

# Introduction to Geology and Resources of Gold, and Geochemistry of Gold

U.S. GEOLOGICAL SURVEY BULLETIN 1857-A



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Chapter A

# Introduction to Geology and Resources of Gold, and Geochemistry of Gold

The Case for Gold—An Introduction to Geology and Resources of Gold in the United States

By DANIEL R. SHAW

Geochemistry of Gold in Hydrothermal Deposits

By SAMUEL B. ROMBERGER

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DANIEL R. SHAW and ROGER P. ASHLEY, Scientific Editors  
LM.H. CARTER, Technical Editor

U.S. DEPARTMENT OF THE INTERIOR  
MANUEL LUJAN, JR., Secretary



U.S. GEOLOGICAL SURVEY  
Dallas L. Peck, Director

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# Introduction to Geology and Resources of Gold, and Geochemistry of Gold

## The Case for Gold—An Introduction to Geology and Resources of Gold in the United States

By Daniel R. Shawe

### Abstract

Gold has long been a store of wealth, whether held by governments or in private hoards. Of the total of about 3 billion troy ounces of gold that has been mined worldwide through man's history, about one-third is held by central banks, another third is held privately, and the last third is fabricated in jewelry (also a store of wealth) and in forms useful in industries such as electronics and dentistry.

Since the British Gold Standard was established in 1717, the price of gold generally has been fixed officially, and thus it has tended to remain stable. The U.S. Congress in 1792 adopted a gold standard of \$19.39 per troy ounce, which lasted to 1834 when the official price was set at \$20.67. In 1934 the official U.S. price (effectively, the world price) was raised to \$35 per ounce. At times during this long period of stable gold price, aberrations such as the American Civil War and financial panics caused either temporary de facto abandonment of the gold standard or suspension of specie payments. The U.S. government declared a de facto abandonment of the standard in 1968 and then an official abandonment in 1971, at the time of the collapse of the Bretton Woods Agreement, which had established the U.S. dollar as the world's monetary standard at gold parity of \$35 per ounce. Thereafter, the world gold price rose rapidly. A peak of \$850 per ounce was reached in January 1980; since then the price has settled in the range of \$300–\$500 per ounce.

Gold production in the United States prior to 1848 was less than 2 metric tons annually. Discovery of gold in California in that year led to annual production of 60–100 metric

tons during the 1850's. Gold production gradually declined thereafter, until discoveries in South Dakota, Alaska, Colorado, and Nevada provided new sources to help finance the country's expanding economy, culminating in peak annual production of more than 150 metric tons just before World War I. Following the war, production declined sharply, until the depression of the early 1930's and the gold price increase in 1934 again stimulated gold mining. An all time high in annual gold production of 187 metric tons was reached just prior to World War II. The government order restricting gold mining in the United States during the war resulted in a precipitous drop in annual production to less than 50 metric tons. After the war, a brief increase in annual production tailed off into a gradually declining trend near 50 metric tons annually. The rapid price increases in the 1970's were not matched by increased gold production until 1981, reflecting the long lead times required to develop gold mines. Annual gold production in the United States presently again exceeds 100 metric tons.

Because of the importance of gold as a store of wealth, and because of the historical bond between gold and money, it is hoped that the descriptions of the geology of gold provided in this series will help increase the supply of gold, and thus they may also benefit the world's monetary systems.

Gold has been mined throughout the world from a great variety of types of deposits and of all geologic ages. Excepting placers, most of the world's gold production has come from Precambrian terranes, and commonly from deep geologic environments. In the United States most production has come from deposits of younger geologic age and shallower geologic environments. Aside from the

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Precambrian-age Homestake deposit at Lead, South Dakota, the United States' largest producer, most of the major gold deposits are of Mesozoic and younger age. They occur predominantly in intermediate to shallow geologic environments such as the mid-level quartz-vein system of the California Mother Lode and numerous porphyry-copper systems of the Western United States, and shallow-level bonanza-type deposits such as the Comstock Lode in Nevada and Cripple Creek in Colorado, and recently, a variety of disseminated deposits mostly in Nevada.

This series describing the geology of gold deposits in the United States consists of chapters on the geochemistry of gold, the distribution of gold in the United States, descriptions of major gold terranes, and descriptions of individual deposits or districts. Deposits are grouped as those in metamorphic rocks; mesozonal deposits consisting of polymetallic replacements and veins, porphyry copper systems, and mid-level gold-quartz veins; a variety of epizonal deposits, including bonanza and disseminated types; and placer deposits.

## INTRODUCTION

The value of gold in international political and commercial relations makes a secure and substantial domestic source of gold a significant national asset. This series is being prepared in the belief that a broader understanding of the geologic occurrence of gold will assure a more extensive and a more efficient exploitation of this valuable resource, and thereby contribute to the national well-being.

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## GOLD AS A STORE OF WEALTH— THE USES OF GOLD

Gold has been prized by man from distant prehistory because of its beauty, rarity, and durability.

From its use as an article of adornment, it grew to be a stable item of trade and eventually became what is now called money. Other metals and printed (paper) money, however, now have replaced gold coinage in circulation worldwide. Though in theory these substitutes represent a reserve of gold that is held as backing by the issuer of the substitute money, in fact, this support of money by means of a gold reserve is seldom strictly true. Nevertheless, with the organization of industrialized nations and the development of international commerce, gold became the primary instrument for settlement of international debt, whether used in direct payment, or as backing, officially or de facto, for national currencies (that is, as monetary reserves). Thus gold is accumulated and held as reserves by national banking institutions, the so-called central banks. But individuals worldwide commonly do not trust the vagaries of national and international politics and economics, and of wars, and they prefer to hold their own reserves as private hoards of gold. Whether held privately, or as a public hoard, gold has long been a store of wealth.

With modern advances in technology, gold now is finding more and more industrial uses, particularly in electronics. However, with respect to the total store of gold the amount involved in industrial uses is minor, and likely to remain so. Because of the high price of gold, industrial applications tend to use very small amounts of gold.

Of the total gold available in the world today—which represents virtually all the gold that has ever been mined—about one-third is held by national central banks and other official agencies such as the World Bank and the International Monetary Fund as a support, albeit imperfect, for monetary systems. At the end of 1983 central bank gold holdings were about 35,000 metric tons (Mining Journal, March 8, 1985). Another third is held in private hoards, as a hedge against inflation and sudden domestic or international instabilities, or for speculation purposes. The last third is in jewelry (in some respects a store of wealth) and in other fabricated uses such as in the electronics industry and dentistry (Stoehr, 1984; Davenport, 1981).

## HOW MUCH GOLD?

Probably at least 5,000 years have passed since the first gold was mined on this planet, during which time slightly more than 3 billion troy ounces (about 94,000 metric tons; fig. A1) have been produced. Most of this has been produced since A.D. 1500 (Kavanagh, 1976), and about half of the total has been mined within the last 35 years (Stoehr, 1984). The increasing quantity of available gold was highlighted by Stoehr (1984) in the following figures: assuming an even distribution of all available gold among all living persons on the planet, in

the year 1800 there was 0.14 oz per person, in 1900 0.31 oz, in 1980 0.71 oz, and projected at current trends to 2000 there will be about 1 oz per person. This remarkable acceleration in gold production has resulted from improved extraction technology and a better understanding of the geologic environments of gold, coupled with an ever-increasing demand that in recent years has substantially increased the price of gold.

Despite the long-term increase in gold production worldwide, gold mining has been sporadic through time and from locale to locale, owing in part to nature's uneven allotment of gold to different geologic environments and to man's unstable political and economic activities. Figure A1 shows the production of gold in the United States and in the world during the period 1845–1987.

## **FACTORS INFLUENCING THE PRICE AND PRODUCTION OF GOLD**

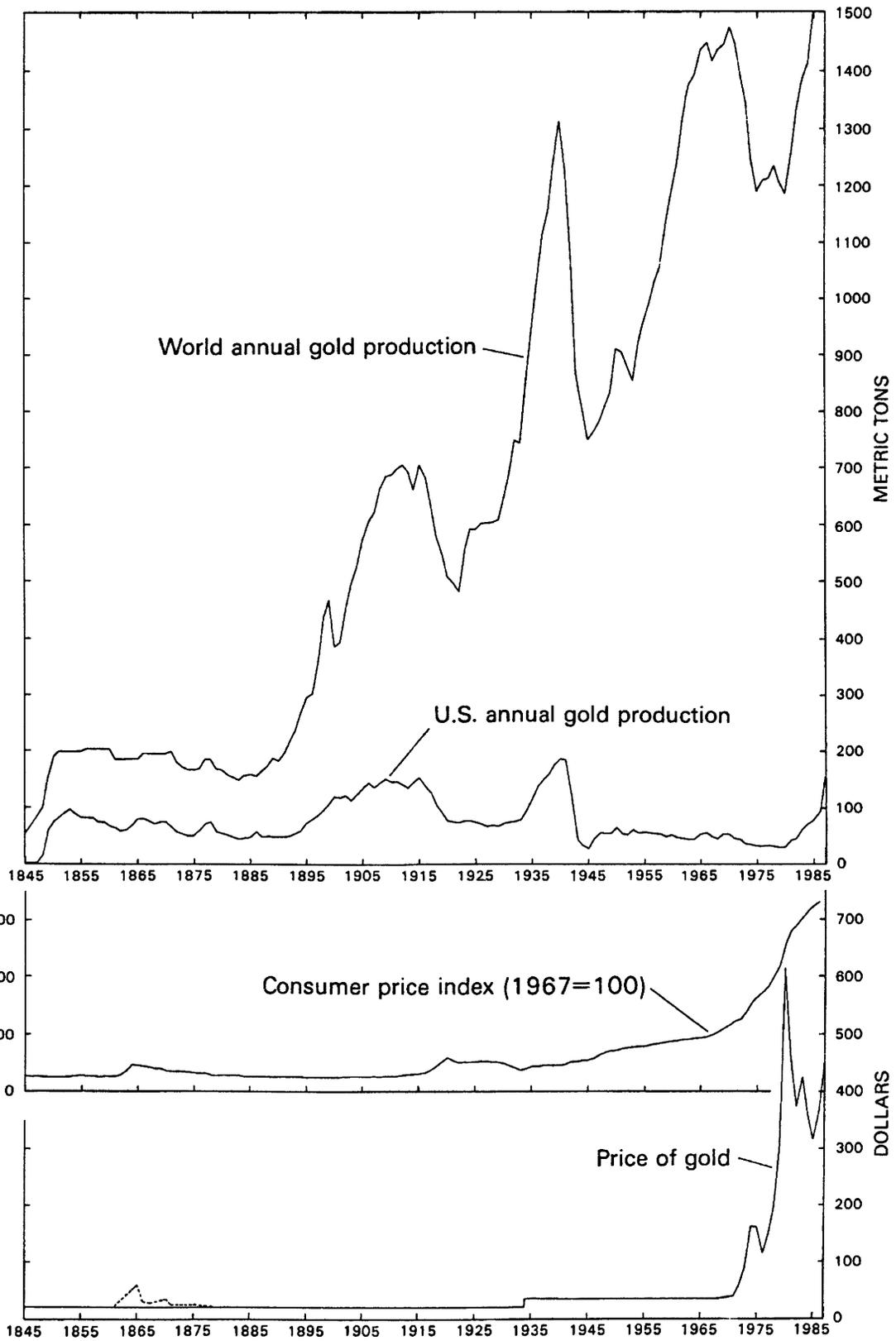
The British Gold Standard was established in 1717 by Sir Isaac Newton, then Master of the Mint, at £4.248 per troy ounce. The standard lasted for more than 2 centuries. In 1792 the U.S. Congress adopted a bimetallic (gold-silver) standard for the new Republic, fixing the price of gold at \$19.39 per troy ounce (U.S. gold price history from Cycles, 1981) at a fixed ratio of 1 to 15 gold to silver, at parity with the British pound sterling. The United States suspended specie (coinage, particularly of gold and silver) payments in August 1814 following the War of 1812 with Great Britain, and resumed them in February 1817. The gold price then remained constant at \$19.39 until 1834, when because of inflation a new price was set at \$20.67, at a fixed ratio of 1 to 16 gold to silver. The financial panic of 1837 brought on a one-year suspension of specie payments. Specie payments also were suspended briefly during the panic of 1857. The Civil War brought on a further specie suspension in December 1861 which lasted until 1879. Unofficial gold prices soared during the war (fig. A1) but dropped substantially on "Black Friday," September 24, 1869, at the time of the "silver panic." With the panic of 1873, the U.S. adopted a de facto gold standard that brought the gold price down close to its earlier fixed price.

In January 1874, Congress provided for redeemability of paper money in gold effective January 1879. This action did not generate a rush for gold, but instead it induced an increase in gold deposits in banks and an increased demand for government securities (Wormser, 1967), because of the strengthening effect of the gold backing upon the nation's monetary system. Thus, specie payments were resumed in 1879 at \$20.67 per troy ounce, and in 1900 the U.S. again officially (de jure) adopted the gold standard. During World War I, between September 1917 and June 1918, free export of gold from the United

States was prohibited. Following World War I in 1919 Britain was forced off the gold standard because of inflation that diminished the value of gold. Gold prices in Britain, as well as in South Africa where the world's most significant gold production was already underway, thereafter improved gradually until 1925, when Britain and South Africa, with inflation controlled, returned to the old standard of £4.248 per troy ounce. Then in March 1933, following the 1929 stock market crash and collapse of the Federal banking system in the United States, the Congress prohibited U.S. citizens from owning gold, and the administration in January 1934 fixed the official price of gold at \$35.00 per troy ounce. But by the end of 1932 the Great Depression had already destroyed the gold standard in Britain. As a consequence, the gold price there rose to £8.40 per troy ounce by January 1940, where it was fixed through World War II. In 1944 as a result of the Bretton Woods Agreement, the U.S. dollar became the world's monetary standard at gold parity of \$35 per ounce (data in part from Mining Journal, Dec. 1986 suppl.) .

In 1968 the U.S. government declared a de facto abandonment of the gold standard, and within 3 years the price increased slightly to about \$40 per troy ounce. The Bretton Woods system collapsed in 1971 (Lehrman, 1986). At that time also the United States officially (de jure) came off the gold standard, and citizens were again allowed to own gold, and thereafter the price rose rapidly. A significant increase in the price of gold to an average of about \$160 per ounce followed the oil-producing and exporting countries' (OPEC's) fourfold increase in oil prices in 1973. After a temporary decline to \$115 in 1976, the gold price soared to a peak of \$850 per troy ounce in January 1980, following further oil price increases, the U.S.S.R.'s invasion of Afghanistan, the Iranian revolution and occupation of the U.S. Embassy in Teheran, and general worldwide economic uncertainty. The average price for the entire year of 1980 was well above \$600 per ounce. Since 1980, and in response to several factors including a strong U.S. dollar, a drop in oil prices, and a drop in interest rates, the price of gold declined, somewhat erratically, to an average price of about \$315 per ounce in 1985. With a weakening dollar and new increases in oil prices and interest rates, the price of gold again climbed, and in May 1987 was above \$450 per ounce, where it now (December 1987) rests.

Gold production in the United States prior to 1848 was less than 2 metric tons annually (fig. A1). Discovery of gold in California in that year led to the great gold rush of 1849, following which, up to the beginning of the Civil War, 60 to nearly 100 metric tons (in 1853) of gold were produced annually. This period was that of peak production from the California goldfields, where placer production exceeded lode production by a margin of 2 to 1.



Depletion of the placers and new laws constraining placer mining were major factors in the subsequent decline in production. During the Civil War, and following the prewar decline in California gold production, U.S. production temporarily increased as unofficial gold prices soared. Although the Comstock Lode (Nevada), which was discovered in 1859, produced silver that financed a large part of the Union's war costs (for example, Smith, 1943), as well as substantial gold, it had little effect on the immediately prewar decline in gold production. Likewise the discoveries of the Homestake deposit in 1876, the Juneau goldfields in 1880, the Yukon placers in 1882, and the Cripple Creek (Colorado) district in 1891 had no immediate effect on a gradually but erratically falling U.S. gold production. However, by 1893 the cumulative effect of the newly discovered sources of wealth, spurred by an ever-growing need for capital to finance a rapidly expanding U.S. economy, sharply increased gold production.

The financial panics in the United States in 1857, 1869, and 1873 had little effect on production of gold. In each instance the panics occurred during or just prior to periods of declining gold production. The 1857 panic was in a period in which gold specie payments continued, whereas the 1869 and 1873 panics were in a period in which specie payments were suspended, and unofficial gold prices were substantially higher than the fixed price of gold (fig. A1).

Discovery of the Nome (Alaska) gold placers in 1897, the Tonopah (Nevada) gold-silver district in 1900, and the Goldfield (Nevada) district and the Fairbanks (Alaska) placers in 1902 added impetus to U.S. gold production, which soared into the range of 100 to more than 150 metric tons annually during the years 1899–1918. This period saw peaks of production of gold from Cripple Creek, Fairbanks, Nome, Tonopah, Goldfield, and the Comstock Lode (Koschmann and Bergendahl, 1968).

During World War I, gold production dropped appreciably, under a fixed price. A precipitous drop

occurred in 1918, following the United States entry into the war and the prohibition of the export of gold. Gold production generally declined until the stock market crash of 1929. Gold production then rapidly increased, culminating at the start of World War II in the largest annual production of gold ever in the United States. This burgeoning gold production was accelerated in 1934 by the official increase of almost 70 percent in the fixed price of gold. Resurgence of gold mining, following the financial crash of 1929 and with the impetus of the 1934 price increase, was made possible by the large reserves of gold still available in the Yukon placers, the Alaska-Juneau lode mine, the Mother Lode mines, the Homestake mine, and lesser districts in Idaho (for example, the Boise Basin), Montana (Virginia City–Alder Gulch), Nevada (Eureka; the Comstock), New Mexico, Oregon, and Washington (Republic). Porphyry copper deposits in Utah, Arizona, Montana, Nevada, and New Mexico also contributed substantial byproduct gold during this period.

An all-time high in annual U.S. gold production of about 187 metric tons was reached in 1940, just prior to United States entry into World War II. The most catastrophic drop in gold production in U.S. history came during World War II, a period of constant gold price, following the government order that closed down domestic gold mines. When the ban on gold mining was lifted at the end of the war, gold production spurted momentarily and then declined irregularly as inflation eroded the value of the fixed gold price of \$35 per oz. Production never again reached its prewar level, for in addition to the damping effect of inflation, mining could not resume in many of the abandoned mines whose workings were caved or flooded. Discovery of the Carlin gold deposit in 1962 and its early production starting in 1965 had little influence on the overall U.S. production of gold. In spite of sharply rising gold prices and increasing discoveries in the years 1973–1980, production of gold continued to fall.

Figure A1 shows that production of gold in the United States between 1845 and the end of World War II closely paralleled that in the rest of the world. However, after a momentary spurt that followed the war, gold production in the United States gradually decreased up to 1980; during the same period, world production soared. The discrepancy probably can be attributed to several factors, including high U.S. wages relative to the rest of the world, and the fact that gold mines worldwide except in the United States were generally maintained during the war. By 1981, even though prices began to drop substantially, gold production rose sharply and it continues to rise. Much of the lag in production can be attributed to the long lead times required to put new gold mines into production. Exploration and development spurred by the gold price increases between 1973 and

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**Figure A1** (facing page). Annual world and United States gold production, United States consumer price index, and yearly average price (per troy ounce of gold), 1845–1987. World gold production from Ridgway (1929), Ryan (1965), Anonymous (1982), Anonymous (1986), and various issues of *Mining Journal* (1980–1987); U.S. gold production from U.S. Geological Survey (1883–1923), U.S. Bureau of Mines (1924–1931), U.S. Bureau of Mines (1932–1984), and various issues of *Mining Journal* (1980–1987); U.S. consumer price index from U.S. Bureau of the Census (1970) and *Facts on File Yearbook* (1971–1986); price of gold (average annual price for 1968–1987) from *Cycles* (1981) and various issues of *Mining Journal* (1980–1987); dotted interval 1861–1879 indicates “unofficial” or black market price during and following the Civil War.

1980 did not begin to reach fruition until 1981. Moreover, a significant advance in the technology of gold extraction during the past decade, notably the development of cyanide heap leaching (Nettesheim, 1987), has greatly accelerated the production of gold in the United States.

## THE ROLE OF GOLD IN WORLD MONETARY SYSTEMS

The importance of gold as a store of wealth, including its role in world monetary systems, is the principal driving force that leads to efforts to find and produce gold. This series, intended to provide a more thorough understanding of the geology of gold and consequently an increase in the supply of gold, thus may have a bearing on gold's influence upon world monetary systems. This brief discussion is not intended to show what the interrelationships of gold and monetary systems ought to be, but instead it is meant only to emphasize the historical bond between gold and money.

The interrelationships between gold and monetary systems are complex and have long been debated; opinions are far from unanimous. Nevertheless, there is a general recognition that a tie exists between the two. The connection has been expressed in many ways. For example: "Whatever mineral you have in your mine, you are mining for gold" (Mining Magazine, July, 1985, p. 5). "The price of gold\*\*\*is determined not only by the supply and demand for gold, but by the supply and demand for money" (Wall Street Journal, Sept. 4, 1986, p. 26). "If there is success in restoring price stability and confidence in our currency, tighter linkage of our monetary system to gold may well become super-erogatory" (U.S. Gold Commission, as reported by Mining Journal, April 30, 1982, p. 5). "Under fixed exchange rates based on a true international gold standard, even during periods of very rapid growth—as during the first century and a half of the Industrial Revolution—global financial balance is maintained by virtue of the fact that total international reserves increase through increased gold production, not increased dollar (or other reserve-currency) debt" (Lehrman, 1986).

Inasmuch as monetary systems are extensions of national policy, and therefore susceptible to the changing world scene, gold transactions also are responsive to world events. Despite the difficulty of predicting even in the short term how gold price and production are going to respond in a free world market, gold nevertheless is a sensitive indicator of certain domestic and international conditions such as inflation and wars. For example, the general parallelism between the price of oil and gold in recent years has been apparent, although this relationship might not persist over the long term. According

to the Mining Journal (Feb. 12, 1982, p. 115), the relative appeal of gold is based on (1) inflation and other anxiety factors, (2) cost of money and the yield on alternative assets, (3) promotional and marketing efforts, (4) price of gold relative to other commodities, and (5) supply-industrial demand outlook for gold. (See also Kaufmann, 1987.) In the last week of February 1983, gold tumbled from about \$500 per oz to about \$400 per oz, in concert with a drop in the U.S. prime interest rate from about 12 percent to 10.5 percent. Under today's uncontrolled gold price, if the value of the dollar falls, the price of gold increases. The great complexity of interplay of various influencing factors however can cause some otherwise reliable indicators to become fallible. What *can* be stated is that a stable gold price reflects generally stable economic conditions worldwide, discounting political and military influences. Furthermore, the gold price is not appreciably influenced by supply factors such as newly mined gold, inasmuch as new gold makes only a trivial impression on the total supply of gold. Effects of short-term fluctuations in the world supply may be apparent, however, as for example when the U.S.S.R. in December 1981 sold a large amount of gold contributing to a moderate decline in the world price (Mackay-Smith and Leger, 1981).

With the discontinuance of a world gold standard instigated by U.S. action in 1971, the price has been controlled by the free market, and it has sought its own level. But discontinuing the use of gold as a world reserve currency has not eliminated the need for such a standard, and the U.S. dollar has assumed this role. A silver-based world monetary system was established as a result of the 1922 Genoa Conference, and continued in 1944 as a result of the Bretten Woods Conference (Mueller, 1986). The system was abandoned by the U.S. in 1971 with suspension of dollar-gold convertibility, as the United States and Britain could no longer redeem currency in gold while other countries used dollars and pounds as official reserves (Lehrman, 1986). The dollar, however, simply by its overwhelming dominance in world economic activity nevertheless retained a de facto role as the world's reserve currency. But because U.S. dollars basically are financing world growth and trade, there cannot be a net increase in world monetary reserves. The dollar, therefore, becomes an asset for foreign central banks but a liability for the United States (Mueller, 1986; Lehrman, 1986).

## WHERE GOLD COMES FROM

Gold has been mined throughout the world from a great variety of deposit types and of all geologic ages (for example, Boyle, 1979). Gold has been produced from the Precambrian shield areas of Africa, North and South America, Australia, India, and Scandinavia, principally

from quartz veins, and in southern Africa and Brazil from widespread "reefs" or "bankets" which generally are thought to be relatively thin fossil placer deposits in conglomerates. The gold-bearing reefs of the Witwatersrand in South Africa have been the world's greatest source of gold, having produced about one-third of the total supply. Paleozoic-age deposits occur widely, but they are concentrated in the Ural Mountains, Kazakhstan, and southern Siberia in the U.S.S.R., in southeastern Asia, in eastern Australia, in the Appalachian region of the United States, and in Europe. These deposits are mostly quartz veins and stockworks. The Muruntau gold deposit in Kazakhstan, a complex of quartz veins and associated stockworks of quartz veinlets in Paleozoic calcareous siltstones, shales, and schists near Paleozoic granodioritic plutons, is the world's largest producing mine. Mesozoic deposits of gold occur mostly in the cordilleran belts at the western margins of North and South America, and in eastern Siberia and China. Quartz veins again are the dominant type, in some districts forming great regional systems such as the productive Mother Lode of California. Deposits of Cenozoic age have a distribution similar to, though wider than, those of Mesozoic age, occurring also throughout southern Europe and eastward through southern Asia to the western Pacific area of Indonesia, New Zealand, and Japan. Gold deposits include bonanza-type quartz veins, porphyry-copper systems, and disseminated types. Finally, gold placers are found throughout the regions of bedrock occurrences of gold. Tertiary and Quaternary placer deposits such as those in Alaska, the western foothills of the Sierra Nevada of California, and Siberia have yielded large amounts of gold.

The types of deposits, excepting placers, that have dominated gold production in the United States have not been the same as those that have been most productive elsewhere in the world. Throughout most of the world, major gold production has come from Precambrian terranes, and commonly from deep geologic environments. In the United States most production has come from deposits of younger geologic age and of shallower geologic environments. Aside from the Precambrian-age Homestake deposit at Lead, S. Dak., the United States' largest producer, most of the major gold deposits have been of Mesozoic and younger age. They occur predominantly in intermediate to shallow geologic environments, as for example the mid-level quartz-vein system of the California Mother Lode and numerous porphyry-copper systems of the Western United States, and shallow-level bonanza-type deposits such as the Comstock Lode in Nevada and Cripple Creek in Colorado, and recently, a variety of disseminated deposits mostly in Nevada.

Historically, the types of gold deposits exploited at any given time have depended on an ever-expanding

understanding of the occurrence of gold, modified by a technology of extraction that has evolved in response to discovery. Primitive societies won their gold from placers, which have remained major but highly varied sources to this day. Lode deposits (in the strict sense of fissure veins) have been major sources for millennia. The highly productive gold-bearing reefs of the Witwatersrand have been mined for just a century. Byproduct gold is a fairly recent phenomenon, and disseminated gold in "Carlin-type" and similar deposits was first recognized quite recently (modified from Shawe and others, 1982).

## SCOPE OF THIS SERIES, AND CONVENTIONS USED

The resurgence of gold mining in the United States in the 1980's, coupled with the present depressed condition of most of the remainder of the mining industry, focuses new interest on the geologic occurrence of gold. Increased understanding of the distribution of gold in the Earth's crust allows a more effective exploitation of this valuable commodity. Localized concentrations of gold (gold deposits) occur in a great variety of geologic environments, and descriptions of important examples of these deposits provide valuable models to guide assessment of gold resources and the search for new gold deposits. The objectives of this series thus are to give descriptions of the major geologic terranes in which gold occurs, as well as descriptions of significant gold mining districts and deposits throughout the United States. Some deposits that have been mined principally for base metals or silver but that have produced significant amounts of gold also will be described. In addition to the recently recognized types of gold deposits that show great promise for substantial future gold production, many "conventional" types of gold deposits offer significant potential. Among these latter are deposits whose production was interrupted by World War II and that never recovered thereafter because of adverse economic conditions, but which with a favorable gold price may be viable again.

An accompanying report in this chapter discusses the geochemistry of gold in hydrothermal fluids. Reports in subsequent chapters will describe the geologic and geographic distribution of productive (>10,000 oz of gold) districts in the United States, and broad geographic clusters of gold deposits that in general also are characterized geologically. Each geographic region (gold terrane) exhibits major lithologic (or lithogenetic) units and structural elements with which gold deposits are associated. Ages of the deposits will be discussed to clarify the relation of gold mineralization to particular geologic events.

Later chapters, the bulk of the series, will describe individual gold deposits and districts. The deposits and districts described are considered significant because they have had production or they contain announced reserves of >1,000,000 troy oz of gold, or because they are considered to represent an important geologic type of deposit. Our coverage has not been exhaustive, and a few deposits that have had significant production will not be described because of similarity to certain described deposits. Also, some important recently discovered deposits are not included among our descriptions. The deposits and districts described have been grouped for convenience as gold deposits in metamorphic rocks; mesozonal gold deposits including polymetallic replacements and veins, porphyry copper systems, and mid-level gold-quartz veins; epizonal gold deposits including bonanza-type and disseminated gold deposits; and placer gold deposits.

This collection of reports was planned initially for publication as a single volume, but now is being published in appropriate groupings as separate chapters in a series, with the hope that late reports can be incorporated in final chapters. Because of the delay entailed in obtaining some reports, a few of those submitted earlier had become outdated. As much as possible, those reports have been updated.

Metric units are used throughout the series generally, except that gold amounts are given as either troy ounces (oz) or as metric tons (t) (1,000,000 troy ounces = 31.1 metric tons and 1 metric ton = 32,151 troy ounces), and gold grades are given as ounces of gold per short ton (oz Au/ton). Descriptions of placer gold deposits give gold grades as ounces of gold per cubic yard (oz Au/yd<sup>3</sup>). No standard conversion exists for oz Au/yd<sup>3</sup> to oz Au/ton, because of variation in the density of placer gravel. The term "fineness" is used to indicate the proportion of pure gold in native gold that is almost universally alloyed with lesser amounts of mostly silver. For example, a fineness of 860 indicates 860 parts per thousand pure gold. The term "tenor" is commonly used interchangeably with grade. Map and cross section elevations, and mine levels, are given in feet.

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# Geochemistry of Gold in Hydrothermal Deposits

By Samuel B. Romberger<sup>1</sup>

## Abstract

The geochemistry of gold in hydrothermal deposits is influenced by the source of transporting solutions, metal source, mechanisms of transport, and the mechanisms of ore deposition. The solutions may have a magmatic source, or may be derived from any one of the following, depending on deposit type: sea water, connate water, meteoric water, or water evolved during metamorphism. Where the solutions have a nonmagmatic source, the gold must be derived from aquifer or other rocks through which the solutions migrate. No one rock type appears to be a favorable source for gold in terms of its abundance. Instead, the suitability of a rock as a source for gold will be controlled by its permeability, accessibility of the gold to the transporting solutions, and the chemical composition of the solutions.

Gold may be transported in aqueous solutions as a variety of complexes; however, aurous chloride or bisulfide species are most likely in hydrothermal systems, depending on temperature and solution composition. In most deposits formed between 200 and 300 °C, gold is best transported as a bisulfide complex; however, at higher temperatures typical of magmatic systems, gold is transported as a chloride complex. That a gold thioarsenide complex may exist is evaluated based on the ubiquitous association of gold and arsenic in primary hydrothermal deposits and the occurrence of thioarsenide species.

If the gold is transported as a chloride complex, reduction, increase in pH, and (or) decrease in temperature may result in deposition. If it is transported as a bisulfide or thioarsenide complex, oxidation, increase or decrease in pH, and (or) decrease in sulfur activity will cause deposition; the effect of temperature on the solubility of these complexes is uncertain. Because oxygen activity strongly affects solubility of gold bisulfide complexes, oxidation is the preferred mechanism of gold deposition. The oxidation of hydrothermal solutions may be produced by boiling, mixing with oxygenated ground waters and (or) contact with a host rock containing an oxidized mineral assemblage. Because of the high solubility of gold bisulfide complexes compared to the amount of gold in the ore deposits and source rocks, the mineralizing solutions seldom may be saturated with gold. Gold may be coprecipitated with sulfides as these minerals use up the sulfur forming the complexes. Recrystallization during metamorphism or other superimposed events would

then produce fine-grained gold along grain boundaries and as patches within the sulfides.

## INTRODUCTION

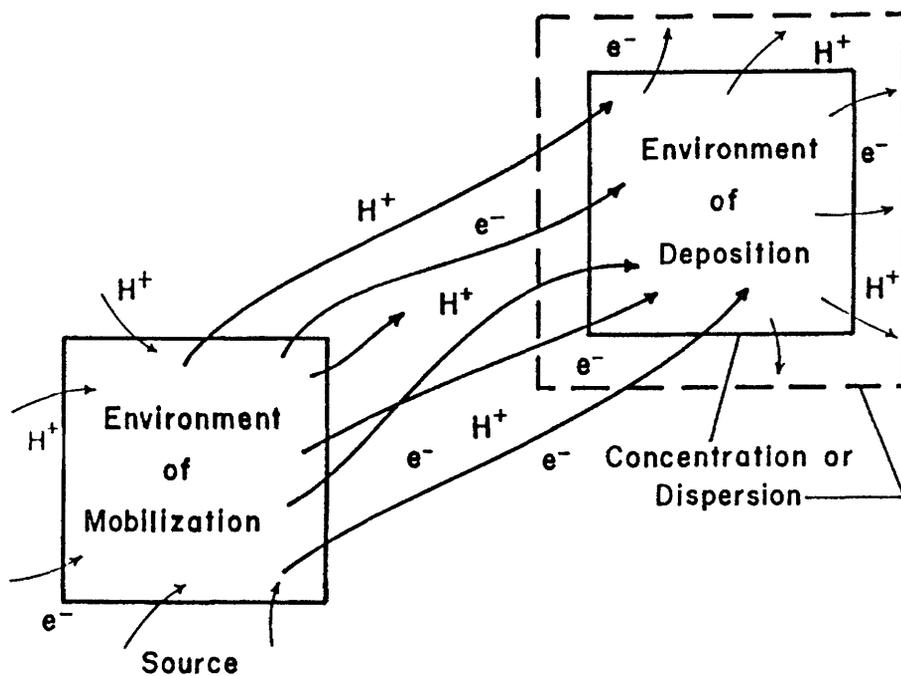
In the development of models for the origin of various types of gold deposits, it is essential to understand how the metal behaves in the geochemical environment. This is true particularly for deposits of hydrothermal origin because of the complex nature of the solution-mineral equilibria for gold. In hydrothermal deposits four factors must be considered in developing an understanding of their origin: (1) nature and source of the mineralizing solutions, (2) source of the gold, (3) mechanisms of gold transport, and (4) mechanisms of gold deposition. Each of these factors will be considered, although emphasis will fall on the sources of gold and the mechanisms of transport and deposition because extensive literature already exists on the nature and source of mineralizing solutions.

Figure A2 is a schematic representation of the general gold mineralizing system which illustrates three of the four factors (parts of the system) given above. It presents the environment of mobilization, or source rock, the environment of transport, and the environment of deposition; note that in the environment of deposition, the gold may be dispersed or concentrated, depending on the physical and chemical nature of the environment. The nature of each part of the system will depend on the composition of the other parts. For example, the mechanisms of gold precipitation in the environment of deposition will depend on how this metal is transported. This, in turn, will depend on the availability of suitable complexing agents in the source environment. In more fundamental terms, the occurrence of gold in the environment of deposition will depend on its availability in the source area. The diagram implies that the transport of gold will depend on the activities of electrons and protons (oxidation state and pH of the solution respectively).

## NATURE AND SOURCE OF SOLUTIONS

The source of solutions responsible for hydrothermal mineralization has been much debated. Five sources have been proposed for various deposit types: (1) meteoric (ground water); (2) sea water; (3) connate, or

<sup>1</sup>Colorado School of Mines, Golden, CO 80401.



**Figure A2.** Schematic diagram of the hydrothermal mineralizing environment illustrating the environments of source rock, transport, and deposition (concentration, solid square) or dispersion (dashed square).

formation, water; (4) magmatic water; and (5) metamorphic water. Taylor (1979) summarized a large number of oxygen and hydrogen isotope data available for precious metal deposits and concluded that the hydrothermal solutions responsible for their formation were dominated by meteoric water. Based on detailed geochemical studies, Radtke and others (1980) concluded that the gold and other materials deposited at Carlin were transported in solutions dominated by meteoric water. In their development of genetic models for epithermal precious metal deposits Buchanan (1981) and Berger (1982, p. 119–126) assumed these systems to be fossil geothermal areas where the hydrothermal solutions were chemically evolved heated ground waters. Their models are based on sound field relationships as well as geochemical studies of known precious metal deposits and active hot spring areas. Finally, Henley and Ellis (1983) discussed similarities between present-day geothermal systems and epithermal gold deposits, implying the importance of ground water in the formation of the epithermal deposits.

The importance of sea water and connate water in the formation of gold deposits is less well documented. Initial concentration of gold by hot spring activity on the sea floor may have been important in the genetic history of Archean vein deposits (Ridler, 1970; Karvinen, 1982). Fripp (1976) concluded that the gold-bearing Archean banded iron-formations of Rhodesia represent chemical precipitates deposited from waters issuing from submarine hot springs. These stratiform ore bodies occur

with sulfide and sulfide-carbonate facies banded iron-formation containing alternating layers of chert, arsenopyrite, pyrrhotite and ankerite. The gold occurs within arsenopyrite grains. Textural and structural features suggest that the gold and sulfides were deposited before deformation and metamorphism. Bavington and Keays (1978) found a significant enrichment of gold in interflow sedimentary rocks in a komatiite sequence in Western Australia. These rocks are interpreted as chemical precipitates formed around hot springs on the Archean sea floor. Even though the associated volcanic rocks contain average (crustal abundance) gold contents, the gold concentration of the interflow sedimentary rocks is as much as several hundred parts per billion (ppb).

Hallager (1984) concluded that the gold-containing iron-rich chemical sedimentary rocks at Jardine, Mont., were deposited by hot spring activity on the Archean sea floor. The gold is closely associated with sulfide facies ironstone which lies within a thick sequence of quartz-mica schists and quartzites. The close association of the gold with a carbonate iron-formation at the Homestake deposit suggests that the gold may have been deposited initially by a process similar to that for iron-formation. These deposits appear to have many similarities to syngenetic massive sulfide deposits that have been interpreted to be formed from deep circulating heated and chemically evolved sea water (Hutchinson, 1973; Ohmoto and Skinner, 1983; Hutchinson and Burlington, 1984).

Fehlberg and Giles (1984) interpreted the Spargoville deposit in the Archean Eastern Goldfields Province of Western Australia to have a volcanic-exhalative origin. Fine-grained gold occurs in conformable bands of arsenopyrite-bearing actinolite-quartz-carbonate rock within a metagreywacke sequence. These sedimentary rocks are associated with a felsic volcanic center within a greenstone belt. Fehlberg and Giles (1984) called upon connate water within the sedimentary-volcanic sequence as a possible source for the mineralizing solutions.

Gold occurs in anomalous amounts in many porphyry copper deposits around the world (Kesler, 1972; Titley, 1978; Sillitoe, 1979, 1980, p. 52–68, 1981). Most geochemical studies suggest that the solutions responsible for primary hydrothermal mineralization in these deposits were derived from magmatic water (Roedder, 1971; Taylor, 1979). However, an overprint of meteoric-water-derived mineralization is often indicated by stable isotope studies. It seems apparent that magmatic water may be important in the transport of gold in the porphyry copper systems.

The importance of waters released during metamorphism in the formation of gold veins has received considerable attention in recent years. Boyle (1959) originally proposed a metamorphogenic origin for the Archean greenstone-hosted veins in the Yellowknife district of the Northwest Territories. Groves and others (1984) interpreted the Archean vein deposits of Western Australia as being formed from hydrothermal solutions liberated during metamorphism. Fyfe and Kerrich (1984) developed a general model for the formation of Archean greenstone-hosted lode gold deposits which relies heavily on the transport of materials by solutions released during metamorphism. This model is based on extensive geochemical data on the distribution of major, minor, and trace elements in the veins and wall rocks (Kerrich and others, 1977; Kerrich and Fryer, 1979; Kerrich and Fyfe, 1981; Kerrich and Hodder, 1982; Kerrich, 1980, 1983).

Buchanan (1981) and Roedder (1984) summarized the composition of gold mineralizing solutions based on fluid-inclusion evidence and inferences from field relationships. In most hydrothermal deposits the solutions which transported and deposited the metals are no longer present in a quantity large enough to analyze and evaluate in detail. Solutions may be present in fluid inclusions in ore and gangue minerals; however, these are commonly too small to analyze directly, or they may represent an event superimposed on the original vein-forming episode. In addition, these fluid inclusions represent mineral-depositing and not necessarily mineral-transporting solutions. Nevertheless, fluid inclusions can yield valuable information on the physicochemical conditions of hydrothermal mineralization (Roedder, 1979; Roedder and Bodnar, 1980; Bodnar, 1983).

The range of temperatures determined for hydrothermal gold deposits is 100–400 °C, with most occurring between 200 and 300 °C. Table A1 summarizes the homogenization temperatures of various epithermal precious metal deposits discussed by Buchanan (1981). The temperature of ore deposition was considered to be similar to that of fluid-inclusion homogenization because these systems were at, or very close to, the boiling curve for the solutions (Buchanan, 1981). In addition, Nash and Theodore (1971) reported temperatures of formation and salinities for gold-quartz veins at Copper Canyon, Nev., to be 250–330 °C and 0.3–12.2 wt. percent NaCl equivalent. Nash (1975a, 1975b) determined formation temperatures for gold veins in the Park City district, Utah, and Sneffels-Telluride district, Colorado, to be 220–300 °C and 250–315 °C respectively. Batchelder and others (1978) gave a temperature for the formation of deposits in the Tintic district of Utah as 150–300 °C and salinities of less than 0.1 to 3.1 wt. percent NaCl equivalent.

Higher temperatures and salinities have been determined for gold-bearing deposits closely associated with magmatic activity. Moore and Nash (1974) reported temperatures and salinities for the Bingham Canyon porphyry deposits of 400–600 °C and up to 36 wt. percent NaCl equivalent, respectively. Huang and others (1978) determined temperatures of 450–600 °C and salinities of up to 42 wt. percent NaCl equivalent for the tactite deposits at Ely, Nev. T.G. Theodore and others (written commun., 1985) gave temperatures of 350–550 °C and salinities of up to 25 wt. percent CaCl<sub>2</sub> for the Tomboy-

**Table A1.** Temperatures of formation and salinities for selected epithermal precious metal deposits (Buchanan, 1981)

[Leaders (--), no data]

District	<sup>1</sup> T <sub>h</sub>	Salinity <sup>2</sup>
Oatman, Arizona .....	220	--
Pachuca, Mexico .....	200–250	--
Comstock, Nevada.....	250–300	--
Guanajuato, Mexico .....	230	< 1
Tonopah, Nevada .....	240–265	< 1
Goldfield, Nevada.....	200–300	--
Creede, Colorado .....	250	--
Eureka, Colorado .....	285–293	0.8
Rochester, Nevada .....	270–310	6
Bodie, California.....	215–245	--
Tayoltita, Mexico .....	265	3.4–8.4
Seven Troughs, Nevada .....	240–318	--
Ramsey-Talapoosa, Nevada .....	221	--
Colqui, Peru.....	270	2–10
Lake City, Colorado.....	250	3

<sup>1</sup>T<sub>h</sub> – temperature of homogenization, °C.

<sup>2</sup>Salinity in weight percent NaCl equivalent.

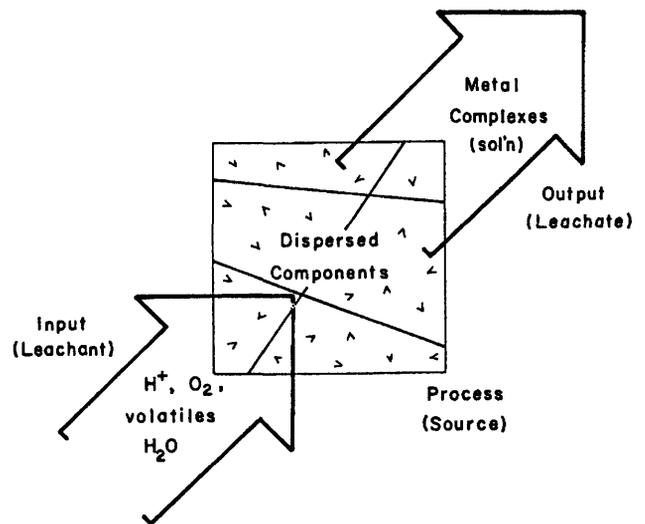
Minnie skarn deposits at Battle Mountain, Nev. Finally, E.W. Tooker (written commun., 1985) indicated a temperature of formation for veins in the Butte, Mont., district of 300 °C.

Geochemical data available suggest that sodium chloride is the most important dissolved compound in the solutions; lesser amounts of calcium and potassium are present also. Carbon dioxide may be present in significant quantities in inclusions from certain types of deposits, particularly those hosted by Paleozoic carbonate sedimentary rocks. Groves and others (1984) reported that fluid-inclusion data from gold veins in Western Australia indicate that the mineralizing solutions were CO<sub>2</sub>-rich and relatively dilute, with salinities generally between 1 and 3 wt. percent NaCl equivalent. Temperatures of formation were between 300 and 450 °C. R.M. Smith (written commun., 1985) suggested that the fluid salinities were very low in the Grass Valley vein deposits in California, and formation temperature was about 500 °C.

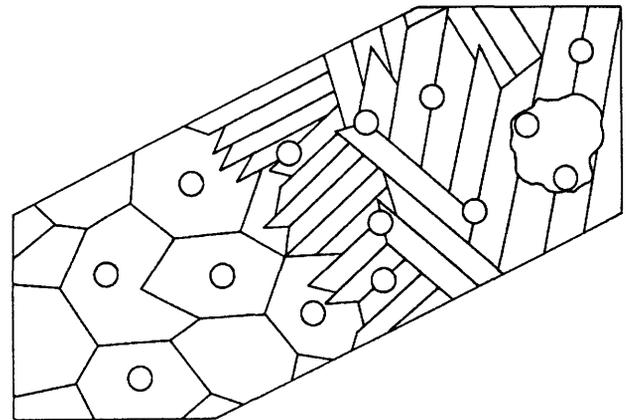
## SOURCES FOR GOLD

If hydrothermal systems responsible for the formation of gold deposits are dominated by meteoric water, sea water, or metamorphic water, source rocks must be somewhere in the flow path of the mineralizing solutions. Figure A3 represents the generation of a mineralizing solution by showing a gold-barren solution of variable pH and oxidation state interacting with a source rock containing dispersed gold. A prerequisite for these solutions to be able to react with the source is that the source rock must be permeable. As the solutions migrate through the rock the gold is released in some soluble form such as complexes. The input solutions may be the source of the complexing agents, or the complexing agents may be derived from the source rock as well. Gold trapped in the crystal structures of rock-forming minerals will not be in a form accessible to the solutions unless these minerals go through complete recrystallization during which the gold can be released. Figure A4 schematically illustrates that impurity components can be removed to accessible sites by various processes of recrystallization where the gold is no longer accommodated by the "new" minerals. Such changes can occur during weathering, diagenesis, metamorphism, or hydrothermal alteration. Gold dissolved in volcanic glass may be released during devitrification. The efficiency with which the gold is subsequently mobilized will depend on the nature of the solutions (see section on mechanism of gold transport and deposition).

Geochemical studies have shown that wall rocks can serve as sources for gold, at least on a local scale. Stephenson and Ehman (1971) reported a depletion of gold in altered metamorphosed intrusive mafic rocks



**Figure A3.** Schematic representation of the generation of a mineralizing solution wherein a barren solution reacts with a source rock containing dispersed gold.

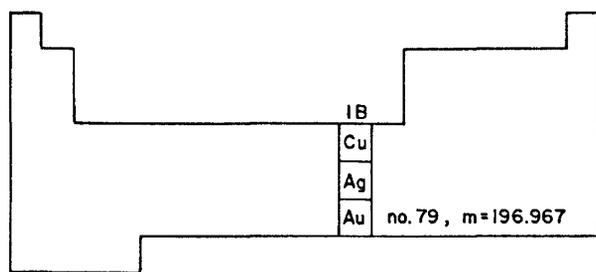


**Figure A4.** Schematic diagram of processes (alteration, recrystallization, devitrification, or metamorphism) responsible for releasing gold (small circles; left side of diagram) to leachable sites (grain boundaries and open spaces; right side of diagram) in a source rock.

adjacent to gold-quartz veins in the Rice Lake-Beresford Lake area of southeastern Manitoba. Jenkins (1980) detected a decrease in gold content in altered Precambrian metamorphic rocks adjacent to veins in the Jamestown district of Colorado. Klein (1980) found a statistical decrease in gold and other related components in altered metamorphosed ultramafic and mafic rocks surrounding veins in the Seminoe Mountains of Wyoming. In addition, other studies have been done to show that other components occurring in veins can be derived from the wall rocks (Kerrich, 1983).

A consideration of sources for gold must begin with its behavior during various geochemical processes. Gold belongs to group IB of the periodic table along with

copper and silver (fig. A5) and very commonly follows these elements during processes such as magmatic differentiation. Analyses of meteorites indicate that gold has a distinct siderophile tendency with a secondary chalcophile tendency, whereas silver and copper have strong chalcophile tendencies. Gold is concentrated in the metallic phase, or in the sulfide phase in the absence of metal. Siderite meteorites contain up to 10 ppm (parts per million) Au with an average of 1.2 ppm. The gold content of chondrites averages between 0.17 and 0.34 ppm, depending on the type. The highest amounts occur in the metal-rich enstatite chondrites, whereas the carbonaceous chondrites contain the least. There is a strong partitioning of gold into the metallic phase compared to the sulfides and silicates in heterogeneous meteorites (Allman and Crocket, 1978).



**Figure A5.** Periodic table of the elements illustrating the relationship between gold, silver, and copper.

In some of the earlier work on the behavior of gold during magmatic processes, Vincent and Crocket (1960) demonstrated a positive correlation between gold and copper, and showed that gold preferred copper sulfides to iron sulfide, oxides, or silicates in the Skaergaard intrusion. Rowe (1969) also found a correlation between these two elements in the Great Lake sheet of Tasmania, a differentiated tholeiitic dolerite. The maximum gold concentration occurred when the magma began to crystallize copper-bearing sulfides. Keays and Kirkland (1972) suggested that gold was derived from mafic to ultramafic dikes containing abundant copper sulfides in the Woods Point dike swarm deposits at the Thomson River copper mine, Victoria, Australia. Keays and Scott (1976) found a correlation between gold and chromium contents in mid-Atlantic ridge basalts and suggested that at least some of the gold is tied up in chromian spinels. They found no strong relationship between the gold and sulfur contents, although their data suggest that the samples high in gold are also high in copper. Finally, Dupuy and others (1981) found a similarity in the behavior of gold and copper in the noncumulate ultramafic rocks of New Caledonian ophiolites, where these metals appear to have been enriched in the liquid relative to the residue during partial melting. However, in the

mafic and cumulate phases gold showed no relationship to copper and appeared to be concentrated during the crystallization of chromian spinel.

Allman and Crocket (1978) and Boyle (1979) tabulated the gold contents of a wide variety of rock types from many different locations. Table A2 lists representative abundances for selected rock types from these tabulations as well as from other recent publications. Significant variations in gold content occur between and within rock types; however, some generalizations can be made about gold abundances and lithology. Ultramafic and mafic rocks appear to be enriched in gold relative to the average crustal abundance (5 ppb), although there are exceptions. Rozhkov and others (1973) determined the gold content of kimberlite and ultramafic inclusions from various Russian localities to average 3.9 and 4.8 ppb, respectively. They concluded that gold contents between 3 and 7 ppb are typical of upper mantle material, and that variations were a result of differences in the degree of partial melting during magma formation. Mitchell and Keays (1981) suggested that the bulk of the gold in the upper mantle was present in an intergranular phase which may represent an immiscible sulfide melt. They determined the average gold content of whole rock spinel lherzolite to be about 0.6 ppb Au. Oshin and Crocket (1982) studied the gold content of ultramafic rocks in the ophiolite complex at Thetford Mines, Quebec. They reported a gold content of 1.5 ppb for tectonite peridotite and 0.27 ppb for dunite lenses within the harzburgite. Cumulate phases within the complex contained similar concentrations. The gold content increased during progressive magma fractionation; gabbros within the complex had the highest concentrations of about 1.7 ppb. These authors suggested that sulfur saturation of the magma may play a role in the enrichment of gold in later differentiation products.

The occurrence of gold-quartz veins in Archean ultramafic and mafic rocks has been attributed to the fact that these rocks were anomalously high in gold and served as good source rocks (Viljoen and others, 1970; Anhaeusser, 1976; Keays and Scott, 1976; Pyke, 1976; Groves and others, 1984). However, there appears to be no detectable difference between the gold content of mineralized and unmineralized rocks (Anhaeusser and others, 1975). Tilling and others (1973) detected no appreciable differences in gold content between granitic and metavolcanic rocks in greenstone belts.

Saager and others (1982) compared the gold content of rocks from South African Archean greenstone belts with that of European Paleozoic ultramafic rocks. For the rocks from greenstone belts they obtained an average of 10.8 ppb (range 0.1–372 ppb), and for the ultramafic rocks they determined an average of 2.0 ppb (range 0.1–25 ppb). They found no relationship between gold content and major and trace element contents and

**Table A2.** Summary of gold contents for selected rock types

[Leaders (-), no data; data selected from Tilling and others, 1973; Allman and Crocket, 1978; Boyle, 1979]

Rock type	Range	Average	No. of samples
	ppb Au		
Granite .....	0.2-3.3	1.7	310
Granodiorite .....	1.3-4.3	3.0	380
Diorite .....	1.4-4.4	3.2	--
Monzonite .....	0.75-0.9	--	261
Syenite .....	1.4-4.4	1.8	--
Gabbro .....	0.5-9.9	4.8	580
Peridotite, dunite, etc.....	1.4-11	6.6	149
Rhyolite .....	0.5-3.5	1.5	188
Andesite .....	0.6-5.4	5.2	696
Basalt .....	0.3-9.5	3.6	
Conglomerate .....	11-100	--	--
Sandstone .....	2.1-109	3.0	105
Siltstone .....	5.9-18	3.0	
Shale .....	2.3-57	2.5	28
Limestone .....	1.1-38	2.0	20
Slate and argillite.....	0.3-10	1.0	135
Schist.....	1.1-13.5	2.2	114
Gneiss .....	0.6-4.3	3.9	37
Quartzite .....	2.4-7.3	4.9	2
Amphibolite.....	2.7-12	--	--
Hornfels.....	6.6-22.5	8.5	43

concluded that the gold was carried by accessory sulfides in the volcanic rocks, with perhaps some atomic gold occurring along grain boundaries. A sulfide-free phlogopite-peridotite from the Paleozoic ultramafic suite contained 0.1-0.5 ppb Au.

Keays and Scott (1976) determined the gold content of pillow basalts on the mid-Atlantic Ridge. The fresh interiors of the pillows contained from 0.2 to 0.7 ppb Au, whereas the glassy rims contained 0.3-2.7 ppb. These authors concluded that the glassy material better preserves the original magma chemistry and the interiors are much more susceptible to post-emplacement alteration by sea water. Crocket and Teruta (1977) obtained similar gold contents for mafic rocks drilled from the mid-Atlantic Ridge, leg 37, Deep Sea Drilling Project. These authors detected a slight increase in gold values with depth. Anoshin and Kepezhinskas (1972) studied recent volcanic rocks of the Kurile-Kamchatka province and found no relationship between gold content and differentiation index in a basalt-andesite-liparite rock sequence. The average gold content for all rocks was about 1.8 ppb. They found the gold to be fairly uniformly distributed in the rock-forming silicates and concluded that it occurred as uncharged atoms. However, mafic

rocks containing sulfides, especially chalcopyrite, were enriched in gold.

The intrusive equivalents of mafic to intermediate lithologies show a slightly higher gold content than do extrusive types. During magma differentiation in a closed system, the gold is excluded from rock-forming silicates and will be concentrated in residual liquids along with the volatile components. Eventually these will be incorporated in the rock if the melt crystallizes totally within the magma chamber. However, if the magma vents to the surface, the gold, volatiles, and other incompatible elements will be lost. This trend appears to be reversed in ultramafic systems, where the gold may be incorporated in early crystallized refractory minerals such as spinels (Keays and Scott, 1976; Dupuy and others, 1981).

Korobeynikov (1981a) concluded that feldspars in igneous and metamorphic rocks are the carriers for background levels of gold, and noted that gold content decreased in these minerals from mafic to felsic igneous rocks. The highest gold values of about 7 ppb were found in plagioclase from intrusive basalts. In porphyritic varieties the plagioclase phenocrysts contained less gold (approximately 1 ppb) than the coexisting groundmass (approximately 6 ppb). Korobeynikov (1981b) also showed that biotite in igneous rocks has the highest gold content of all rock-forming silicates. The highest values (15-90 ppb) were found in biotites from gabbroic rocks.

There are fewer data on the gold content of various types of metamorphic and sedimentary rocks compared to igneous rocks (table A2). There appears to be a decrease in gold with increase in grade of metamorphism in quartzofeldspathic terranes. This is probably due to the removal of gold in solid solution and along grain boundaries during recrystallization. The gold is mobilized in the fluids released during prograde metamorphism. However, Pchelintseva and Feldman (1973) concluded that the gold content of metamorphic rocks was controlled by the original composition of the protolith and not by the grade of metamorphism. Sighinolfi and Santos (1976) obtained an average gold content of 1.5 ppb for Archean granulites from Brazil. They concluded that high-grade metamorphism may not significantly affect the distribution of gold and that the composition of the protolith is important in determining its content. They conceded that gold may be mobilized during dehydration but emphasized that most of it will be reprecipitated not far from the source.

A review of the preceding geochemistry reveals three factors which are important in any discussion of possible source rocks for gold: (1) no one rock type appears to be enriched in gold; (2) gold content in mafic rocks may increase slightly with increasing age; and (3) gold content in mafic varieties varies significantly depending on geographic location. Exceptions to the lack of enrichment of gold are the chemical sediments

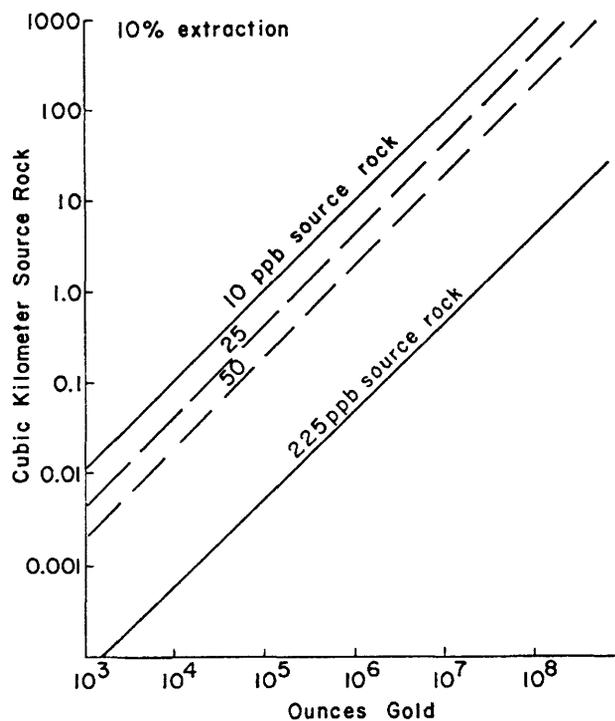
occurring as interflow units in volcanic terranes and iron-formation (Fripp, 1976; Bavington and Keays, 1978; Saager and others, 1982). These rocks may represent protore concentrations in the eventual formation of metamorphogenic veins in greenstone terranes. In the absence of such enrichments, certain rock types may serve as sources because the gold occurs in an easily mobilized state. Saager and others (1982) suggested that gold occurring in association with sulfides is readily available to later hydrothermal solutions, and a metamorphic overprint is very important in the genesis of gold-quartz veins in greenstone terranes. Most such rocks have been metamorphosed to at least greenschist facies, during which the gold could have been released into a more accessible site.

The increase in gold content with age in mafic rocks is less well documented and not well understood. This relationship is particularly noticeable in comparing Archean with Paleozoic ultramafic and mafic suites (Saager and others, 1982). The increase in gold content with age may be related to the progressive differentiation and depletion of metals and volatiles in the upper mantle (Keays, 1984). The geographic variation in gold content in mafic rocks has been interpreted to be due to inhomogeneities in the mantle (Anoshin and Kepezhinskas, 1972; Tilling and others, 1973; Saager and others, 1982). However, these inhomogeneities may have been produced by different degrees of partial melting at different times and places during an earlier differentiation of crust or upper mantle.

Consideration of source rocks with near normal abundances of gold requires that the volume of rock accessible to the leaching solutions is large enough to supply all the gold in a given deposit. Figure A6 gives the calculated volume of source rock required to form a deposit containing a given amount of gold. If a source rock contained 10 ppb Au, approximately 10 km<sup>3</sup> of the rock would be required to produce a deposit containing 10<sup>6</sup> ounces. Approximately 1 ppb would be removed from the source, a depletion which would be very difficult to detect using present analytical methods. If the source rock contained 225 ppb Au, only 0.05 km<sup>3</sup> would be required. Of course, if the efficiency of extraction was increased, the volume of source rock required would be decreased proportionately.

## MECHANISMS OF GOLD TRANSPORT AND DEPOSITION

The solution chemistry of gold is not well understood because of its apparent low solubility in most solutions of geologic interest. Previous studies on the transport of gold in hydrothermal systems have contrasted its solubility as chloride species in acid oxidizing solutions with that as various sulfide species



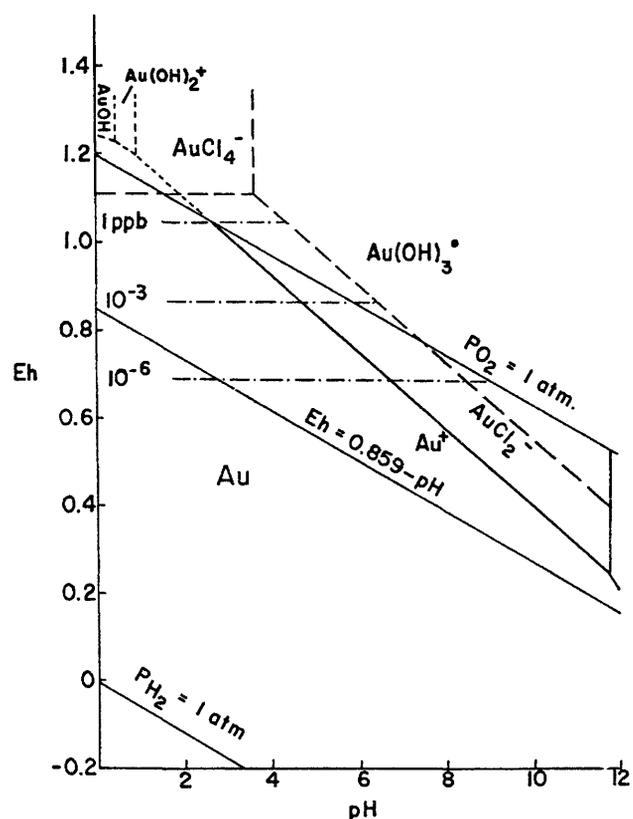
**Figure A6.** Calculated volume of source rock required to form gold deposits containing various amounts of gold. The diagram assumes a 10-percent efficiency in extraction and deposition, meaning that 10 percent of the gold in the original source ends up in the deposit. Three lines shown are for sources with 10, 25, and 50 ppb Au. A fourth line for 225 ppb was used to determine the volume of rock required to produce the gold veins in parts of the Front Range mineral belt where bostonite dikes containing this amount of gold occur (Budge, 1982).

under reducing conditions. As early as 1887 Becker (1887) suggested that gold was soluble in sulfide-containing solutions, based on his studies of mercury deposits in California. Stokes (1905) and Lenher (1918) demonstrated experimentally that gold is soluble in various chloride solutions at elevated temperatures. In the first relatively comprehensive experimental study on gold solubilities, Ogryzlo (1935) was able to dissolve significant quantities of this metal in weak hydrochloric acid solutions and in sodium bisulfide solutions at elevated temperatures and pressures. He concluded that in acid systems gold is transported as a chloride complex and deposition occurs as a result of reduction and (or) neutralization. In reduced sulfide solutions gold is transported as a bisulfide complex and deposition occurs through oxidation. Krauskopf (1951) arrived at the same conclusions based on a theoretical treatment of gold solubility. Smith (1943) concluded that gold is transported as sulfide complexes because in order for it to be soluble as chloride complexes, the solutions must be free of reducing agents. He stated that natural systems will have significant amounts of ferrous iron and H<sub>2</sub>S which will tend to reduce the gold out of solution.

In more recent studies, Helgeson and Garrels (1968) evaluated gold solubilities as chloride complexes and concluded these species to be important in the formation of hydrothermal deposits. Henley (1973) experimentally evaluated the solubility of gold in chloride solutions at temperatures between 300 and 500 °C. He concluded that the gold was transported as an uncharged gold chloride complex at high temperatures, but conceded that ionic or sulfide complexes may predominate at lower temperatures. In contrast, the transport of gold as various aqueous sulfide species has been supported by Weissberg (1970), Seward (1973, 1984), and Grigoryeva and Sukneva (1981). The most quantitative of these studies is that of Seward (1973), who evaluated the solubility of gold as bisulfide complexes as a function of temperature, pH, and concentration of various sulfide species. Solubilities were observed that were far higher than required to form gold deposits (see p. A17) under reasonable geologic conditions. In addition, he was able to postulate the complex stoichiometries  $\text{Au}(\text{HS})_2^-$  and  $\text{Au}_2\text{S}(\text{HS})_2^{2-}$  from the solubility measurements. Grigoryeva and Sukneva (1981) suggested that arsenic and antimony also may be involved with gold complexing as well as reduced sulfur species in some natural hydrothermal systems.

Several aspects of the behavior of gold in aqueous systems can be summarized using the Eh-pH diagram in figure A7. This is a standard diagram calculated at 25 °C showing the upper and lower stability limits for water at 1 atm. pressure and the upper limit of typical surface and near-surface water compositions labelled  $\text{Eh} = 0.859 - \text{pH}$  (Sato, 1960). This diagram and others to follow have been calculated using thermodynamic data from Wagman and others (1969), Naumov and others (1974), Robie and others (1978), and Barner and Scheuerman (1978). In solution gold can be in the aurous ( $\text{Au}^+$ ) or auric ( $\text{Au}^{3+}$ ) state depending on the oxidation potential. However, auric species occur only at high Eh values at or above the stability limit of water, particularly with 20 ppm chloride present. This value was chosen because it represents the average chloride content of near-surface ground water in the vicinity of weathering sulfide deposits. Therefore, it may be concluded that in hydrothermal systems gold will most likely occur either as the aurous ion or as a complex containing this species.

Table A3 gives the possible aurous complexes taken from various sources listed in the preceding paragraph. Many of these need not be considered because they require solution compositions outside the range that are typical of hydrothermal systems ( $\text{AuOH}^0$ ,  $\text{AuBr}_2^-$ ,  $\text{AuI}_2^-$ ,  $\text{Au}(\text{CN})_2^-$ ,  $\text{AuS}^-$ ). The thiosulfate complex appears to be quite stable, as thiosulfate complexes are used in some heap leaching procedures (Berezowsky and Sefton, 1979). However, the existence of thiosulfate is unknown in most hydrothermal systems.



**Figure A7.** Calculated Eh-pH diagram for the system Au-Cl-H<sub>2</sub>O at 25 °C assuming an aqueous chloride concentration of 20 ppm.

Thioarsenide complexes have been postulated (Grigoryeva and Sukneva, 1981; Romberger, 1984) because of the common occurrence of arsenic with gold in a wide range of deposit types from Archean quartz veins to Tertiary hot springs. However, the stability relationships for such complexes, if they do indeed exist, are unknown. The same rationale was used to suggest the existence of a telluride complex (Romberger, 1984).

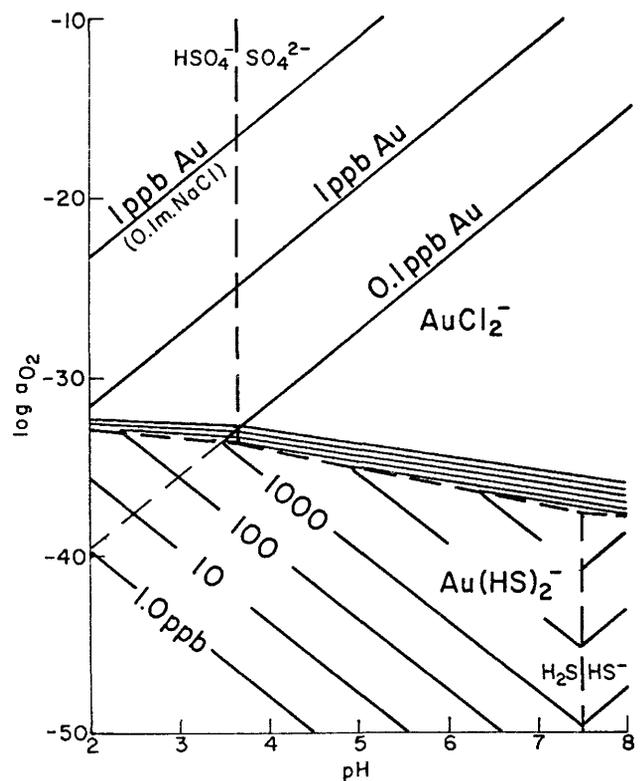
**Table A3.** Partial list of aqueous gold species occurring in natural systems

$\text{Au}^+$ , $\text{Au}^{3+}$ ,
$\text{AuOH}^0$ , $\text{AuOH}^{2+}$ , $\text{Au}(\text{OH})_2^+$ , $\text{Au}(\text{OH})_3^0$ ,
$\text{Au}(\text{OH})_4^-$ , $\text{Au}(\text{OH})_5^{2-}$ , $\text{AuO}_3^{3-}$ ,
$\text{AuCl}_2^-$ , $\text{AuCl}_3^0$ , $\text{AuCl}_4^-$ ,
$\text{AuOHCl}_3^-$ , $\text{Au}(\text{OH})_2\text{Cl}_2^-$ , $\text{Au}(\text{OH})_3\text{Cl}^-$
$\text{AuBr}_2^-$ , $\text{AuBr}_3^0$ , $\text{AuBr}_4^-$ ,
$\text{AuI}_2^-$ ,
$\text{Au}(\text{HS})_2^-$ , $\text{Au}_2\text{S}(\text{HS})_2^{2-}$ , $\text{AuS}^-$ ,
$\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ ,
$\text{Au}(\text{CN})_2^-$ ,
$(\text{AuAsS}_2^0, \text{Au}(\text{HTe})_2^-)$

The solubilities and relative stabilities of the chloride and bisulfide complexes are shown in figure A8, which is an oxygen activity-pH diagram calculated at 250 °C and assuming a solution containing 1 molal NaCl and 0.01 molal total sulfur (5.8 wt. percent NaCl and 320 ppm S, respectively). This 250 °C temperature is based on temperatures of formation for a wide variety of epithermal gold deposits (table A1). The solution composition is considered to be in the right order of magnitude for hydrothermal gold-depositing systems; significant changes in these solution parameters would be required to change the solubility relationships appreciably. The gold solubility as chloride complexes is calculated using thermodynamic data from Wagman and others (1969); the solubility of the bisulfide complexes is calculated from stability constants derived by Seward (1973). Only the  $\text{Au}(\text{HS})_2^-$  species is considered here; the effect of including  $\text{Au}_2\text{S}(\text{HS})_2^{2-}$  would be to increase gold solubility in the alkaline region. This diagram confirms the conclusions of earlier investigators that gold will be soluble as the chloride complex in acid oxidizing solutions and as the bisulfide complexes under reducing conditions in solutions where sulfur would occur as either  $\text{H}_2\text{S}$  or  $\text{HS}^-$ . It is apparent from the shape of the contoured solubility surface that in the case of the chloride complex, increase in pH and (or) reduction can result in gold deposition from a saturated solution. The maximum solubility of gold as bisulfide complexes occurs at slightly alkaline pH's just below the boundary between sulfide and sulfate. Both increase and decrease in pH can result in gold deposition, depending on the starting composition of the solution. However, because of the steep slope on the solubility surface towards increasing oxygen activity, oxidation is a much more efficient mechanism for gold deposition.

Henley (1973) and Seward (1973) showed that the solubility of gold as chloride and bisulfide complexes respectively increased with increasing temperature. Therefore, cooling would be an adequate mechanism for gold deposition from a saturated solution. However, temperature affects other parameters, such as oxygen activity, which may have a greater influence on solubility, so that temperature effects in natural systems are difficult to evaluate. This discussion will assume temperature to be relatively constant, which is not unreasonable considering that geothermometric studies indicate little temperature variation within any one mineralizing episode.

Pressure is even more difficult to assess. Generally, increase in pressure increases mineral solubility; however, Seward (1973) noted that its effect on gold solubility in sulfide solutions depended on both temperature and pH. In epithermal systems where the pressure-temperature conditions are very close to the liquid-vapor curve for the solution, the only significant



**Figure A8.** Calculated oxygen activity-pH diagram for the system Au-NaCl-S-H<sub>2</sub>O at 250 °C showing the relative solubilities of gold chloride and bisulfide complexes: 1 m. NaCl and 0.01 m. S in aqueous solution.

effect of pressure will be to influence the solubility of volatile components such as carbon dioxide and sulfur gases. These are very important in controlling the pH and oxygen fugacity of the solutions, as will be discussed later (Drummond, 1981).

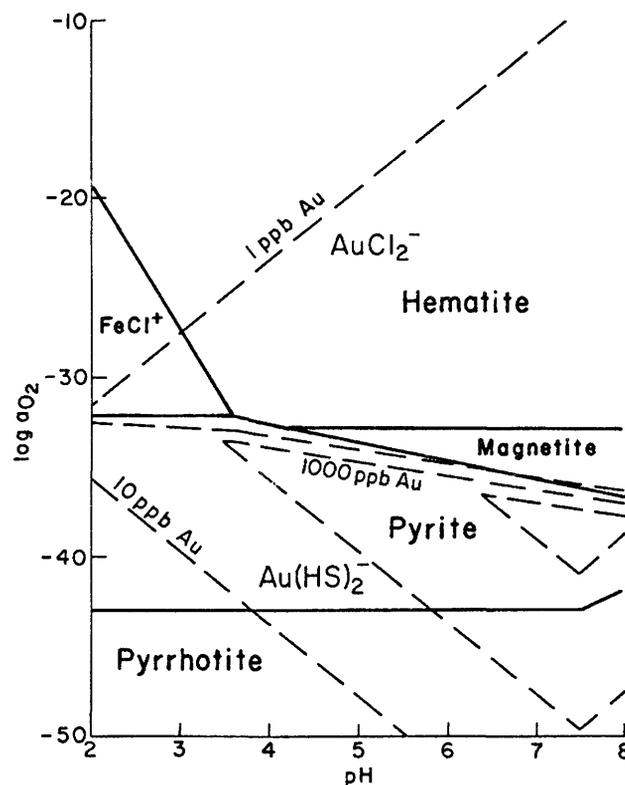
The solubilities shown for bisulfide complexes far exceed values expected in typical hydrothermal mineralizing systems even if in error by one or two orders of magnitude. For this reason Romberger (1984) suggested that mineralizing solutions may be undersaturated with respect to gold, and the gold is coprecipitated with sulfides during their deposition. The gold is subsequently released to the native state through some process of recrystallization. If this is the operating process, the usefulness of these phase relations is limited to show how the gold is transported and the stability relationships of the associated minerals; little can be concluded about the mechanisms of deposition of the gold itself.

Figure A9 superimposes the phase relations for iron sulfide and oxides on the gold solubility relationships plotted in figure A8 assuming the concentration of dissolved iron to be 10 ppm. The quality and usefulness of this and subsequent diagrams will depend on the reliability of the thermodynamic data used for their

calculation. The patterns will remain the same; however, the absolute limits on the coordinates will change somewhat with small (a few kilocalories) differences in thermodynamic parameters. Therefore, even though the data may not be of the highest quality, these diagrams are conceptually very useful in establishing relative solution-mineral equilibria and trends in parameters which influence the systems. The stable common minerals shown here, and others discussed later, serve as indicators of the conditions of ore deposition, so that the presence of pyrite in a hydrothermal mineral assemblage suggests that the oxygen activity-pH conditions of the solutions responsible for gold deposition fall within the pyrite field. Pyrite is very common in many hydrothermal gold deposits, and in most of these a close paragenetic relationship obtains between pyrite and gold. Figure A9 clearly shows that for these deposits the gold is most likely transported as a bisulfide complex and the most likely mechanisms of deposition are oxidation, diminished activity of dissolved sulfur, and (or) coprecipitation with pyrite. In contrast, in natural systems dominated by oxidized species such as hematite, gold would be transported as a chloride complex and deposition might occur as a result of neutralization and (or) reduction.

Figures A8 and A9 were prepared assuming the concentration of dissolved sulfur remains constant. However, this may not be the case in natural systems, because the precipitation of sulfides will decrease the activity of dissolved sulfide species, as will the loss of volatile sulfur species if the hydrothermal system is boiling. Figure A10 shows the gold solubility relationships superimposed on the relative stability of various iron minerals in terms of the activities of oxygen and sulfur gas at 250 °C and a constant pH of 5. The positions of the pyrite, pyrrhotite, and hematite fields are shown as in the earlier diagram. However, chlorite is shown here to replace the magnetite field because of the common occurrence of chlorite as an alteration mineral in gold deposits and the nearly total absence of magnetite. (See Barton and others, 1977, for the rationale used for replacing magnetite with chlorite in these diagrams.) The diagram shows that within the stability field of pyrite, the solubility surface slopes steeply in the direction of lower  $S_2$  activities so that gold and pyrite can be coprecipitated as a result of declining sulfur activity. The diagram also does not preclude the coprecipitation of gold with pyrite in a hydrothermal system undersaturated with respect to gold.

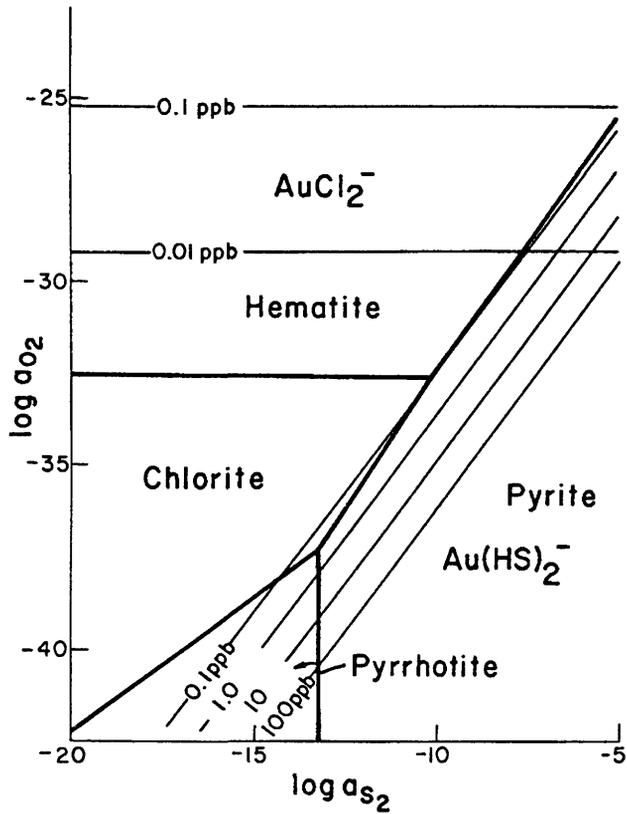
Many hydrothermally altered rocks contain abundant chlorite and pyrite, which would suggest that these rocks would buffer the system in terms of oxygen and sulfur activities along the boundary between these two minerals. However, the solubility contours are sub-parallel to this boundary, suggesting that gold would not



**Figure A9.** Calculated oxygen activity-pH diagram for the system Au-Fe-NaCl-S-H<sub>2</sub>O at 250 °C showing relative stabilities of various iron minerals (heavy solid lines) superimposed on the gold solubility relationships (dashed lines) from figure A8; 1 m. NaCl, 0.01 m. S and 10 ppm Fe in aqueous solution.

be deposited in systems buffered by this assemblage; yet, the contrary is observed. An alternative explanation is that the gold is coprecipitated with pyrite. In addition, Romberger (1984) showed that if gold is transported as a thioarsenide complex, the solubility contours are oblique to this phase boundary, and deposition would occur as a result of reductions in both oxygen and sulfur activities.

Alteration and gangue minerals that occur with the ore assemblage can be very useful in indicating the chemical conditions of deposition and also the chemical changes associated with ore precipitation. In addition, when the temperature and residence time for solutions in source rocks or aquifers are sufficient, the solutions begin to take on a chemical character which is governed by those source rocks. For example, solutions derived from carbonaceous sedimentary rocks will be reducing and can be assumed to be high in reduced sulfur species. It is the contrast between the geochemical environments of the host and source rocks which commonly is responsible for the chemical changes causing ore deposition.



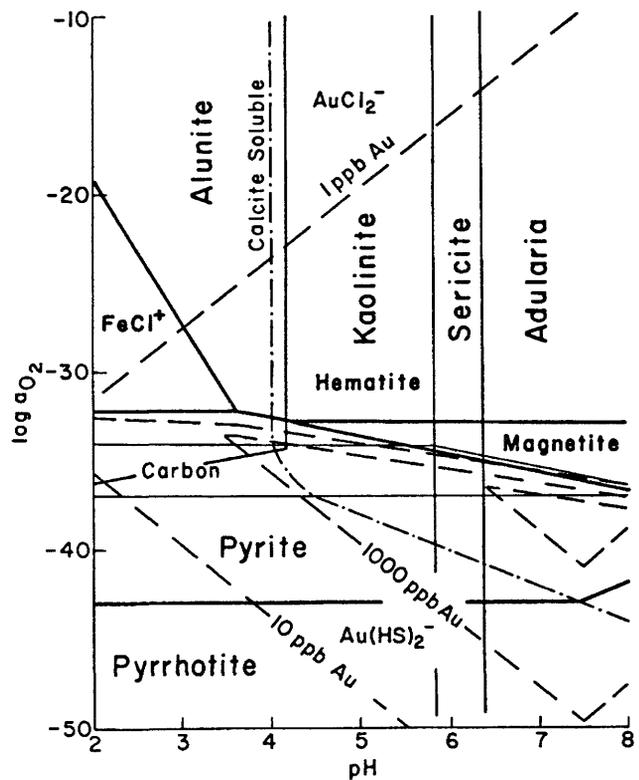
**Figure A10.** Calculated oxygen activity-sulfur activity diagram for the system Au-Fe-NaCl-S-H<sub>2</sub>O at 250 °C and pH 5 showing the relative stabilities of various iron minerals (heavy solid lines) and gold solubility relationships (light solid lines); 1 m. NaCl in aqueous solution.

Figure A11 superimposes the stability relationships for the common potassium aluminosilicate alteration minerals and the phase relationships for various forms of carbon onto the earlier derived solution-mineral equilibria at 250 °C and assuming an aqueous potassium concentration of 100 ppm, a calcium concentration of 100 ppm, and CO<sub>2</sub> partial pressure of 1 atm. Alunite and kaolinite would characterize alteration assemblages produced by acid to slightly acid solutions; sericite would be formed by neutral to slightly alkaline solutions; and potassium feldspar would be a product of alkaline solution alteration (neutral pH at 250 °C is approximately 5.5). Carbonate minerals would be deposited by solutions with oxygen fugacities above the graphite field and at pH's above the carbonate solubility line shown. At lower oxygen fugacities below the carbon field, methane would be stable. In this diagram the stability field of graphite has been calculated. However, the stability field of more complex forms of carbon would have the same shape and be in a similar position to that

shown. Hydrocarbon fields would fall between methane and graphite, depending on the carbon-to-hydrogen ratio.

Figure A11 shows clearly that solutions which attain chemical equilibrium with pyritiferous carbonaceous sedimentary rocks would be reduced in nature and be of the composition appropriate for the solution of gold as bisulfide complexes. The pH of these solutions would be determined by CO<sub>2</sub>:CH<sub>4</sub> ratios or the silicate assemblage in the source rocks.

Sericite is a common mineral occurring in alteration haloes around gold veins in a wide variety of deposit types and geologic terranes from veins in Tertiary volcanic rocks (Casadevall and Ohmoto, 1977) to veins in Archean greenstone terranes (Boyle, 1979). Spatial relationships suggest that the sericite is genetically related to gold deposition in many places. Figure A11 shows that the stability field of sericite overlaps the area of maximum gold solubility as a bisulfide complex, and therefore sericite would be expected as the most common potassium aluminosilicate in alteration



**Figure A11.** Calculated oxygen activity-pH diagram for the system Au-Fe-CaO-K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-NaCl-C-S-H<sub>2</sub>O at 250 °C and CO<sub>2</sub> partial pressure of 1 atm. showing relative stabilities of aluminosilicate alteration minerals (light vertical solid lines) and carbon (lightest solid lines) superimposed on the stability relationships for iron minerals (heavy solid lines) and gold solubilities (dashed lines); 1 m. NaCl, 0.01 m. S, 0.1 m. Ca, 100 ppm K and 10 ppm Fe in aqueous solution.

assemblages produced by solutions originating in this field if simple oxidation was the prevailing mechanism of deposition.

Adularia (orthoclase) is commonly found spatially associated with precious metals in many epithermal gold deposits (Buchanan, 1981). In a vertically zoned hydrothermal system, the adularia zone usually narrows and disappears less than 100 meters above the ore zone. In figure A11 adularia indicates alkaline pH's. The presence of this mineral in hydrothermal veins can be due to increases in pH as a result of the loss of carbon during boiling (see p. A22), or the original solutions had a higher initial pH.

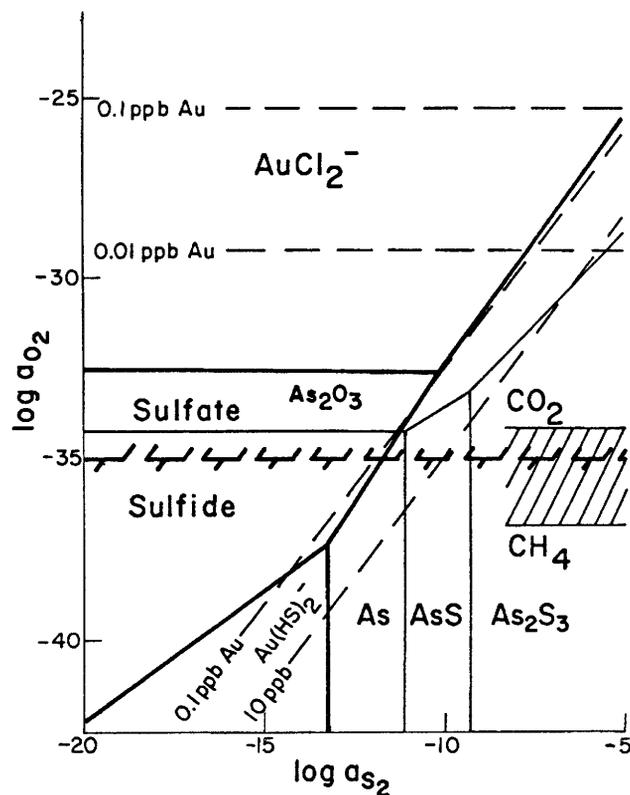
Argillic alteration assemblages are widespread in many gold districts and may occur as haloes around relatively deep precious and base metal veins, or in quite shallow precious metal and hot springs systems. These assemblages may consist of varied proportions of kaolinite, montmorillonite, illite, sericite and (or) alunite. All of these indicate solution pH's at or below 5. Kaolinite-alunite-silica assemblages also are found as layered caps around hot spring centers, many of which contain anomalous amounts of gold. Figure A11 shows that alunite and kaolinite would be expected in assemblages formed by acid oxidizing solutions, and these minerals are referred to commonly as the acid assemblage. Alunite would not be expected to form directly from solutions transporting gold as bisulfide complexes even though there appears to be a genetic relationship between alunite and gold deposits. The acid assemblage has been interpreted to be a result of downward-percolating sulfuric acid solutions which, in turn, had been a product of mixing of oxidized ground waters with H<sub>2</sub>S vapors rising from below. This assemblage is diagnostic of epithermal gold deposits showing evidence of boiling, and it may be a reflection of events occurring at depth in a vertically zoned hydrothermal system (Berger, 1982; Henley and Ellis, 1983).

Arsenic occurs ubiquitously in hydrothermal gold deposits of all types, so a consideration of the phase relations for this element is appropriate here. In primary ores arsenic occurs most commonly as realgar or arsenopyrite, depending on deposit type. Orpiment occurs associated with realgar in certain sedimentary rock-hosted deposits. Figure A12 shows the stability fields for various arsenic minerals and compounds superimposed on the oxygen-sulfur activity diagram previously given as figure A10. The presence of arsenic sulfides limits the oxygen fugacity in these hydrothermal systems. In chemically complex natural systems, arsenic oxide would be replaced by other phases such as scorodite, FeAsO<sub>4</sub>·2H<sub>2</sub>O. This mineral is found in some disseminated gold deposits; however, it is a weathering product of the original sulfide ores. Also shown are the

position of the carbon field at a CO<sub>2</sub> pressure of 1 atm. and the boundary between reduced and oxidized sulfur species.

In view of these phase relationships, it is noteworthy to recognize that a very common, if not ubiquitous, assemblage in many disseminated gold deposits is pyrite, realgar, and gold in a carbonaceous host. Figure A12 shows that solutions in equilibrium with this assemblage would transport gold as the bisulfide complex, and deposition from saturated solutions would occur as a result of oxidation or reduction of sulfur activity. Solution compositions conducive to the transport of gold as the chloride complex lie at oxygen fugacities well above the stability fields of sulfides, and chloride complexing is considered unimportant at temperatures typical for most gold deposition.

Figure A13 shows the stability field for arsenopyrite in terms of the same parameters used above. Certain Precambrian gold deposits are dominated by the assemblage chlorite, arsenopyrite, and iron sulfide, either pyrrhotite or pyrite. Even though the temperature of formation of these deposits is higher than 250 °C (Groves



**Figure A12.** Calculated oxygen activity-sulfur activity diagram for the system Au-Fe-As-NaCl-C-S-H<sub>2</sub>O at 250 °C, pH 5, 1.0 m. NaCl, and CO<sub>2</sub> partial pressure of 1 atm., superimposing the relative stabilities of arsenic (light solid lines) and carbon phases (diagonal line pattern) on the relationships shown in figure A10.

and others, 1984), the phase relations shown here suggest that the mineralizing solutions were dominated by reduced sulfur species and gold was most likely transported as bisulfide complexes.

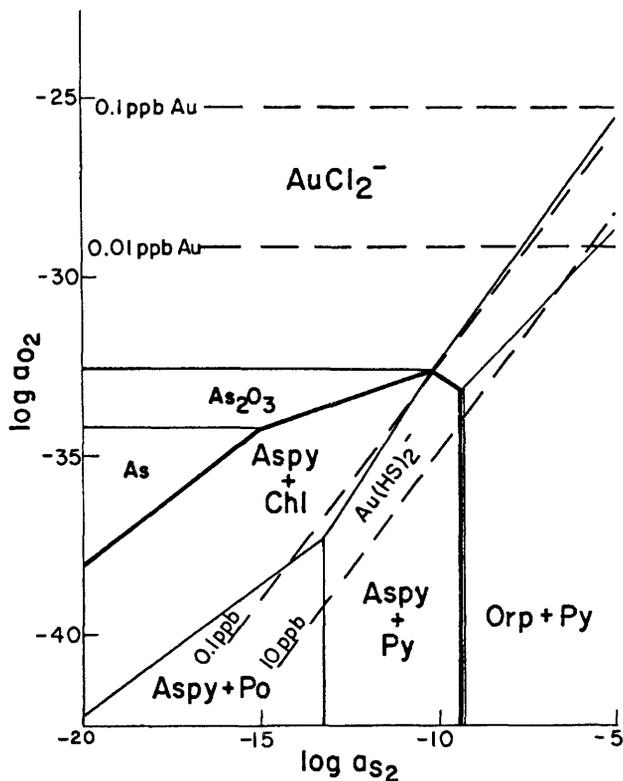
To summarize the solution chemistry described herein, in hydrothermal systems where gold may be accompanied by pyrite and various arsenic sulfides, the composition of the solutions had to be such that the gold was transported as bisulfide complexes. Gold chloride complexes would predominate only in a few systems dominated by hematite or other oxides, or at higher temperatures than those determined for typical epithermal deposits. Alteration assemblages containing sericite and (or) potassium feldspar are consistent with the solutions being near neutral or slightly alkaline. Even though the acid assemblage, including alunite and kaolinite, commonly occurs in gold deposits, it is probably formed above the zone of gold deposition by processes which are indirectly related to those responsible for the precipitation of gold itself. Gold may occur with alunite as a result of the expansion of the hydrothermal system from below and the superposition of a depositional event

onto an earlier formed argillic assemblage. The evidence for this is the occurrence of fresh euhedral pyrite with alunite and (or) kaolinite, an assemblage not predicted to form contemporaneously based on the phase relationships.

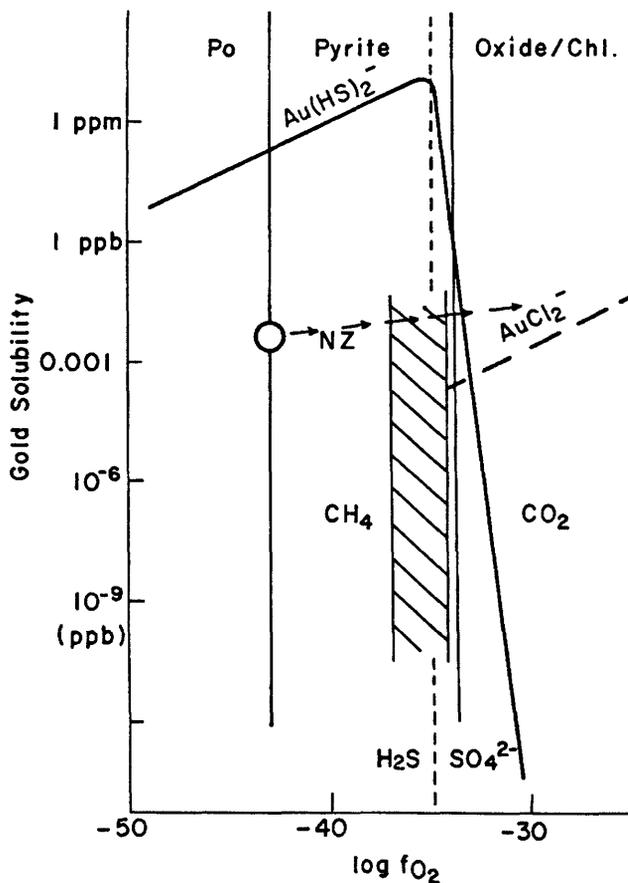
If the gold is transported as bisulfide complexes, the most efficient mechanisms of deposition from saturated solutions at relatively constant temperatures are oxidation and (or) decrease in sulfur activity. Changes in pH probably are not important in the deposition of gold itself, although they do occur as evidenced by the zoned nature of alteration assemblages (Buchanan, 1981). Hydrothermal solutions most certainly are not saturated with respect to gold through most of their existence. Figure A14 shows the path that a solution may take starting out with a gold concentration of 0.004 ppb and buffered by the mineral pair pyrrhotite plus pyrite (Weissberg and others, 1979). The solution would not become saturated with respect to gold upon oxidation until the composition intersected the solubility surface (crosslined on fig. A14) as shown. However, upon piercing the saturation surface, the solubility of gold decreases rapidly and deposition would occur. Alternatively, the solution may never become saturated and the gold could be coprecipitated with sulfides. Once these mechanisms of deposition have been established, the possible natural processes responsible for these changes must be addressed. Processes occurring in hydrothermal systems which may result in solution oxidation are boiling (or effervescence), mixing with more oxygenated ground waters, or contact with a more oxygenated host rock. Processes which may result in reduction in sulfur activity are boiling and (or) effervescence and precipitation of sulfides.

Drummond (1981) addressed the chemical changes occurring during both boiling and fluid mixing. During boiling there will be a partitioning of reduced volatile components into the vapor phase, resulting in oxidation of the residual liquid. Drummond (1981) calculated the solution paths for several compositions in terms of oxygen fugacity and pH at 250 °C and found that, depending on the starting composition, the solution has an initial increase in pH followed by a sharp increase in oxygen fugacity. His solution composition paths are consistent with transport of gold as a bisulfide complex and precipitation as a result of oxidation due to boiling.

Many epithermal gold deposits have shown evidence that boiling was occurring in the mineralizing system; the results of several studies have been summarized by Buchanan (1981). Numerous more recent studies also result in the conclusion that boiling is an important part of the mineralizing process, as there appears to be both a spatial and temporal relationship between a boiling event and precious metal deposition. The models proposed by Buchanan (1981) and Berger



**Figure A13.** Calculated oxygen activity-sulfur activity diagram for the system Au-Fe-As-NaCl-S-H<sub>2</sub>O at 250 °C, pH 5, and 1.0 m NaCl, showing the stability field of arsenopyrite (heavy solid lines) superimposed on the solution-mineral equilibrium relationships of figure A10. Aspy, arsenopyrite; Orp, orpiment; Py, pyrite; Chl, chlorite; Po, pyrrhotite.



**Figure A14.** Calculated gold solubility versus oxygen activity at 250 °C, pH 5, 1.0 m. NaCl, 0.01 m. S, and CO<sub>2</sub> pressure of 1 atm. showing the solution path during oxidation of a solution starting with 0.004 ppb Au buffered by the mineral pair pyrite-pyrrhotite. NZ, New Zealand.

(1982) incorporate boiling into their mineralizing systems. The mineralization commonly is restricted to a relatively narrow vertical range and its elevation commonly shows a spatial relationship to a paleosurface. The geology of many of the deposits suggests that they formed at relatively shallow depths, commonly with evidence of hot spring activity, so boiling of solutions at temperatures in the vicinity of 250 °C is not an unexpected event.

In addition to oxidation and gold deposition, boiling will have other relevant effects on the mineralizing system. Alteration assemblages within the narrowly telescoped vertical zonation may be explained by changes in the pH of the solutions, which itself is a result of loss of acid volatiles such as CO<sub>2</sub>. The acid assemblage already described is a product of sulfuric acid solutions formed by the oxidation of H<sub>2</sub>S vapors, which had to originate in a boiling system. This same loss of H<sub>2</sub>S would result in the decrease of sulfur activity in the residual liquid and may cause gold deposition from a

saturated solution if the gold is transported as bisulfide complexes. Finally, gold itself may be transported in the vapor phase as the highly speculative thioarsenide species AuAsS<sub>2</sub><sup>0</sup>, as this is a neutral molecule. This species would redissolve in the condensate forming in the cooler, shallow parts of the system and precipitation would result from oxidation. This mechanism would result in a very shallow near-surface zone of gold deposition, a feature recognized in many hot spring and hydrothermally mineralized systems.

Mixing of rising hydrothermal solutions with cooler oxygenated ground water may be an important mechanism for gold deposition in some systems. Theoretically, deposition should occur along the mixing interface. However, these are very dynamic systems, and convection, turbulence in open structures, and refluxing would destroy any regular mixing surface, so that kinetics would be more important in controlling mineralization than simple solution-mineral equilibria. The same would be true for transporting solutions entering oxygenated host rocks, particularly where the water:rock ratio is high. The rocks would take on the chemical characteristics of the hydrothermal solutions with time, and the driving forces for deposition would disappear until a change in the hydrologic regime occurred. Earlier formed ore minerals may be redissolved by later solutions dominated by either ascending hydrothermal solutions or descending ground water in areas of recharge in a convecting system. The result will be periods of acidification and (or) oxidation alternating with those of reduction and (or) neutralization, producing complex and unpredictable zoning and paragenetic relationships.

Thus, geochemical models can be postulated which incorporate plausible natural processes and at the same time are consistent with fundamental solution-mineral equilibrium principles. However, care must be taken when applying these models so that equilibrium principles fit paragenetic relationships, and also it must be understood that the deposits are commonly products of multiple events. Each event will have its own compositional history in terms of oxidation state, pH, and sulfur activity, among other parameters; and the result of superimposing these events one upon the other must be considered. Finally, the hydrologic environment is very important in controlling ultimate source rocks, the affected hosts for ores, and the kinetics of the reactions responsible for ore deposition.

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