerals now present.

Frondel (1938) seems to have been one of the last investigators to experiment seriously with colloidal gold under hydrothermal conditions. He found that gold sols were protected by silica colloids against electrolytes (NaCl) and spontaneous coagulation by increase of temperature. He also noticed an increase in the stability of protected gold sols with increase in temperature, and found that the protected sols were stable up to 350°C. From the experimental data Frondel concluded that in acid hydrothermal solutions gold is very probably transported in true solution; part or all of the gold salt, however, may be carried as an adsorbed electrolyte on colloidal silica. With approaching neutrality or alkalinity of the originally acid solution, the gold is precipitated out as sol, protected by colloidal silica. The protected gold sol may be coagulated in various ways – by decrease of temperature, dilution, changes in pH, mixing of the gold sol with other solutions carrying different kinds and concentrations of electrolytes and adsorption of the sol on mineral surfaces and gel surfaces.

More recently Vilor and Shkarupa (1971), experimenting with the $Au$-$SiO_2$-$H_2O$ system at 100 to 400°C and at $H_2O$ pressures up to 1000 atm, observed that the gold and silica contents in the solution were about equal and independent of pressure up to 200°C. At higher temperatures they increase with temperature and pressure, and the gold is present as $[AuO_2]^-$ and colloidal particles. The colloidal particles are stabilized by dissolved and polymerized $SiO_2$.

Finally, Fijii and Haramura (1976) have noted that a solution of $HAuCl_4$ can be reduced to a gold colloid in silica solution without adding reducing agents. In their experiments at room temperature and pressure they used (1) silica solution + $HAuCl_4$ solution + silica gel and (2) silica solution + $HAuCl_4$ solution. The concentration of the silica solution was about 50 ppm $SiO_2$. In the first experiment deposition of aggregates of colloidal purple gold and quartz crystals were observed. Colloidal purple gold was also absorbed in silica gel giving the gel a darker colour. Dissolution of the silica gel by alkali solution revealed the presence of fine purple gold and growth of gold and quartz crystals. In the second experiment, deposition of aggregates of fine purple gold, quartz crystals and a small amount of silica gel were observed. The colloidal purple gold did not adhere to the quartz crystal surfaces. The authors concluded that although the experiments were simple and at room temperature and pressure, they suggest that both colloidal and true solution processes are involved in the origin of some gold-quartz veins.

Despite all of the favourable experiments and speculations indicating the colloidal transport of gold it should be pointed out that no one has yet shown that gold is present in natural waters as a colloid. My investigations using dialysis methods have all been negative, but this is not surprising since gold in natural waters is present in such low amounts (circa 0.005 ppb) that one can probably not hope to attain success with present day apparatus. I have, however, noted that gold travels with other sols, e.g., hydrous ferric oxides, manganese sols, humic colloids, etc., but its state is unknown. It is probably largely present in an adsorbed form.

14. As aerosols and vapours in water gas (steam): the constitution of the aerosols would be varied. In some cases they would probably be colloidal gold particles or gold compounds of various types; in others the gold would probably be adsorbed to hydrated silica, $SiO_2 \cdot nH_2O$, hydrated alumina, $Al_2O_3 \cdot nH_2O$, etc. Gold aerosols are probably present in volcanic emanations or in steam impregnated rocks near the surface. There are few data on these phenomena: Goleva *et al.* (1970*a,b*) found from 0.8 to 1.6 ppb Au in the HCl fumaroles of the Ebeko volcano on Paranushir Island, Kurile Islands, Kamchatka, U.S.S.R. They concluded that the gold was present mainly as the chloride complex $[AuCl_4]^-$. There are a number of other volatile compounds of gold that could conceivably exist as aerosols or vapours under natural conditions, e.g., $AuFeCl_6$ and $AuAlCl_6$. These have considerable volatility in the range 200 to 500°C (Heinen and Eisele, 1974).

15. As an integral part of or adsorbed to the various humic complexes (colloids) that commonly occur in surface waters and in some underground waters: this is probably an important mode of transport in regions where decaying organic matter is present. Further details are given in 11 and 13 above.

16. As an integral part of or adsorbed to suspended particulate matter: in some places this is a major mode of transport of gold (and silver) in surface waters and also in waters leaching porous deposits undergoing oxidation. We have repeatedly found gold (and silver) in colloidal and particulate hydrous iron oxides, hydrous manganese oxides and fine silt, and in these substances with an abundant humic component in both surface and underground waters. The nature of the gold in these materials is discussed in the section on gold in other minerals in this chapter (e.g., limonite, wad, etc.) and in 13 above. The content of gold in these colloidal and particulate substances is variable. Where the so-called 'flour gold' is present (*see* 1 above) the contents are very high; in more normal environments as in the Keno Hill area and elsewhere the fine silt and other particulate matter in the streams averages about 0.05 ppm.

Fischer (1966) reports gold in amounts up to 0.1 ppm in the suspended silt of the Saale River in Germany. In the Aldan Shield of U.S.S.R. Razin and Rozhkov (quoted in Trofimov, 1969) found that 'floating gold' ('flour gold') and gold in suspended matter predominates in ground and creek waters. Their values for these materials range up to 0.037 ppm. In their paper on gold migration in the vicinity of the 'Kuranakh type' of gold deposit in Yakutia, Razin and Rozhkov (1963) found an average of 0.001 ppm dissolved gold and 0.009 ppm in suspended matter in waters rich in dissolved iron and manganese. Gosling *et al.* (1971), in their research on the gold content of natural waters in Colorado, found that the particulate solids in the waters ranged from nondetectible to 9.6 ppm, with most of the values falling between 0.1 and 0.7 ppm.

17. As an integral part of or adsorbed to various free swimming or floating micro-animal organisms and plants: Krauskopf (1956) showed experimentally that plankton adsorbs silver strongly. Gold probably behaves in a similar manner. (*See also* the section on the biogeochemistry of the element.)

The migration of gold in natural waters can be summarized in the following statements:

In ground, spring and surface waters gold is present in only small amounts generally of the order of 0.03 ppb. Much of this gold is apparently present as a colloid or adsorbed to organic, inorganic or organo-inorganic colloids and particulate matter. The remainder of the gold is in a soluble form in a variety of complexes depending on the environment of migration of the metal. In hypogene (hydrothermal) solutions the gold is evidently largely present in a complex form mainly as some species combining sulphide, antimony-arsenic-sulphide or telluride-sulphide. Under acidic condition the metal may also be complexed as some form of the chloro complex. Judging from the elemental associates of gold in its epigenetic deposits (*see* the section on epigenetic gold deposits in Chapter III), the nature of the wall-rock alteration zones associated with gold deposits (Chapter III), and the nature of thermal waters now depositing gold, a reasonable estimate can be made of the type of solution or diffusion current from which epigenetic gold deposits have been or are being precipitated. This solution is probably relatively dilute containing no more than 1 ppm Au, generally much less. Its pH is nearly neutral, and its constitution is varied but in most cases it contains the principal elements in the following forms:

Alkalis (Na, K, etc.) as carbonates, bicarbonates and sulphates
Alkaline earths (Mg, Ca, Sr, Ba) as bicarbonates
Boron as borates and boric acid
Silicon as colloidal silica, alkali silicate or $Si(OH)_4$
Arsenic and antimony as As-Sb-sulphide complexes
Sulphur as $H_2S$, various sulphide complexes and sulphates
Tellurium as telluride-sulphide complexes
Fluorine as alkali fluorides
Chloride as alkali chlorides
Iron and manganese as bicarbonates
Base metals (Cu, Zn, Hg, etc.) as sulphide, bisulphide and polysulphide complexes
Gold and silver as sulphide, bisulphide, As-Sb-sulphide and tellurium-sulphide complexes

The alkali carbonates and $H_2S$ appear in many cases to control the migration and solution of gold mainly through formation of alkali sulphide and hydrogen sulphide complexes which render gold soluble. The formation of sulphide and bisulphide ion in solutions of alkali carbonates and $H_2S$ probably follows reaction such as:

$$K_2CO_3 + H_2S = K_2S + H_2O + CO_2$$
$$KHCO_3 + H_2S = KHS + H_2O + CO_2$$

When arsenic and antimony are present in the system gold may be rendered soluble as complexes of these elements.

Changes in temperature, pressure and concentration of solutions and gases containing dissolved gold species commonly lead to the precipitation of gold. In near surface (supergene) processes changes in temperature, pressure, etc. are usually small and hence have only minimal effects, although they may be important at the orifices of springs where evaporation of solutions takes place, or where sublimation phenomena prevail at the vents of fumaroles. Under deep seated primary vein forming conditions, however, changes in temperature, pressure and concentration have marked effects. When highly heated water gas under high pressure and charged with K, Na, $SiO_2$, Cl, $CO_2$, $H_2S$, As, Sb, Te and gold in the form of various complexes, enters dilatant fractures or other structures it undergoes a decrease in pressure with consequent precipitation of various minerals including gold. Similar effects are produced as these gases (or solutions) rise toward the surface where they come into contact with cooler rocks, where they mingle with cool, circulating groundwaters or where they react with the wall-rocks.

In addition to changes in temperature, pressure and concentration there are a number of other mechanisms by which gold may be precipitated from natural waters and vapours. These are:

1. Decomposition of gold complexes due to changes in pH and other parameters: most dissolved gold species are complexes, some stable only in acid solutions, viz. the halide complexes such as $[AuCl_4]^-$, others stable only in neutral and alkaline waters, viz. the thiosulphate complexes such as $[Au(S_2O_3)_2]^{3-}$ and the thioaurite complex $[AuS]^-$. Changes in pH lead to the precipitation of gold from these complexes depending on the availability of complexing ions and other factors. Considering the acid halide complexes, neutralization of solutions containing these leads to the decomposition of the complexes and the precipitation of native gold where ions capable of complexing the element under neutral and alkaline conditions are absent. Similar conditions prevail during the neutralization or acidification of alkaline solutions containing complex ions of the type $[Au(S_2O_3)_2]^{3-}$ and $[AuS]^-$. In this case the complexes are decomposed and native gold is precipitated where ions capable of complexing gold under acidic conditions are absent.

Shifts in the pH of gold-bearing solutions through the neutral region into the acid and alkaline ranges must be common in nature. Acidic gold-bearing chloride solutions coming into contact with carbonates either under supergene or hypogene conditions generally rapidly and quantitatively precipitate their gold as one can readily see by simply adding powdered calcite to a solution of dilute gold chloride in a test tube. The effect in this case seems to involve an initial precipitate of gold hydroxide or oxide which is unstable, and which is ultimately reduced to native gold. Similarly, neutralization of alkaline waters containing dissolved gold in the form of alkaline complexes leads to precipitation of the metal where such waters come into contact with acid waters in oxidized zones or in humic environments whose waters are invariably buffered on the acid side of the pH scale. In hypogene environments loss of alkalis such as K, Na, Rb and Cs by reaction with wall rocks (sericitization, albitization, etc.) leads to a shift in the pH toward the acid range, the decomposition of the alkaline complexes and the precipitation of native gold or its compounds. Similarly, withdrawal of sulphide and arsenide ions by reaction with iron in the host rocks (formation of pyrite, aresenopyrite, etc.) leads to the breakdown of the gold sulphide and arsenide complexes and the consequent precipitation of gold. Dilution of solutions containing $[AuS]^-$, likewise, leads to a reduction of the sulphide ion concentration and the precipitation of gold. Oxidation (change in Eh) results in the precipitation of gold from sulphide, arsenide and antimonide complexes.

Decomposition of gold complexes in solution due to changes in pH, Eh and a variety of reactions involving the withdrawal of alkali and alkaline earth metals (the balancing cations of the complexes) and sulphide ion are probably the most important modes of precipitation of gold in both hypogene and supergene environments.

2. Adsorption and/or coprecipitation of soluble gold complexes and colloids: this is probably the second most important mode of precipitation of gold in natural settings. Concomitant with these phenomena there are invariably a variety of reduction reactions, which lead to the precipitation of metallic gold in the systems. Flocculation invariably takes place in the case of the gold colloids.

In the supergene environment gold (and silver) is strongly adsorbed and/or coprecipitated by natural gels, particularly hydrous iron oxides (limonite), hydrous manganese oxides (wad), silica-alumina gels, clay minerals and humic gels. Some of these gold-bearing substances are mentioned in the section on mineralogy, and analyses of these materials are given in Tables 12 and 22. Other data are given in Chapter IV.

The reasons for the adsorption and/or coprecipitation of gold by the various natural gels, clay minerals, etc. is a particularly complicated problem, mainly because experimentation with these natural substances is difficult, the results obtained being often strange and nonreproducible. The reason for this is that these natural precipitates, gels and resultant mineral complexes are never pure, and their composition varies widely as one can see by a glance at the analyses given in Boyle (1965*a*, 1972) and Dyck (1971). In addition to a great variation in the major constituents such as Fe, Mn, Si, Al, Mg, Ca, etc., there are also marked variations in the content of the humic constituents, which are inextricably mixed with the gels of Fe, Mn, Si, etc. Dyck (1971), experimenting with the adsorption of silver on these natural substances in our laboratories, found that in general they adsorb much larger quantities of silver than do laboratory preparations of hydrous oxides of iron and manganese under similar conditions of pH and equilibrium silver concentrations. He attributes this to the presence of ions in the colloidal complexes, which form insoluble compounds with silver. Gold behaves in a similar manner judging from natural and experimental data obtained by the writer. However, gold does not form many stable compounds, and ions associated with the gels do not have the same precipitating effect as found by Dyck (1971) for silver. On the other hand gold is readily reduced to the metal by practically any organic compound and by a great variety of ions such as $Fe^{2+}$, $Mn^{2+}$, etc. Once in the metallic form it is not easily desorbed (dissolved) by natural solutions, except where relatively high concentrations of complexing anions such as $[S_2O_3]^{2-}$ and $[Cl]^-$ are present.

The metallic gold colloid carries a negative charge in the pH range 4 to 8, which is that found in most natural waters. Reversal of the charge is possible by the addition of various salts (Weiser, 1933). Most of the common gold complexes carry a negative charge, e.g., $[AuCl_4]^-$, $[Au(S_2O_3)_2]^{3-}$. Some of the natural colloids and gels carry positive charges under certain conditions. Below a pH of approximately 7.5 (the isoelectric point) hydrous ferric oxide carries a positive charge; above this pH the sol is negative. From this it follows that hydrous ferric oxide would adsorb and/or coprecipitate and carry colloidal and anionic gold extensively in natural solutions with an acidic and neutral reaction. Under alkaline conditions hydrous ferric oxides would tend to repel and disperse colloidal and anionic complexed gold. These features seem to account for the common enrichment of gold in many limonitic gossans and for the transport of gold adsorbed to colloidal ferric oxides in acidic and neutral surface and groundwaters during the oxidation of gold deposits.

Aluminum hydroxide and hydrous alumina behave in much the same way as hydrous ferric oxide, the isoelectric point being approximately at pH 8.4. Aluminosilicates behave similarly, the isoelectric point shifting to a more acid pH as silica is substituted in the system $Al_2O_3$-$SiO_2$. With 57 per cent $Al_2O_3$ the isoelectric point is at a pH of 7.0 whereas with 34 per cent $Al_2O_3$ the isoelectric point is at 5.0 (Johansen and Buchanan, 1957). Much more complex are adsorption phenomena involving kaolinite and other clay minerals. In kaolinite the negative charge on the 001 face is always greater than the positive charge on the edge faces and the aluminum mineral invariably carries a net negative charge down to a pH of 3.6 (Street and Buchanan, 1956). One would expect, therefore, that gold colloids and anionic complexes would be repelled by the clay minerals. Such, however, is not the case as shown by Mering *et al.* (1953). They found that gold sols were extensively adsorbed by kaolinite, particularly on the edge faces (i.e., the sites of positive potential). These features explain why gold is frequently concentrated in clay mineral aggregates and mixed limonite–clay mineral–silica aggregates in the oxidized zones of some gold deposits (*see also* Chapter IV). The phenomena may also account for the rich primary shoots of gold in certain highly kaolinized and argillized rocks, which owe their condition to sedimentation processes or hydrothermal alteration. Foster (1971*a*) considers this probable at Carlin, Nevada, but Radtke and Scheiner (1971) disagree and state that there is no apparent correlation between the amount of gold deposited in these disseminated orebodies and the total clay or illite content. The reason why certain clay minerals such as kaolinite do not always adsorb negative gold colloids or complexes probably has something to do with the fact that as the adsorptive sites of clay minerals become saturated with phosphate, arsenate and other negative anionic complexes they become negatively charged and hence repel the gold species. This has been shown experimentally as far as phosphated edges are concerned (Marshall, 1964).

Many other gels and sols carry negative charges, examples being silica, hydrous manganese dioxide, humic substances and various sulphide sols. Theoretically these should repel and disperse the metallic gold colloid and anionic gold complexes. In nature, however, the theory does not in general apply for we find that many of these substances are avid for gold and tend to precipitate the element extensively as one can see by a glance at Table 22. The reasons for this are complicated and only imperfectly known. The answer probably lies in the fact that seldom are these gels found in a pure state. Most are highly contaminated by hydrous ferric oxide and alumina gels, and these are probably mainly responsible for the adsorption and/or coprecipitation of gold in the composite gels. Other possibilites also exist: the hydrous MnO or $Mn(OH)_2$ gel is positively charged and adsorbs anions such as sulphate strongly. It would be expected, therefore, that the gold colloid and anionic complexes would also be adsorbed. Hydrous MnO is probably one of the initial manganese precipitates in neutral and alkaline environments characterized by a low oxidation potential, such as gossans, stream sediments, etc. During maturation of the gels the MnO or $Mn(OH)_2$ gel is oxidized, ultimately yielding $MnO_2$ and other manganese oxides. The problem is also concerned with the adsorption of gold by humic substances and the formation of gold organic compounds. Since humus is invariably a constituent of the composite sols in the surface environment, this mechanism may also be important in the enrichment of gold in gels. Finally, natural sols and gels tend to adsorb a great variety of substances which change their effective surface charges. Adsorption of a variety of cationic complexes by negative sols and gels may give them an effective positive charge, which permits them in turn to adsorb the negative gold sols and anionic complexes.

3. Changes in oxidation-reduction potential: gold is the most noble of metals and hence the lowest member of the electrochemical series, the potentials in acid solutions being as follows (Latimer, 1952):

$Cu = Cu^{2+} + 2e^-$ $E^0 = -0.337$

$Fe^{2+} = Fe^{3+} + e^-$ $E^0 = -0.771$

$Ag = Ag^+ + e^-$ $E^0 = -0.7991$

$2H_2O = O_2 + 4H^+ + 4e^-$ $E^0 = -1.229$

$Mn^{2+} + 2H_2O = MnO_2 + 4H^+ + 2e^-$ $E^0 = -1.23$

$Au = Au^{3+} + 3e^-$ $E^0 = -1.50$

$Au = Au^+ + e^-$ $E^0 = -1.68$

From a consideration of these and other redox couples it can be seen that all the metals and most of their ions can reduce gold from its ionic state to the metal. The effect produced by iron and manganese is marked. Thus, an increase in the redox potential with the consequent production of ferric ion and $MnO_2$ renders gold more soluble and mobile if complexing agents are available. Alternatively a decrease in the redox potential permits greater concentrations of ferrous and manganous ions, which precipitate gold. Increase in the oxidation potential in solutions containing iron has other effects. Ferric iron undergoes hydrolysis and is precipitated as hydrous oxide gel which carries a positive charge. This results in the strong adsorption of anionic gold complexes and gold colloids as noted in 2 above.

Changes in the oxidation-reduction potential are effective in precipitating gold from natural solutions in a variety of supergene environments – in the sea, in freshwater bodies, in manganese and iron bogs, in precipitates at spring orifices and in the zones of oxidation of gold deposits. Similarly, these changes greatly affect the mobility of gold during hypogene processes. Where the oxidation potential is high, gold is maintained in the oxidized (ionized) state, permitting its transfer for considerable distances. Where the oxidation potential is low or where reducing substances are present the mobility of the metal is restricted. Finally, changes in the oxidation potential have a marked effect on the solubility of gold as sulphide, arsenide and antimonide complexes. Oxidation of these complexes results in the rapid and nearly quantitative precipitation of the metal.

The effects of various anions in solution may influence the coprecipitation of gold and silver on sulphides as shown by the researches of Sakharova *et al.* (1976). They found that the influence of the anions $Cl^-$, $F^-$, $CO_3^{2-}$, $HCO_3^-$ and $PO_4^{3-}$ upon the precipitation of gold and silver in the system $HAuCl_4 + AgNO_3 + NH_4OH$ was marked. The presence of $Cl^-$ and $F^-$ lowers the overvoltage of the silver reduction reaction and raises the overvoltage of gold reduction leading to a decrease in the fineness of the gold-silver precipitates. The influence of $CO_3^{2-}$ and $HCO_3^-$ ions results in a sharper rise of the overvoltage of the process of silver reduction than that of gold and consequently the formation of precipitates with a high fineness. The $PO_4^{3-}$ ion exerts no appreciable influence upon the coprecipitation of Au and Ag.

4. Decrease in $H_2S$, $S^{2-}$ or $Cl^-$ concentration of vapours, gases or solutions: where gold is carried as the sulphide or chloride complexes, reaction of the vapours, gases or solutions with the wall rocks or gangue minerals may reduce the concentration of $H_2S$, $S^{2-}$ or $Cl^-$ as a result of the formation of pyrite, chloride-bearing minerals, etc. This breaks up the sulphide and chloride complexes causing the precipitation of gold in one form or another. Similar effects probably result when gold is transported as complex S-Se-Te and S-Sb-As compounds and the $S^{2-}$, $HS^-$ or As ion concentration is reduced by reactions with iron (formation of pyrite and arsenopyrite) in the wall rocks.

Reactions such as those noted above appear to be partly responsible for the primary precipitation of gold (and silver) in a number of epigenetic deposits in basic rocks and in certain types of sedimentary rocks. These reactions may also operate in a modified way in the zones of reduction (secondary sulphide zones) of oxidized gold deposits.

5. Precipitation of gold as a result of the reaction of gold-bearing solutions, gases and colloids with various natural materials: the process is evidently one of reduction although other mechanisms such as adsorption and colloidal coagulation may also be involved. Whatever the cause it has been shown by a great number of investigators (Liversidge, 1893*c*; Rickard 1896; Lenher, 1909; Palmer and Bastin, 1913; Morris 1918; Sakharova and Lobacheva 1967; Radtke and Scheiner, 1970*a*; Shabynin, 1970; Zaitseva *et al.*, 1973; Lakin *et al.*, 1974; Sakharova *et al.*, 1975; and others) that most minerals and rocks precipitate gold from its solutions. The most efficient precipitants appear to be the sulphides, arsenides, tellurides, sulphosalts, native metals including gold, calcite, clay minerals, finely divided chlorite, graphite, carbon, carbonaceous matter, organic carbon compounds, pyritiferous carbonaceous slate and schist, carbonate rocks, sapropel and so on. Charcoal has long been known to be an active precipitant of gold (and silver) mainly by adsorption (Gross and Scott, 1927). Morris (1918) was able to grow beautiful dendritic crystals of gold on calcite in hydrothermal bombs charged with gold chloride. Shilo *et al.* (1974) have shown that gold and silver can be precipitated as a solid solution on pyrite. Limonite, wad, jarosite, scorodite and a veritable host of other supergene minerals precipitate, adsorb or otherwise incorporate gold from solution. Hydrogen in serpentine (mainly in magnetite) is considered by Coveney (1971) to have been the effective precipitant of gold from aqueous gold species in the Oriental Mine, Alleghany, California. The stability of the various soluble gold complexes in the presence of the various earth materials noted above varies widely and depends on many parameters. Generally speaking the halide complexes are the most readily reduced followed by the thiosulphate, thiocyanate, cyanide and various S-As-Sb complexes in about that order. Considering the great variety of natural precipitants of gold one wonders how the element is capable of migrating in any environment.

6. Coagulation of colloids: colloidal gold, colloidal gold compounds and gold adsorbed to various inorganic and organic colloids can be precipitated by a great variety of chemical changes such as a decrease or increase in pH, coprecipitation by other colloids and precipitation by electrolytes. Pyrite, arsenopyrite, galena and various other sulphides, arsenides and sulphosalts also coagulate gold on their surfaces as shown by Zvyagintsev and Paulsen (1940) and a number of earlier workers. The coagulating effect of minerals like quartz, mica, barite and calcite is less marked than that of the sulphides, etc., but is effective over long time intervals.

There are no data on the presence of gold colloids in natural hydrothermal solutions, and hence the effect of coagulation processes in primary vein formation is a matter of speculation. In natural fresh- and seawater it is probable that much gold is precipitated as a result of the coagulation of colloids.

7. Sublimation: this process is probably effective mainly in volcanic and fumarolic processes. The sublimates incorporate the available gold either in their structures or in an adsorbed form.

8. Decomposition of organic (humic) complexes due to oxidation: humic complexes, carrying gold in an adsorbed state or as an integral part of their structure, on oxidation yield $CO_2$, $H_2O$, etc. and liberate the gold. This gold may then be precipitated by a variety of mechanisms.

9. Sedimentation of particulate matter carrying gold: this process acts in all sedimentary basins in lakes, seas and in the oceans. The gold is incorporated in the sediments in a variety of forms.

10. Death and sedimentation of gold-bearing plants and organisms: numerous organisms and plants in natural fresh and saline waters absorb gold into their vital parts, or like plankton adsorb the element on their surfaces. On their death their remains are deposited on the bottoms of lakes, seas and the oceans. There, further reactions attendant on the decay of the organisms and plants fix the gold in the sediments. One of the most common of these reactions in a reducing environment is the bacterial degradation of the protein complexes of the organisms with the consequent production of $H_2S$, which precipitates iron and other sulphides which incorporate the gold. Legedza (1967) considered that sedimentary pyrite absorbs gold dissolved as the thiosulphate during sedimentation and diagenesis in the following manner:

$$FeO + H_2S + nH_2O \rightarrow FeS{\cdot}nH_2O$$

$$2\ FeS{\cdot}nH_2O + Au(S_2O_3)_2^{3-} \rightarrow 2\ FeS_2 + Au + 2SO_3 + nH_2O$$

11. Precipitating action of organisms: certain types of bacteria precipitate gold directly from natural waters. (*See* the section on biogeochemistry.) In addition iron and manganese bacteria play an indirect part since they oxidize $Mn^{+2}$ to $Mn^{+4}$ and $Fe^{2+}$ to $Fe^{3+}$, which then undergo hydrolysis and are precipitated as hydrous manganese and iron oxides. During these reactions gold may be coprecipitated or adsorbed by the hydrous oxides.

> Gold is elaborated by vegetable growth in soils where there are no pretended geological indications; it is found occasionally in rain water; it may, for anything I know to the contrary, exist in the air, vapourized and afloat, as reguline.
>
> –W.B. Clarke, (Southern Gold Fields, Sydney, 1860)

## Biogeochemistry of gold

Gold is a microconstituent of many plants and animals, including man. The literature on the biochemistry of the element is extensive, but is scattered through a great variety of medical and biological journals, many not readily accessible to the geologist and geochemist. Only a few of the most important papers have been consulted during the preparation of the following compilation.

Gold has been used in dentistry and as a medicine for centuries. The potable gold known to the alchemists was a dilute solution of the metal in aqua regia. Many medicinal virtues were ascribed to this potion, including those of the elixir of life. In more recent times gold solutions (thiosulphates) were used in the treatment of syphilis; today gold compounds still find a medicinal use in the treatment of rheumatoid arthritis.

Gold has long been known to be a constituent of plants and animals. The Czechoslovakian alchemist Paterson Hain Janos is said to have found gold in Hungarian grapes, and he wrote a treatise on the occurrence of gold in vegetation entitled *"De Auro vegetabili et vitibus Hungariae aureis"*. V.I. Vernadsky cites the researches of Rouelle and d'Arcet who found gold in French wines in 1779, and C.-L. Berthollet the famous French chemist is said to have determined the content of gold in the ashes of vegetables. In more recent times a number of voluminous compilations dealing with gold in plants and animals have appeared. Among these the works by Berg (1928) and Bertrand (1932) summarize their own work and that of those before them. Other exhaustive reviews, replete with many references, covering some 10 years of research and about all that was known concerning gold in plants and animals at the time, are the works by Babička (1943) and Babička *et al.* (1945). More recently Jones (1970) has compiled most of the data available on the gold content of plants and animals and added a commentary. The reader will also find a valuable discussion on the biogeochemistry of gold (and silver) in the recent compilation by Manskaya and Drozdova (1968) on the geochemistry of organic matter.

### *Gold in plants*

The gold content of plants varies over a wide range, and hence average values are practically meaningless. It is difficult to comment on the analyses quoted in the literature since they have been done by many different investigators and by a great variety of different methods over a period of some 50 years. Table 23 shows the ranges in various types of plants. For particulars the reader should consult the extensive compilation by Jones (1970) and the various references noted in the table.

Table 23. Gold content of plants*

| Type of plant | Au in ash (range) (ppm) |
|---|---|
| *Nonvascular* | |
| Bacteria | no data |
| Algae (marine) | 0.00015–1.7 |
| Algae (terrestrial) | no data |
| Fungi (terrestrial) | trace–11.6 |
| Lichens | 1–1.3 |
| Mosses | 0–19.2 |
| *Vascular* | |
| Herbs | |
| Grasses and sedges | 0–8.6 |
| Forbs | 0–610 |
| Shrubs | 0–600 |
| Trees | |
| Coniferous | 0–6 |
| Deciduous | 0–10 |
| *Miscellaneous* | |
| Honey | not detected |
| Wine (U.S.S.R.) | 0.030–0.758<br>μg/L (ppb) |

*Compiled from data by: Aferov *et al.* (1968)
Aripova and Prikhid'ko (1965)
Aripova and Talipov (1966)
Babička (1943)
Beridze *et al.* (1969)
Boyle (unpublished)
Cannon *et al.* (1968)
Curtin *et al.* (1968)
Erämetsä (1954)
Fukai and Meinke (1962)
Kaspar *et al.* (1972)
Khotamov *et al.* (1966)
Korotayeva and Polikarpochkin (1970)
Lungwitz (1900*a,b*)
Razin and Rozhkov (1963, 1966)
Schiller *et al.* (1971*a,b*, 1973)
Stark (1943)
Warren and Delavault (1950)
Zvyagintsev (1941)

There are insufficient data on the gold content of nonvascular plants to draw any satisfactory conclusions about the capacity of these plants to accumulate gold. Certain species of fungi (*Boletus*) seem to accumulate gold. Fungi (mushrooms) also appear to accumulate silver in places (*see* the compilation by Boyle, 1968*b*). Razin and Rozhkov (1966) analyzed five samples of various lichens and found an average of 1.0 ppm Au in the ash, about twice that found in their soil substrates. Lichens tend to concentrate copper, silver and other elements where they are available in the substrate (Lounamaa, 1956; LeRoy and Koksoy, 1962), and may well be accumulators of gold where it is available either in the substrate or in surface waters.

Shacklette (1965) did not detect gold in his study of various liverworts and mosses, but Razin and Rozhkov (1966) found up to 19.2 ppm Au in various species of bryophytes. The amount of gold in the ashes of the mosses generally exceeded that present in their substrates.

Fungi and bacteria may have an important role in the cycle of gold in nature. Hatschek (1919) and Williams (1918) noted that colloidal preparations of gold produced by the addition of tannic acid tend to become mouldy, and that the mould, in the course of time, removed the metal from solution. Williams' (1918) experiments with colloidal gold solutions and fungi showed the following:

1. Conidia of *Penicillium glaucum* and *Oidium lactis* developed in colloidal gold solutions which contained tannin or gum arabic.
2. The living fungus, during growth, removed the metal from the solution. Retention occurred in such cell walls as are not cuticularized.
3. The process goes on more irregularly when masses of dead fungus were introduced into solutions.
4. Solutions with a higher rate of diffusion coloured the fungus more quickly than those with a lower rate. In all cases the accumulation of gold finally produced a blue coloration.
5. No explanation of the process could be given.

There are also a number of other scattered references to the capability of fungi to extract gold from solution. In one interesting reference (selected abstracts from the technical literature on gold by Johnson, Matthey and Co. Ltd. for 1969, p. 1) it is reported that the Novosti Information Service in Moscow states that mould fungi extract gold from solution. Active fungi extracted 98 per cent of the metal in 15 to 20 h. Babička (1943) mentions that *Penicillium glaucum* is capable of depositing colloidal gold on its membranes and in its vicinity, and suggested that fungi in the surface parts of gold deposits and mines probably have a great influence in the transition of gold from the ionized to the colloidal state. The same author cites a number of references, which bear on the deposition of gold mainly as a colloid by various micro-organisms. Barbieri (1935) describes various gold-bacterium complexes, which are formed when bacteria are treated with solutions of $AuCl_3$.

Parès and Martinet (1964) carried out an extensive investigation of the role bacteria can play in the cycle of gold. They found that gold from laterites and other gold-bearing materials could be solubilized by autotrophic bacteria, such as the nitrogen fixing species, and to a much smaller extent by various heterotrophic bacteria existing in the soil, water and air. The solubilization of gold by bacteria can be marked, but several factors influence the phenomenon, such as the pH, the age of the cultures, the quality of inoculum, the concentration of gold in the medium and the nature of the nitrogenous and carbonaceous nutritive substances. These and other factors discussed by the authors should be referred to in the original paper. It is of particular interest to note that the solubilization activity of the various bacteria was strongest with strains obtained from soils over gold-bearing deposits.

In a Canadian patent, A. A. Mayling (Chemical Abstracts, v. 66, 13120b, 1967) describes the use of bacteria to keep aerated ferric chloride solutions oxidized for leaching ores containing Au, Ag, Cu and Pb. Suitable bacteria are *Ferrobacillus ferrooxidans* and *Thiobacillus ferrooxidans.* At acid pH (1–3) and temperatures ranging from 15 to 40°C these Fe-oxidizing bacteria depress the normal reduction of ferric chloride resulting from reaction with the metals or sulphide in the ore. Presumably the gold taken into solution is complexed as chloride. The implication of the action of such bacteria in the mobilization of gold in the oxidized zones of gold deposits containing abundant iron minerals is obvious, considering the fact that the Fe-oxidizing bacteria are of common occurrence and that complexing substances such as Cl and organic compounds are, likewise, common in some environments.

Lyalikova and Mokeicheva (1969) examined the role of bacteria in the migration of gold during the oxidation of gold deposits. They found that numerous heterotrophic bacteria have the ability to dissolve gold, and that various sulphur compounds (e.g., thiosulphates) that accumulate in solutions during the oxidation of sulphides by sulphur bacteria contribute to the solution of gold. A culture isolated from the Zodsk gold deposit, similar to *Bacillus alvei* was the most active and dissolved 500 to 600 μg/L (ppb) Au in 3 weeks. The largest amounts of gold solubilized in the experiments were obtained when stibnite was present – an interesting fact and one that supports the writer's contention that gold is frequently transferred in nature as some form of antimony compound. The authors concluded from their laboratory experiments and microbiological examination of the Zodsk gold deposit that bacteria play a significant role in gold migration.

In a recent report K.G. Doxtader (U.S.Geol. Surv., Circ. 622, p. 13) summarized his work involving the testing of the ability of various soil bacteria and fungi to grow in liquid media containing different concentrations of the metals including gold, silver, mercury, copper, lead, manganese, cobalt, chromium, molybdenum, tin, cadmium, uranium, vanadium, tungsten, zinc and palladium. He found that one fungus could grow in a concentration of 25 ppm Au, and 12 species of bacteria and fungi could grow in cultures containing 10 ppm Au. On the other hand, cultures containing >5 ppm Ag or Hg were found to be lethal to all organisms tested; some organisms could grow in saturated solutions of copper, manganese, molybdenum, lead, uranium, tungsten and zinc. Two bacteria species (not named in the report) previously reported to be capable of solubilizing native gold (up to 1.5 ppm in solution) were also tested for a period of 3 weeks, with negative results.

In a more detailed account of his work Doxtader (*in* Lakin *et al.,* 1974) concluded as follows:

> In the microbiological studies, elemental gold was added to liquid nutrient media which were then inoculated with pure cultures of bacteria and fungi either obtained from stock collections or isolated from soil. In a glucose-peptone medium containing colloidal gold, significant gold solubilization occurred. In other media or with powdered gold, metal solubilization was slight. The microbial strains showed various abilities to solubilize the noble metal. In sterile glucose-peptone medium gold solubilization occurred, but, in the same medium inoculated with various microorganisms, the solubilization of gold increased.

Doxtader (*in* Lakin *et al.,* 1974) also tested soils and stream sediments from Cripple Creek, Colo., to determine whether specific bacteria or fungi occurred in materials containing gold. No significant differences in numbers or kinds of micro-organisms present were found between gold-bearing and barren samples.

During recent investigations of the effect of organisms on the geochemical cycle of gold Mineev (1976) concluded that the dissolution, colloidal formation and precipitation of gold take place in nature with the participation of various micro-organisms.

Of the vascular plants the herbs have received the most attention with respect to their gold content. Razin and Rozhkov (1966) analyzed a number of samples of various grasses and sedges, including entire plants and the stems, leaves and fruit of the plants. Their values range from 0.005 to 8.6 ppm in the ash. Over some of the placer deposits in the Beauceville area of Quebec the writer has found an average of 2.4 ppm Au in the ash of various grasses (whole plants, excluding roots; 9.3% ash, mainly silica). This compares with an average of 9.2 ppm Au in the ash of *Equisetum* in the same area (whole plants, excluding roots; 26% ash, mainly silica). It would appear from these values that there is a relationship between the gold and silica content of plants, the higher the silica the greater the gold content, all other things being equal. This feature is also mentioned by Babička (1943) and Thyssen-Bornemisza (1942).

The gold contents of grasses and maize (*Zea mays*) have been investigated recently by Schiller *et al.* (1973) using neutron activation analysis with a view to determining the influence of seasonal variations of samples in a gold-bearing area. The contents in the ash of maize ranged from 0.008 to 0.103 ppm Au; in the ash of grasses the values were 0.009 to 0.040 ppm Au. Marked seasonal variations were noted between the three seasons, spring, summer and autumn. These are important data for biogeochemical prospecting purposes. The investigators recommend that sampling should be done preferably in the spring since this is the time when the maximum amount of gold is taken up by the plants due probably to higher rainfall and movement of elements in soil waters, etc.

Considerable work on the gold content of various forbs has been done in the last 40 years. The range in the values is from 0 (not detected) to 610 ppm Au. Babička (1943) and his colleagues carried out investigations on the gold content of a variety of forbs for some 10 years, paying particular attention to plants such as corn, beans and horsetails (*Equisetum*). In the ash of *Equisetum palustre* (marsh horsetail) he found 610 ppm Au in the andesitic region of Oslany, Czechoslovakia, where the gold content of the soil averaged about 0.2 ppm. In two other samples of *Equisetum arvense* contents of 16 and 63 ppm Au were reported in the ash. These results seemed to indicate that *Equisetum* is a gold accumulator. However, Cannon *et al.* (1968) found that *Equisetum* averages only 0.17 ppm Au in the ash in the samples they investigated from a number of mineralized areas in the conterminous United States; in samples from Alaska they found up to 0.5 ppm Au in the ash. These values are about the same as those reported by Warren and Delavault (1950) and Razin and Rozhkov (1966) in various varieties of *Equisetum.* Cannon *et al.* (1968) concluded that the high values quoted by Babička and other workers may be erroneous since a study of the analytical procedures that were used suggest that other metals in the plants, some of which are relatively high (e.g., zinc, copper), may have been measured and reported as gold.

Our research on *Equisetum* seems to indicate that horsetails may be accumulators of gold. Over some of the placers of the Beauceville area, Quebec the ash of horsetails contained up to 9.2 ppm Au (whole plants, excluding roots; 26% ash). *Equisetum* ash from the Ramore area of Ontario, well removed from gold mineralization, contained 0.095 ppm Au; the corresponding silver value was 2.4 ppm. *Equisetum* growing on old tailings piles on the Hollinger property at Timmins, Ontario contain considerable amounts of gold according to a personal communication to the writer from Mr. C.D. MacKenzie, Chief Geologist of Hollinger Gold Mines (1970). The gold content of the ash of these plants ranged from 0.01 to 0.25 oz Au/ton (0.3 to 8.5 ppm).

The gold content of shrubs ranges from 0 to 600 ppm. Babička (1943) found 600 ppm in the ash of the seeds of *Clematis vitabla* (virgins' bower) in the andesitic region of Oslany, Czechoslovakia. The soil and weathered debris contained 0.2 ppm Au. In the wood and fruit of the same shrub and of *Corylus avellana* (hazel nut) and *Rosa Canina* (dog rose) from Oslany and other areas in Czechoslovakia the same author found gold contents ranging from trace to 110 ppm in the ash. It is interesting to note that relatively large amounts of gold occur in seeds. This is also true for silver as pointed out by the writer (Boyle, 1968*b*). Warren and Delavault (1950) found only small amounts of gold (nil and $<0.03$ ppm) is the ash of *Juniperus communis* (dwarf juniper) in the North Fork of Watson Bar Creek in the Clinton Mining Division of British Columbia. Gold occurs in quartz veinlets in this area. Razin and Rozhkov (1966) analyzed a number of shrubs in the vicinity of the Kuranakh gold deposits, Yakutia. Their values range from 0 (not detected) to a maximum of 10 ppm Au in the ash; this can be compared with a maximum of 8 ppm Au in the soil. However, they found that in some 65 per cent of the soil and shrub ash samples that the maximum gold contents in the soil exceeded those in the ashes of the shrubs. Aripova and Talipov (1966) investigated the gold content of a number of shrubs and herbs in the gold belts of Uzbekistan. The species sampled were wormwood (*Artemisia terrae-alba*), salsola (*Salsola* sp. and ferula (*Ferula* sp.). The largest amounts of gold were found in the ash of wormwood (up to 125 ppm Au). The average gold content in the plants over auriferous zones ranged from 20 to 50 ppm Au and greater. The largest amounts of gold were found in the plants during springtime and early summer (May-June), the blooming and fruiting period. Khotamov *et al.* (1966) used neutron activation methods to determine the gold content of a number of shrubs and their organs in one of the ore fields of the gold-bearing Kyzyl-Kum district, U.S.S.R. Their values ranged from 0.3 to 36 ppm in the ash. The soil substrates contained from 0.2 to 1.5 ppm Au. The leaves of some shrubs contained more gold than the stems and roots, whereas in other plants the gold content was relatively uniform in all organs. The largest amounts of gold (and arsenic and antimony) in the plants were observed during the period of intensive growth and the smallest amounts in dried (dead) plants. No relationship was detected between the ash content and the overall content of gold (and arsenic and antimony). Arsenic and antimony were also determined by activation methods on the vegetation and soil. A direct correlation between gold and antimony was found in the soil and plant ash, whereas a correlation between gold and arsenic in the soil and plant ash was not always observed.

The gold content of trees ranges from 0 (not detected) to 10 ppm in the ash. Lungwitz (1900*a,b*) appears to have been one of the first to report the presence of gold in trees, specifically in what he called 'iron wod' from the Omai Valley in British Guiana. The work was done mainly to prove that gold migrates in surface waters. Babička (1943) records up to 10 ppm Au in the ash of the blossoms of *Tilia parvifolia* (linden). Warren and Delavault (1950) found from 0 to 1.02 ppm Au in the ash of *Pinus contorta* (lodgepole pine), *Pinus ponderosa* (western pine), *Pseudotsuga taxifolia* (Douglas fir), *Salix* sp (willow) and *Populus tremuloides* (aspen) in the North Fork of Watson Bar Creek, British Columbia. In areas unmineralized with gold (negative areas) the gold contents in the ash of these trees ranged from nil to 0.03 ppm. In the vicinity of quartz veinlets carrying gold (positive areas) the contents in the ash ranged from nil to 1.02 ppm. Silver was also determined in the ash of the trees. Calculations based on the values given indicate that the Au/Ag ratio in the ash is about 0.06. Other investigations of the gold content of trees include those by Zvyagintsev (1941), Razin and Rozhkov (1963, 1966), and Khotamov *et al.* (1966). Their values range from 0 (not detected) to 6 ppm in the ash of various species.

Concerning plant products Berg (1928) did not detect gold in honey. In wines from the U.S.S.R., Beridze *et al.* (1969) by activation analysis found from 0.030 to 0.758 μg/L (ppb) Au. The level of the gold content in red wines was considerably higher than that in white wines. Most of the gold was thought to have come from the soil with minor contributions from the apparatus used in the processing of the vineous spirit.

Seasonal variations in the gold content of plants have been noted by some investigators, but the data are insufficient to draw adequate conclusions. Aripova and Talipov (1966) report that the ash of Artemisia (wormwood) contains from 10 to 20 times more gold (and copper, lead and chromium) in May than in October, and that these metals tend to be highly concentrated in plants in desert regions. Khotamov *et al.* (1966) found that the largest amounts of gold (and arsenic and antimony) occur in plants during the period of intensive growth and the least in plants that have died and dried up. As noted above Schiller *et al.* (1973) noted marked seasonal variations in the gold content of plants, the maximum concentrations being present during springtime.

With respect to the content of gold in the various organs of plants, Khotamov *et al.* (1966) state that the largest amounts of gold are concentrated in the above ground portions of plants, particularly in the leaves of some species. Seeds may be concentrators of gold in a manner similar to that found for silver (Boyle, 1968*b*).

There appears to be no particular relationship between the gold content and the ash content of plants. There may, however, be a relationship between the silica content of plants and their gold content, but more work is required to confirm this. Khomatov *et al.* (1966) found a definite direct correlation between gold and antimony in the ash of plants, a correlative feature that also holds in most gold deposits. The correlation with arsenic was less definite.

The data with respect to the ratio – Au in soil/Au in plant ash – are conflicting. Some investigators have found this ratio to be less than 1 whereas others have found the reverse. It is well known that this ratio depends on a veritable host of factors, and one would expect wide variations and reversals to be general, even locally, as some of the data in the literature clearly show. A detailed study by Razin and Rozhkov (1963) over the Kuranakh (karst) type of gold deposits in Yakutia showed that there was a direct relationship between the content of gold in the ashes of the plants and the content in the soil substrate.

The uptake and translocation of gold by plants has been studied by a number of investigators including Zvyagintsev (1941), Babička (1943), Razin and Rozhkov (1963), Shacklette *et al.* (1970) and Schiller *et al.* (1971*a*).

Zvyagintsev (1941) speculated that the solutions secreted by the root hairs of plants were capable of solubilizing gold in their vicinity, and that the gold entered the plant in an ionized form.

Babička and his colleagues after more than 10 years of study on the gold content of plants concluded the following:

1. Only a few plants can take up gold in large amounts.
2. The concentration of gold is characteristic for certain plants; it is not, however, definitely known whether gold has a favorable effect on the growth and the life functions of these plants.
3. The gold taken up by the roots of a plant spreads throughout the plant and becomes concentrated in certain organs. In the case of seed-bearing plants, this is usually in the seeds. With increasing age of a plant there is a progressive increase in the gold content.
4. Plants absorb ionized gold derived from solid particles of gold, particularly when the metal is in the colloidal state. In nature, colloidal gold is concentrated mostly in the rhizosphere (root layer), perhaps by the actions of plants and organisms generally. If gold occurs in the soil in the form of small nuggets, tablets, fine wires, etc. it is practically unavailable to plants.

Razin and Rozhkov (1963) concluded from their data on gold in plants and soils over the Kuranakh (karst) type of gold deposits in Yakutia that the gold is assimilated by plants in the ionized form.

Shacklette *et al.* (1970) experimented with the uptake and translocation or radioactive ($^{198}$Au) and nonradioactive gold ($^{197}$Au) by impatiens (*Impatiens holstii*), garden balsam (*I. balsamina*) and onion (*Allium cepa*). They found that colloidal gold was not absorbed by the roots of these plants, and that of the solutions of gold used (chloride, cyanide, bromide, iodide, thiocyanate, thiosulphate and gold cyanide solution *via* flax) the gold cyanide is the most readily absorbed by roots and transported in largest amounts to the leaves. They concluded that if gold is present in the soil and if cyanogenic plants are rooted in this soil, a mechanism is present for the entrance of gold into the biogeochemical cycling process.

Schiller *et al.* (1971*a*) experimented with the uptake of radioactive gold by barley from solutions containing in one case aurothiomalic acid-Au-198-sodium salt and in another case colloidal gold (Au-198) (particle size range up to 200 Å) stabilized with gelatin. In both cases the uptake of gold was almost quantitative, from which the authors concluded that gold accumulation by plants, both in colloidal and ionized form, is possible.

In recent papers Talipov *et al.* (1975, 1976) have noted that the accumulation of gold (and a number of other elements) in plants in the Karamin Range, U.S.S.R., depends to a large degree on the concentration of the element(s) in the groundwaters and soils. In particular they noted a linear correlation between the Au, Ag, Cu, Zn and Pb contents of plants and that of soils and waters. They also observed that some elements have an antagonistic effect on the uptake of certain elements in plants; thus high calcium contents in groundwaters decreased the migration of gold and hence its accumulation in plants.

The nature of gold in plants is not known. It may be present largely in the chlorophyll (a porphyrin), since a gold (III) porphyrin, which is relatively stable, has been synthesized (Fleischer and Laszlo, 1969). It may also be present as an organometallic compound, perhaps as a protein complex, since the metal, like silver, is apparently concentrated in seeds which are especially high in protein. The role of gold, if any, in plant metabolism is unknown.

According to Babička (1943) small quantities of gold stimulate the growth of plants and micro-organisms, whereas large amounts are toxic. He cites a number of researches to support this contention. Felippe and Martins (1926) found that native gold had an oligodynamic (growth inhibiting) action on *B. dysenteriae* Flexner, and Nadson and Stern (1934) observed that native gold placed at a distance of 2 to 3 mm from white mustard seeds retarded the germination of the seeds and the growth of the sprouts. Shacklette *et al.* (1970) found that concentrated solutions of radioactive gold cyanide were extremely toxic to all *Impatiens* whereas low concentrations of the compound were not toxic. Radioactive gold bromide solutions were very toxic to *Impatiens*, and radioactive gold iodide solutions were found to be extremely toxic to all plants experimented with. Radioactive gold thiocyanate was toxic to unrooted cuttings of *Impatiens*, whereas the nonradioactive solutions were less toxic. Gold thiosulphate solutions were only slightly toxic to all *Impatiens.* The toxic effects manifested by gold solutions on plants are principally wilting of leaves and stems, necrosis and chlorotic symptoms. None of these effects have been observed by the writer in plants growing in soils and placers rich in gold in Canada, nor are there any references in the literature to such effects attributable to the presence of gold in other countries. The writer has also not observed any stimulative effects on plants that could be related to the presence of small amounts of gold in soil and soil solutions.

Some plants appear to be gold accumulators. The case for *Equisetum* needs verification, and further careful studies should be carried out on this plant, especially where it grows on gold-enriched soils. Grasses also appear to accumulate gold in places. Fungi and lichens are probably accumulators of gold where the element is readily available, and some mosses also appear to concentrate gold according to the data provided by Razin and Rozhkov (1966). Khotamov *et al.* (1966) state that *Lagochilus intermedius, Artemisia terrae-alba* and *Cousinia hamadae* are concentrators of gold in the Kyzyl-Kum region of U.S.S.R. Certainly some of the wormwood shrubs (*Artemisia*) are greatly enriched in gold (up to 125 ppm Au in the ash) in the arid regions (Tamdynsk Mountains) of Uzbek, U.S.S.R. according to the data of Aripova and Talipov (1966). The average for these shrubs over gold-bearing zones in many cases ranges from 20 to 50 ppm Au. According to a later communication by Talipov and Khotamov (1974) a number of desert and arid land plants in the Tamdynsk Mountains (central Kyzyl-Kum) concentrate large amounts of gold, including *Lagochilus intermedius* (36 ppm in the ash), some *Salsola* (saltwort) species, *Artemisia* and *Stipa* grasses. Certain plants such as *Spiraea* and honeysuckle accumulate large amounts of gold when growing on or near auriferous deposits in the Chatkal-Kurama region of U.S.S.R. (Talipov *et al.* 1976). In India Dekate (1971) has noted that plants producing hydrocyanic acid such as *Sorghum saccharatum* are capable of preferentially absorbing gold from the soil over auriferous deposits, at times, to the extent of depleting gold in the soil in the proximity of plant roots. (*See also* the section on biogeochemical prospecting in Chapter V.)

Direct gold indicator plants appear to be rare if in fact such plants actually exist. Dorn (1937) says that "Gold indicator plants are up until the present only known from Brazil where *Cecropia laetivirens Hub., C. palmate Willd, C. lyratiloba, Alpinia speciosa Schum., Typha dominguensis Kunth,* and *Typha latifola L.* not only contain gold in their ashes but also according to F. Freise are reliable indicators of gold placers." Babička (1943) mentions that prospectors searching for gold and silver deposits in Queensland, Australia, looked for the shrub *Lonicera confusa DC,* which grows preferentially on gold- and silver-bearing soils. A shrub in California is also said by R.H. Stretsch to indicate the presence of gold, but no details of this plant are given.

It is interesting to note that the early Chinese considered some plants to be indicators of gold and silver deposits. Needham (1959) quotes Tuan Chlêng-Shịh in the *Yu-Yang Tsa Tsu* written *circa* 800 A.D. as saying:

"When in the mountains there is the *tshung* plant (ciboule onion; *Allium fistulosum*), then below silver will be found. When in the mountains there is the *hsiai* plant (shallot; *Allium bakeri*), then below gold will be found."

There are numerous other similar statements pertaining to gold in the old Chinese literature on geological and mining subjects, but space precludes their mention here. One is of interest, however, namely that the Chinese noted the presence of the *chhi* (essence) of gold in the rape-turnip (*Brassica rapa-depressa*) (Needham, 1959).

It is worth noting that the coincidence of occurrence of the onion species (*Allium* sp.) and the precious metals, silver and gold, is probably an indirect one, the relationship being more dependent on the presence of sulphur. The writer has noted that various species of wild onions and the meadow garlic (*Allium canadensis*) often proliferate where an abundance of sulphate is available from the oxidation of sulphide deposits, some of which may be auriferous. It is also well known that the *Allium* species, especially garlic, is generally rich in sulphur, and some species seem to take up more than average amounts of arsenic, an element universally associated with gold and silver. The turnip is likewise rich in sulphur.

According to a recent report (Engineering and Mining Journal, v. 177, p. 32, 1976) (Chem. Abstr., v. 34, 111234h) the water hyacinth (*Eichhornia crassipes*) is an accumulator of gold and silver. If experiments are successful it is planned to use the plant to recover the two precious metals from solutions leaching old Cripple Creek mining tailings. In the article it is stated that "under a regular harvesting program, an acre of hyacinths can yield silver at a rate of a pound every four days, and similar results are anticipated for gold."

Contents

### *Gold in animals*

Gold has been determined in only a few animals, the data available being shown in Table 24. Reviews of the gold content of animals have been published by Babička (1943), Vinogradov (1953) and Jones (1970).

Noddack and Noddack (1939) found from 7 to 30 ppb Au in the dry matter of a number of marine organisms, contents similar to those found by neutron activation methods in a variety of sea animals by Fukai and Meinke (1962) and Bowen (1968). Their values range from 0.0012 to 126 ppb Au in the dry matter. The average gold content for all marine organisms done by activation methods is 23.84 ppb. Compared with the average gold content of the sea (0.02 ppb) the enrichment factor of gold in the dry part of marine organisms is 1200. Enrichment factors similar to this figure are not unusual in marine organisms.

Babička (1943) and his colleagues analyzed june bugs from the auriferous Oslany region of Czechoslovakia finding an average of 25 ppm Au in their ash. In another location, which is nongold bearing, near Stříbrná Skalice (Bohemia) they found no gold in the ash of these insects. They reasoned that the june bugs feeding on the leaves of gold-bearing plants accumulate gold, whereas those feeding on nongold-bearing plants do not have the opportunity of concentrating the metal. To prove this they starved the gold-bearing june bugs for a time, then fed them on leaves which contained no gold. A reduction of the gold content from 25 to 18.5 ppm was observed in their ash. Razin and Rozhkov (1966) did not detect gold in the water beetle (*Dytiscus* sp.) or in the carpenter ant (*Camponotus vagus*) but found 400 ppb Au in the ash of a bee (*Vispidae* sp.).

Table 24. Gold content of animals

| Type of animal | Au | Reference | Remarks |
|---|---|---|---|
| *Marine animals* | (ppb) | | |
| Sponge | 10 | 1 | In the dry matter |
| Sponge (various) | 18–126 | 2 | In the dry matter |
| Sea urchin | 7 | 1 | In the shell |
| Starfish | 30 | 1 | In the dry matter |
| Sea cucumber | 24 | 1 | In the dry matter |
| Jelly fish | 7 | 1 | In the dry matter |
| K. fische (Lippfische) | 10 | 1 | In the dry matter |
| Clam (*Tapes japonica*) | 5.7 | 3 | In the dry matter of the soft parts |
| Prawn (*Pandalus* sp.) | 0.28 | 3 | In the dry matter of the soft parts |
| Mackerel (*Pneumatophorus japonicus*) | 0.12 | 3 | In the dry matter of the muscle |
| *Terrestrial animals* | | | |
| Crustaceans (crab) | 0 | 4 | In the shell |
| Insects | | | |
| June bugs | 25000 | 4 | In the ash |
| Bee (*Vispidae* sp.) | 400 | 5 | In the ash |
| Water beetle | 0 | 5 | In the ash |
| Carpenter ant | 0 | 5 | In the ash |
| Birds | | | |
| Various | 0–1500 | 5 | In the ash |
| Animals | | | |
| Various | 0–14000 | 4,6 | In wet and dry matter |

Reference: 1. Noddack and Noddack (1939.)
2. Bowen (1968).
3. Fukai and Meinke (1962).
4. Babička (1943).
5. Razin and Rozhkov (1966).
6. Jones (1970).

Razin and Rozhkov (1966) analyzed a number of birds, including crossbills, buntings, pipits and a thrush in the vicinity of the Kuranakh gold deposits, southern Yakutia. The gold contents in their ashes ranged from 0 (not detected) to 1.5 ppm. There are numerous references to the occurrence of gold nuggets in the crops of birds.

Gold has been detected in a number of animals and in man. Babička (1943) and his colleagues detected relatively high contents of gold in the ash of the antlers of deer and in the hair. Contents from 0 (not detected) up to 68.6 ppm Au were found in the antlers and other parts of deer in the gold-bearing Oslany region of Czechoslovakia. The highest contents of gold were found in the tips of the antlers. No gold was found in the antlers of deer from the barren Malacky area in western Slovakia or in the eastern Carpathian Mountains. A wild boar bagged in the Oslany area contained no detectable gold. Jones (1970) found only 0.5 to 28.3 ppb Au in the ashes of the antlers of 15 mule deer (*Odocoileus hemionus*) harvested from four gold-mining regions in the United States. The largest amounts of gold occurred in the tips of the antlers. The contents found by Jones are much less than those recorded by Babička; they approximate the contents found in common rocks.

Bertrand (1932) detected gold in cow liver and brains, and in human blood, feces and urine. His values range from 0.2 to 14 ppm Au, the largest amount being in the cow brains. In wet human liver Parr and Taylor (1963) found from 0.013 to 0.79 ppb. In human blood and its components the gold content ranges from 0.06 to 0.8 ppb (Bagdavadze *et al.,* 1965). Human hair appears to be enriched in gold according to the data given by Bate and Dyer (1965). They recorded means ranging from 2.7 to 43 ppb Au in people from Tennessee and New Zealand.

The data on the gold content of animals is inadequate, scattered, unsystematic and often conflicting. Conclusions seem unwarranted except to note that marine animals seem to have slightly lower amounts of the element than terrestrial animals. Gold seems to be concentrated in relatively large amounts in the proteinaceous substances of animals (hair, brains, muscle of fishes), which suggests that the element may be largely present as gold-protein complexes in animals, probably bound to the thiol groups in the complexes. In this respect gold behaves much like mercury, its adjacent element in the periodic table. The role of gold, if any, in animal metabolism is unknown.

There appears to be no auriferous animals as far as the data goes. Animals in gold-bearing regions may contain larger amounts of the metal, but the data provided by Babička (1943) and Jones (1970) are conflicting with respect to the antlers of deer. The subject should be further investigated.

It is interesting to note that the old literature is replete with references of unusual occurrences of gold in animals. Gold nuggets and particles of auriferous quartz have been found in the crops of partridges, hens, ducks and geese in many gold-bearing regions of the world, but particularly in Rumania and Hungary. Gold, plating the teeth of goats, sheep and cattle grazing in auriferous regions, is also recorded in some old manuscripts. Buried human skulls in certain auriferous streams have been observed to contain particles of attached gold.

*Homo sapiens* is a concentrator of gold and silver but in ways other than biochemical. Since the beginning of early gold mining (circa 4000 B.C.) man has accumulated an estimated hoard of some 3 billion ($3 \times 10^9$) oz in his vaults, a small amount (0.00008%), however, compared with the total amount of gold in the earth's crust ($3.8 \times 10^{15}$ oz). By contrast man has won about 35 billion ($35 \times 10^9$) oz of silver from the earth. The ratio of extraction of Au/Ag is, therefore, 3/35 or 0.08, a value near that for the ratio found for the two elements in the earth's crust (0.1).

*Gold in humus, peat bogs, muskegs and marshes*

Gold, in common with many of the metals, tends to become enriched in humus and humic deposits. The reasons are the strong adsorptive and absorptive capacity of humus for metals and the presence in humic deposits of various reducing substances and $H_2S$.

Goldschmidt (1935) found 0.2 ppm Au in the ash from beech humus in the Sababurg area near the Weser River in Germany. Deul (1958) noted the presence of gold in the ash of humic acid fractions separated from peat. He did not detect the element in plant ashes, in the whole peat ash, nor in any other fraction separated from the peat. This suggests that gold in the peat is mainly associated with the humic components. Curtin *et al.* (1970) and Lakin *et al.*, (1974) found from <0.04 to 5.1 ppm Au in samples of mull (forest humus layer) taken from gold-bearing areas in U.S.A. (*see* Table 20). They were able to leach small amounts of gold (27–120 parts per trillion, $10^{12}$) from the mull with demineralized water and concluded that much of the gold in the leachates was present mainly in the form of extremely small colloidal particles ($<0.05\ \mu$ diameter) with minor amounts of gold in the ionized state as thiocyanate and cyanide. My research on gold in soil profiles indicates that gold is commonly enriched in the humic layer of the soil (*see* Table 20 and the section on gold in soils in this chapter), and I think that much of the gold in the humic horizon of soils is bound mainly as a humate, perhaps in a chelated or other organometallic configuration.

The organic matter in bogs, muskegs and marshes is enriched in gold in certain areas. The copper bog near Sackville, New Brunswick, which contains up to 4 per cent copper, is also enriched in gold in amounts up to 2.3 ppm and in silver in amounts up to 5 ppm in the dry matter (Boyle, 1977). Bog manganese in peat in some places in New Brunswick carries from 0.01 to 1.4 ppm Au and from 0.8 to 2 ppm Ag in the dry matter (Table 22).

Other types of humic deposits also seem to be high in gold and silver in places. Blanchard (1933) mentioned organic (probably humic) substances with relatively large amounts of manganese near seepages in New Guinea that carry up to 27 920 ppm Au and 15 660 ppm Ag (Table 22). Decaying wood tends to concentrate gold from solution. There are numerous references in the older literature to the occurrence of relatively high amounts of gold in pit props and mine timbers. Babička (1943) also refers to the facility with which decaying wood concentrates gold from solution. Palmer (1935) found marked enrichments of gold and silver in petrified (silicified and carbonized) logs in the Aspen district of Nevada. Samples taken of one log contained 18.26 oz Au/ton and 10.8 oz Ag/ton (624.5 and 369.3 ppm respectively). He concluded that the carbonized wood had precipitated the gold from circulating solutions.

In U.S. Geological Survey, Circular 560, p. 17 (1968) it is reported that 12 samples of peat, muck and driftwood from streams and wet areas near the Front Range mineral belt in Colorado were analyzed for gold on a dry sample basis. Muck from Elk Park and peat from Rudolphs Bog contained 0.3 ppm gold; driftwood from Clear Creek and soft peat from Caribou Peat Bog contained 0.2 ppm. All other samples had less than 0.1 ppm.

Bensusan (1942) records data on an interesting concentration of gold in Lower Burma, which is probably at least partly due to organic agencies. He states:

> Between Tenasserim and Mergui, and impinging on the latter, there exists a very remarkable auriferous deposit in which it is estimated there is upwards of £200,000,000 worth of gold in one concession alone of about 120 square miles. This statement might appear to be exaggerated, but it is a fact, nevertheless. The writer had to investigate this occurrence as well as the deposit at Tenasserim and he was asked to find a means of recovering the gold. Research work was carried out both in Burma and in London with the help of skilled chemists, metallurgists and geologists for nearly a year working on a ton sample sent for the purpose. While hundreds of assays on large samples show without any doubt that the material carries an average of about 4.0 grains of fine gold per ton (0.285 ppm Au), no means could be found for recovering it by any straking or amalgamation method. The gold appears to be in colloidal form as repeated examinations of sample and concentrate under high power microscope failed to show any free gold. In spite of all that was done the tailings from the tests always assayed as much as the heads. No satisfactory theory has yet been put forward as to the origin of the gold nor as to the form in which it exists.
>
> It has been shown that the deposit, which is mangrove swamp mud, could be exploited by means of a suction dredge at a cost of 3d. or 4d. per cubic yard, i.e., as far as excavation and delivery of alluvium to strakes or other appliances used on dredges for alluvial gold recovery are concerned: and since the average value of the mud can be very conservatively taken at 1/6 per yard, there is a fortune waiting for anyone who can devise an economical method of extracting the gold.
>
> A number of boreholes were put down in the mud in various places to depths of about 30 ft. and every sample taken showed gold by fire assay. One borehole was put down to 90 ft. without meeting bed rock and samples roughly taken from the bank of the river always showed values.
>
> In all the straking experiments a small amount of concentrate was recovered which consisted of pyriticised foraminifera, very beautiful microscopic shells of innumerable shapes, but this concentrate yielded only a few grains of gold per ton as well as traces of platinum and iridium.

The manner of occurrence of gold in humic deposits is relatively unknown. In some deposits a small part of the gold appears to be in an adsorbed form, since it can be removed by weak cyanide and aqua regia solutions. The remainder, generally the greater part, is tightly bound in the brown humic complexes. Ong and Swanson (1969) consider that gold is present mainly as a colloid stabilized by a protective layer of organic molecules around the gold in an organic environment (*see also* the section on natural waters in this chapter). Shabynin (1970) observed experimentally that gold is absorbed by peat in about the same amounts as by quartz. He concluded that organic gold compounds are formed, part of which remain in the peat and part of which are soluble and render the gold mobile.

### *Gold in coal*

Gold is a frequent microconstituent in a number of coal seams, but is generally present in amounts less than 0.05 ppm in the ash (Table 25). Certain coal seams, however, appear to be greatly enriched in gold and silver. Lock (1882) and Maclaren (1908) mention the presence of gold in the pyrite of coal, in coaly matter or in sandstones and conglomerates of coal measures in Borneo; Gippsland, Victoria; Tallawang, New South Wales; New Zealand; Tasmania; Deadwood, South Dakota; and the Witwatersrand. The last is probably not coal but thucholite which carries abundant gold in the Rand (*see* the section on the Witwatersrand in Chapter III). Rose and Newman (1937) mention the presence of a rich deposit of gold in lignite in Japan but give no details. There is also a reference to gold in coal in the Batrina Mine in Verespatak, Transylvania in the old literature but again no details. In a summary on gold in coal Lincoln (1911*b*) and Gibson and Selvig (1944) mention the presence of the element in a number of Cretaceous coals in the western United States. The ashes of some of these contain up to 0.5 oz Au/ton. Details are given in the papers by Chance (1900), Jenny (1903), Parsons (1907) and Stone (1912). Jones (1969) mentions, however, that more recent analyses have not confirmed these high figures. Thus, it is reported in U.S. Geol. Survey, Circular 560, p. 17 (1968) that some 400 samples of coal and associated rocks from Colorado, Wyoming, Utah and Idaho contain <0.020 ppm Au. Samples from the Cambria coal field near Newcastle, Wyoming reported in the early literature to contain up to 0.5 oz Au/ton (17 ppm) were found to contain less than 0.1 ppm Au. Some western coals, however, were found to contain small amounts of gold, particularly in coal from Kemmerer, Wyoming and Wales, Utah. No values are given for these coals since the analyses were nonreproducible, suggesting that the gold may be particulate. In U.S. Geol. Survey, Circular 622, p. 10 (1969) it is further stated by J.D. Vine that 100 samples of coal ash from U.S. Appalachian and interior coal fields all showed less than 0.05 ppm Au.

In Canada, Tyrrell (1915) mentions the presence of traces of gold in the coal of the Cretaceous Edmonton Series on the North Saskatchewan River.

At the Tyozin Mine in Japan Tertiary coal beds intercalated with sandstones are exceptionally rich in gold (Watanabe, *in* Newhouse 1942). Similarly in the Coromandel Peninsula, New Zealand, thin coal seams are rich in gold where the auriferous Tertiary veins cross them. In these cases, the gold is apparently hydrothermal in origin.

The gold content of the Carboniferous coals of the Maritime Provinces of Canada is relatively low. The coalified plant fragments in the Carboniferous sandstones are greatly enriched in silver in places, but as a general rule the gold content rarely exceeds 0.08 ppm Au, despite the presence of abundant pyrite, chalcocite and other sulphides.

There seem to be no detailed investigations on the gold content of the different ranks of coal or of the different components, viz. fusain, vitrain, clarain and durain. Analyses for gold of specialized types of coal such as torbanite, cannel, boghead, jet and natural coke are lacking as are also those for the various resinous substances such as amber associated with

Table 25. Gold content of coal

| Locality | Remarks | Au (range) | Ag (range) | Au/Ag ratio | Reference |
|---|---|---|---|---|---|
| | | (ppm) | | | |
| Germany and England | In ash | 0.2–1.0 | 0.5–10 | ~0.1 | 1 |
| U.S.A.; Wyoming and South Dakota | Ashes of Cambria coal | 17.1 (0.5 oz/ton) | – | – | 2 |
| | Sandstone roof of Cambria coal bed (pyritiferous) | 0.1 | – | – | 2 |
| | Coke made from Cambria coal | 4.2 (av.) | 14.7 (av.) | 0.28 | 2 |
| Western U.S.A. | Coal | <0.020 | – | – | 3 |
| Eastern U.S.A. | In ash | <0.05 | – | – | 4 |
| Yugoslavia; Timok Basin | In ash of lignite, bituminous and semianthracite coals | 0.117–0.573 | 2.56–6.07 | – | 5 |
| Canada; Gaspereau River area, Cape Breton Island, N.S. | In ash; Pennsylvanian coal | <0.01 | 0.78 | <0.01 | 6 |
| Canada; Harbour seam, Sydney, N.S. | In coal; Pennsylvanian coal | <0.001 | 1.2 | <0.0008 | 6 |
| Canada; Stonehaven, N.B. | In the ash; Pennsylvanian coal | <0.01–0.015 | 2.3 | ~0.004 | 6 |
| Canada; Shubenacadie, N.S. | In the coal; pyritized Cretaceous lignite | <0.005 | 1.3 | <0.004 | 6 |
| Canada; Walton, N.S. | In the coal; pyritized coal fragments near faults in Mississippian sandstones | 0.034 | 5.47 | 0.006 | 6 |
| Canada; Walton, N.S. | Pyrite and other sulphides separated from pyritized coal fragments near faults in Mississippian sandstone | 0.6 | 77.3 | 0.0008 | 6 |
| Canada; Port Hood, N.S. | Pyrite; Pennsylvanian coal | 0.04 | 0.17 | 0.23 | 6 |
| Canada; Dorchester Mine near Sackville, N.B. | Coal fragments containing chalcocite in Pennsylvanian sandstones | <0.01–0.03 | 2–190 | <0.005 | 6 |
| Canada; Shippegan Island, N.S. | Coal fragments containing chalcocite in Pennsylvanian sandstones | 0.01–0.08 | 27.5 | ~0.002 | 6 |

References: 1. Goldschmidt and Peters (1933).
2. Stone (1912).
3. U.S. Geological Survey Circular 560 (1968).
4. U.S. Geological Survey Circular 622 (1969*b*).
5. Popovic (1954).
6. Boyle (unpublished).

coal or derived from it. These substances would seem to provide an interesting field of investigation.

The occurrence of gold in coal seams is generally erratic. Judging from the writer's experience with silver (Boyle, 1968*b*) and the limited analyses for gold in coal, the distribution of gold in the seams can be summarized as follows:

1. Higher contents of gold (and silver) are generally recorded from coal seams low in ash and rich in other trace elements such as copper, lead and zinc.

2. Higher contents of gold (and silver) often accompany parts of the coal seams or their overlying or underlying rocks that are enriched in sulphides particularly pyrite. Splits containing abundant pyrite are sometimes greatly enriched in silver and gold as well as in various other chalcophile elements.

3. A parallel enrichment of the following elements has been noted in some coal seams in Nova Scotia: gold, silver, copper, zinc, lead, cobalt, nickel, tin, molybdenum, arsenic, antimony and barium. This relationship is marked in coalified fragments in the Walton area in Nova Scotia.

4. Higher gold and silver contents tend to occur in the coal near the top and the bottom of individual seams. There are also a number of references in the literature to higher contents of silver, gold and other trace elements in the rocks immediately overlying the seams.

5. In some coal seams, and in sandstones containing coal fragments, higher gold and silver contents tend to occur in the coal or in coalified fragments near faults, fractures or crushed zones.

The mode of occurrence of gold in coal and coalified fragments has not been extensively investigated. Some general observations from the literature and the writer's research follow:

1. In some coal seams the gold is present as macroscopic and microscopic forms. Much of this gold is commonly of hydrothermal origin.

2. Some gold is probably associated with the coaly substance of coal and may be bound as an organometallic complex. Bouška *et al.* (1963) concluded that gold is bound principally to the organic part of the coal.

3. A very small amount of the gold in coal may be adsorbed to the coaly substances.

4. Much gold (nature unknown) is present in or associated with pyrite (Tables 11 and 25), and some gold is generally observed in the small amounts of galena, chalcopyrite, arsenopyrite, bornite, sphalerite and marcasite that are found in some coal seams. Popovic (1954) noted that the noble metal content of the coals he studied varied with the sulphur content, especially the chemically bound sulphur – the higher the bound sulphur content the higher the noble metal content.

5. The gold in coalified fragments in most sandstones and shales is either in or associated with pyrite, chalcocite, bornite and galena. Its nature is unknown.

6. In the weathered parts of coal seams gold (and silver) may occur in jarosites and iron oxides; also in the native form.

Gold may be concentrated in coal by one or all of the following processes:

1. Goldschmidt (1933*a*, 1935) originally suggested that gold and other trace elements were first concentrated by the coal plants, and these in turn contributed the elements to the humic substances that are the mother of coal: we have seen in the section on the biogeochemistry of the element that gold is a microconstituent of numerous plants, and hence it seems logical to conclude that some of the gold in coals came directly from the accumulated plant material.

2. Precipitation of gold from surface waters flowing into or through the ancient coal swamps: humus in bogs and swamps tends to adsorb and absorb the available gold from surface waters and thus becomes relatively enriched in the metal. Some gold may also be precipitated by bacteria. During humification and coalification processes this gold is incorporated in the coal.

3. Precipitation of gold from circulating groundwaters that course through the coal seams during and after coalification processes: in this case the source of the gold may be the coal itself, and the element is simply redistributed within the seam. More generally, however, much of the gold probably comes from the enclosing sedimentary rocks. Some investigators maintain, however, that the gold is of hydrothermal origin, especially where the element is precipitated in zones containing coal fragments in sandstones.

In coal seams and zones of coalified fragments gold circulating in aqueous systems is precipitated by adsorption processes, probably by chelation and other organometallic binding processes, and by reduction of the complex gold ions to the metal. Gebler and Stramkovskaya (1957) experimented with the adsorption properties of lignite for Cu, Ag and Au. For copper and silver they found a 4.31 and 5.2 per cent copper and silver ion absorption by weight of lignite. For gold they found no absorption but a strong reduction of the gold in solution to the metal.

The enrichment of gold in most coal seams and in coalified fragments in sandstones seems to be best explained by the circulating water hypothesis.

### *Gold in organic shales, petroleum and other natural hydrocarbons*

Shales and other rocks containing organic matter, bitumen, kerogen and their degradation products tend to be slightly enriched in gold compared with normal shales. The distribution of gold in these rocks is, however, commonly erratic. Commercial recovery of gold and silver from oil shales and tarry residues is suggested in a patent by Petty (1968). For further details see the section on gold in sedimentary rocks.

There are relatively few data on the gold content of petroleum. Colombo *et al.* (1964) and Shah *et al.* (1970) determined the gold content by neutron irradiation methods in oil and asphalt samples from a number of fields in Italy, U.S.A. and Libya. Their values range from $<0.1$ to 3.012 ppb in the oil (Table 26). In the asphalt the values ranged from 0.1 to 1.0 ppb. Al-Shahristani and Al-Atyia (1973) report the presence of gold in some Iraqi crude oils but give no quantitative data.

Hitchon *et al.* (*in* Yen, 1975) report the presence of gold in four samples from a total of 88 crude oils from the Alberta fields of Canada. The average concentration of gold in these samples was 0.438 ppb; the maximum was 1.32 ppb.

The mode of occurrence of gold in petroleum is unknown. It seems probable, however, that the element is combined as some type of organo-gold complex or as a chelated complex, perhaps a porphyrin, since the element is capable of forming porphyrins easily (Fleischer and Laszlo, 1969). Shah *et al.* (1970) also analyzed the 10 crude samples shown in Table 26 for Sc, Ni, Fe, Co, Zn, Se, Sb, Cr, As, Eu, Hg and U. A study of the correlation coefficients between these elements and gold indicates a significant correlation between Au and Sb and also between Au and Sc, Fe, Co and Cr.

Table 26. Gold content of crude oil and asphalt

| Sample number and type | Locality | Gold content (ppb) |
|---|---|---|
| Data from Colombo *et al.* (1964) | | |
| Crude oil | Alanno, Italy | <0.1 |
| Crude oil | Chieuti, Italy | <0.1 |
| Crude oil | Cercemaggiore, Italy | <0.1 |
| Crude oil | Avanella, Italy | <0.1 |
| Asphalt | Gela, Italy | 0.5±0.2 |
| Asphalt | Noto, Italy | 1.0±0.1 |
| Asphalt | Vittoria, Italy | 0.2±0.1 |
| Asphalt | Ragusa, Italy | 0.2±0.1 |
| Data from Shah *et al.* (1970) | | |
| Crude oil, 010 | California, U.S.A. | 1.238±0.032 |
| Crude oil, 011 | California, U.S.A. | 0.723±0.039 |
| Crude oil, 012 | California, U.S.A. | 1.174±0.06 |
| Crude oil, 013 | California, U.S.A. | 1.911±0.34 |
| Crude oil, 014 | California, U.S.A. | 3.012±0.40 |
| Crude oil, 015 | Libya | 0.666±0.032 |
| Crude oil, 016 | Libya | 1.365±0.076 |
| Crude oil, 017 | Libya | 1.242±0.261 |
| Crude oil, 018 | Louisiana, U.S.A. | 0.668±0.06 |
| Crude oil, 019 | Wyoming, U.S.A. | 1.489±0.051 |

The gold in petroleum may be derived from the following sources.

1. From the original plants and animals whose remains gave rise to the petroleum: in the present section on biogeochemistry we have reported that many marine plants and animals concentrate gold, and it seems logical to suppose that some gold in petroleum came from this source.

2. By adsorption and absorption processes from sedimentary rocks: petroleum migrating through sedimentary rocks on its way to reservoirs probably adsorbs and absorbs some gold from these rocks.

3. By contact with connate and other waters: these waters probably carry small amounts of gold, which may be absorbed by petroleum when the two solutions come into contact.

There are relatively few data on the gold content of the natural bitumens and asphalts and the various solid hydrocarbons such as gilsonite, ozokerite, grahamite, anthraxolite, thucholite, etc. Thucholite is commonly greatly enriched in gold in the Witwatersrand quartz-pebble conglomerates of South Africa (Liebenberg, 1955) (*see also* Chapter III). The thucholite in the skarn-type gold deposits of the Richardson Mine near Madoc, Ontario is also phenomenally enriched in gold. Other solid hydrocarbons and bituminous materials analyzed by the writer vary widely in their gold content as shown in Table 27. With respect to the possible migration of gold as a complex hydrocarbon species see the section on the origin of the Witwatersrand in Chapter III.

Table 27. Gold content of bituminous materials and solid hydrocarbons

| Description | Location | Au (ppm) | Ag (ppm) | Au/Ag ratio | Remarks |
|---|---|---|---|---|---|
| Thucholite* | Richardson Mine, Eldorado, Ont. | >1000 | >2 | ~500* | In the solid hydrocarbon |
| Thucholite | Witwatersrand | >1000 | >10 | 12 | In the solid hydrocarbon (*see also* the discussion on the Rand in Chapter III) |
| Albertite | Albert County, N.B. | <0.005 | <0.3 | ~0.01 | In the ash of the solid hydrocarbon |
| Vanadium-bearing hydrocarbon-shale | Quadra Island, B.C. | 0.25 | 47 | 0.005 | In the solid hydrocarbon and shale |
| Antraxolite | Sudbury, Ont. | 0.03 | 2.5 | 0.012 | In the ash of the solid hydrocarbon |

*By electron probe the ratio Au/Ag of the visible native gold is 99.8/0.2. *See* the papers by Boyle and Steacy (1973), Steacy *et al.* (1973) and Steacy *et al.* (1974*a,b*).

## Gold in the atmosphere

Relatively little data are available on the gold content of the atmosphere. The element is mentioned as being present in rainwater in the old literature, but no quantitative data are given. Peirson *et al.* (1973) have measured the gold content of rainwater and air by neutron activation at various sites in the United Kingdom. They give values of 0.01 μg/L for rainwater and an average of less than 0.003 ng/kg for air.

Nearly all of the gold in the atmosphere is present in particulates; some may be present as volatile methylgold as Wood (1974) has suggested, or as some other volatile gold-organic compound arising from microbiological activity. The source of the particulates of which gold is either an integral constituent or present in an adsorbed form is probably multiple and includes: terrestrial aerosols raised from the surface of the land and ocean by winds; volcanic aerosols; industrial pollutant aerosols; and extraterrestrial particles (meteoritic dust) from sources unknown. There are no data on the contribution, which each of these makes to the gold content of the atmosphere.

Gold is a constituent of certain terrestrial gases and aerosols, especially in volcanic areas. These are discussed in the section on natural waters.