Research brief

Hydrothermal alteration and gold deposition: a general overview

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Abstract

As it falls, the hydrothermal fluid leaches metals and precipitates minerals. Hydrothermal oreforming fluids are multicomponent aqueous electrolyte solutions that carry gold to ore-depositing environments deep inside the Earth's crust. Hydrothermal ore deposits account for a major share of the world's natural gold endowment. Changes in the chemical and physical environment through which the hydrothermal ore fluid migrates cause the deposition of elemental gold and goldcontaining minerals. A buoyantly rising hydrothermal fluid may come into contact with a permeable zone, causing volatile phase separation and/or boiling, or a deep fluid may come into contact with and mix with colder, steam-heated water with a lower pH. The changing stability of the gold-containing complex ions in reaction to these new conditions determines whether or not gold precipitates in certain scenarios. As a result, hydrothermal gold deposition can occur over a wide range of temperature, pressure, and fluid composition, encompassing varied habitats. Other common minerals, including as quartz, hematite, pyrite, chalcopyrite, calcite, and barite, are frequently precipitated or pulled out of the fluid when the gold is deposited. The gold is referred to as ore, and the other minerals are referred to as gangue. The axial zonation of gold-bearing mineral ore parageneses includes the association of indicator elements of Au, Ag, As, Sb, Pb, Zn, Cu, Bi, Mo, Be, and Co, whereas the association of Au, Ag, As, Sb, Pb, Zn, Cu, Bi, Mo, Be, and Co is thought to be the transverse zonation of the primary haloes. The regional metallogenic units are structural-metallogenic zones with varying degrees of mineralization. Understanding hydrothermal changes is critical because it provides insight into the genesis of ore fluids as well as the chemical and physical properties of ore deposit development.

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1. Introduction and General Background

Gold has historically been a critical strategic commodity, and the genesis of gold deposits has long been studied (Andrew, 2013). Gold is the only economically important metal or a major byproduct in 11 well-characterized deposit types, including paleo placer, orogenic, porphyry, epithermal, Carlin, placer, reduced intrusion-related, volcanogenic massive sulfide (VMS), skarn, carbonate replacement, and iron oxide-copper-gold (IOCG); it also dominates several deposits of uncertain or unknown origin. From the Mesoarchean to the Pleistocene, major gold concentrations formed worldwide, from the Earth's surface to mid-crustal paleodepths, alone or in association with silver, base metals, and/or uranium, and from hydrothermal fluids of predominantly metamorphic, magmatic, meteoric, seawater, or, more rarely, basinal origins, as well as from mafic magma or ambient surface water. The majority of Neoproterozoic and Phanerozoic deposits were generated in accretionary orogens (Richard et al., 2020).

The construction of a simple classification scheme for gold deposits, as provided here, was undertaken with full recognition of the numerous problems connected with ore deposit classification in general. Historically, various classifications and nomenclatures for lode gold deposits have been reached depending on whether they were examined from a genetic, geochemical, economic, or tectonic standpoint (Emmons, 1937; Boyle, 1979; Cox and Singer, 1986; Bache, 1987). Furthermore, classification schemes for subsets of gold deposits have been devised, such as those regarded as epithermal (Heald et al., 1987), intrusion-related (Sillitoe, 1991), bulk mineable (Bonham, 1989), or epigenetic Archean (Gebre-Mariam et al., 1995). These have added new perspectives and broadened the nomenclature surrounding the topic of gold deposit categorization. According to an evaluation of existing categorization schemes, the key geological criteria indicate that the combination of geological environment, mineralization nature, and hydrothermal alteration is unique for practically every deposit type (Robert et al., 1997). As a result, the geological characteristics of deposits represent a key discriminating criterion to be utilized in the establishment of a classification scheme.

Precipitation from hydrothermal solutions has created by far the greatest number of mineral deposits (Skinner and Barton 1973). Because of physicochemical disequilibrium between rocks and fluid, a heated, aqueous solution containing met and other components precipitates minerals in ore traps (Skinner 1997). Fluids passing through rocks cause mineral reactions that accommodate such severe disequilibrium, resulting in the formation of novel hydrothermal mineral associations. Hydrothermal ore deposits account for a considerable fraction of the world's natural gold endowment (Frimmel, 2008). Many studies over the last 25 years have shown a close relationship between vein-hosted gold deposits and alteration halos caused by hydrothermal fluid infiltration (e.g., Böhlke 1989; Boiron et al. 1991; Eilu and Mikucki 1998; Garofalo et al. 2002; Garofalo 2004a, b; Yang et al. 2006; Phillips and Powell 2009; Esmaeily et al. 2012). Fluids move through fault-fracture systems formed by mixed brittle-ductile shear zones that are mostly active in the mesozonal environment. Large amounts of fluid are injected along the shear zones during the faulting process, generating mesh structures. Hydraulic extensional veins are associated with shear fractures, resulting in mineral precipitation (Sibson and Scott 1998; Cox 1995; Zoheir 2008a, b; Bark and Weihed 2012).

2. Environmental constraints on gold mineralization and hydrothermal alteration

Three first-order assumptions are required for physical properties shared by known gold deposits:
a) gold extracts from a local or proximal source to a structurally controlled context;

b) fluids transport gold into the structure; and

c) tectonic forces drive lode-gold mineralization.

Fluids are crucial in gold deposition. In fact, the fluids provide:

1) a transport medium for soluble material;

2) a driving force for fracturing; and

3) they modify the mechanical/rheological properties of rocks, hence influencing the nature and degree of deformation.

Hydrothermal fluid, a common agent and result of metamorphism, is composed of hot H2O- and CO2-rich fluid produced from deep de-volatilizing intrusions or lateral advection from wall rocks during deformation.

Different theories about fluid composition are related to each of the conceptual models discussed above. According to the depositional concept, hydrothermal fluid is universal within a large mineralizing system. The model predicts that structural conduits transport non-unique fluids in extremely varied hosting lithology. This results in a variety of mineralization and alteration forms (Colvine, 1989). However, the composition, temperature, and pressure of most fault fluids vary geographically and temporally; there is no such thing as a typical fault fluid (Parry, 1998). Individual fault mineralogy and fluid-inclusion features suggest discrete fluids with different chemical compositions but the same state qualities. This reinforces the idea that the environment of deposition, rather than the fluids, must be prioritized. A source of gold, on the other hand, may or may not be produced from metamorphic fluids and may or may not be remobilized in accordance with the depositional model. Compressive or least-compressive tectonics are required for lodegold mineralization. Regardless of the gold supply or fluid composition, lode-gold mineralization relies on crustal instabilities caused by a primary stress differential to drive fluid movement and fractures. Heat from intrusive magmas can also cause fluid movement and, as a result, fractures. Stress field involvement is supported by structural asymmetries (e.g., fractures, faults, and veins). As a result, a genetic model is acceptable for explaining lode-gold quartz vein systems.

3. Hydrothermal alteration and gold deposition

The reaction between fluid and host rocks is known as hydrothermal alteration. When heated, mineral-rich fluids interact with rocks and minerals, the mineral composition, texture, and structure of the rocks and minerals change. It varies with temperature, pressure, and, most crucially, fluid composition (Reed 1997, Rose and Burt 1979). Fluids involved in hydrothermal alteration can be formed from magma or other deep sources, and they can transport dissolved metals and minerals through the Earth's crust. Because wall rock interaction along the transport pathway affects fluid composition, the fluid that arrives to the ore trap is not the same as the "primary" or "source" fluid, such as magmatic brine or warm saltwater (Reed, 1997). Temperature gradients between fluids and wall-rocks, as well as differences in wall-rock composition, are major factors influencing such transformation. Although the physicochemical gradient is often significant, the reaction time of metasomatic processes is restricted, implying that final equilibrium between various phases is rarely established (Zhu et al., 2011). As the crust devolatilized progradely, the shearing event may have been accompanied by the formation and transport of hydrothermal fluid. This fluid could have leached ore components from one portion of the granite pluton and concentrated them in veins in another part of the same pluton (Deb and Sarkar, 2017). Hydrothermal alteration can occur in a wide range of geological contexts, including volcanic environments, hot springs, and geothermal systems. Hydrothermal alteration is often associated with various types of quartz-vein mineralization, and some altered wall-rocks can contain high concentrations of metals (e.g., Vallance et al. 2003; Zhu et al. 2011; Andrada de Palomera et al. 2012; Cepedal et al. 2013). Intensive host-rock alteration around the quartz vein reveals distinct mineralogical changes that are indicative of metasomatic processes as a result of the interaction with external hydrothermal fluids. Hydrothermal deposits a large group of mineral deposits formed from the sediments of hot aqueous solutions that circulate deep inside the earth (fig.1). The amount of precipitation of native elements and the type of hydrothermal alteration minerals are strongly dependent on the physical– chemical nature of the mineralizing fluids and the host-rock composition. Chemical variations around mineralized rocks in hydrothermal gold deposits are critical both when it comes to constraining genetic models and, ultimately, as a tool for exploration. Prospectors and geologists have long recognized the link between gold mineralization and volcanic and geothermal hot spring activity. The large literature reporting the alteration demonstrates the significance of geochemical approaches. Several gold deposit studies (e.g., Lowell and Guilbert 1970; Klein et al. 2002; Yang et al. 2006; Su et al. 2008; Modabberi and Moore 2004) have detailed the mineral associations of the various wall-rock alteration zones, as well as the chemical features of the fluids associated with the alteration processes. For the hydrothermal gold deposits investigated in the world, many authors related in their gold deposit that, the proximal alteration zones are bleached in hand specimen due to the dominance of quartz, calcite, ankerite, albite, sericite, pyrite, and chalcopyrite, and the absence of epidote, chlorite, Fe±Ti oxides (in all rock types), and hematite (in syenite). Albite and sericite compositions are similar in proximal to distal alteration zones, and are comparable in all mineralized veins. Calcite and ankerite occur in all hydrothermal alteration zones (Duuring et al. 2000, Zhu et al., 2011). Some writers argue that wall-rock alteration is inextricably linked to the mineralogy of the host rock (e.g., Callaghan 2001; Miur 2002; Botros 2004; Deksissa and Koeberl 2004; Kister et al. 2006). Nonetheless, very few attempts have been made to define the entire evolutionary path of the alteration by quantifying mass changes in different alteration zones during hydrothermal fluid reactions (e.g., Kolb et al. 2005; Phillips and Powell 2009; Andrada de Palomera et al. 2012; Esmaeily et al. 2012). Similarly, research on fine-scale fluctuations in element contents in hydrothermally altered wall rocks with increasing distances to mineralized veins are uncommon (e.g., Silberman and Berger 1985; Warren et al. 2007).

Ascending gold, sulfur, and metal-rich hydrothermal fluids were directed upward along significant fracture and fault zones (Edwards and Atkinson, 1985); elements were leached from the pluton's previously hardened parts. The fluids would have moved higher and outward, following fissures in the solidified part of the granite pluton, causing ore minerals to precipitate in veins and modifying the wall rocks (fig.2). Changes in physicochemical circumstances such as temperature, pressure, oxygen fugacity, and sulfur fugacity are effective gold precipitation mechanisms. Gold can be found in fractured rock as lode deposits or veins. It could possibly be found in the Earth's crust. When hot fluids move through gold-bearing rocks, they take up gold and concentrate it in new sites in the crust. In these regions, hydrothermal fluids generate gold-bearing quartz veins. Many various types of lode deposits are formed by chemical differences in fluids and rocks, as well as physical changes in the rocks (Edwards and Atkinson, 1985). The geochemical makeup of ore-forming fluids is reflected in the mineral assemblages generated during hydrothermal alteration. At high temperatures and pressures, gold tends to concentrate in the vapor phase of fluids. Rock and mineral alteration can result in the production of new minerals and, in some cases, the concentration of precious minerals like gold and silver.

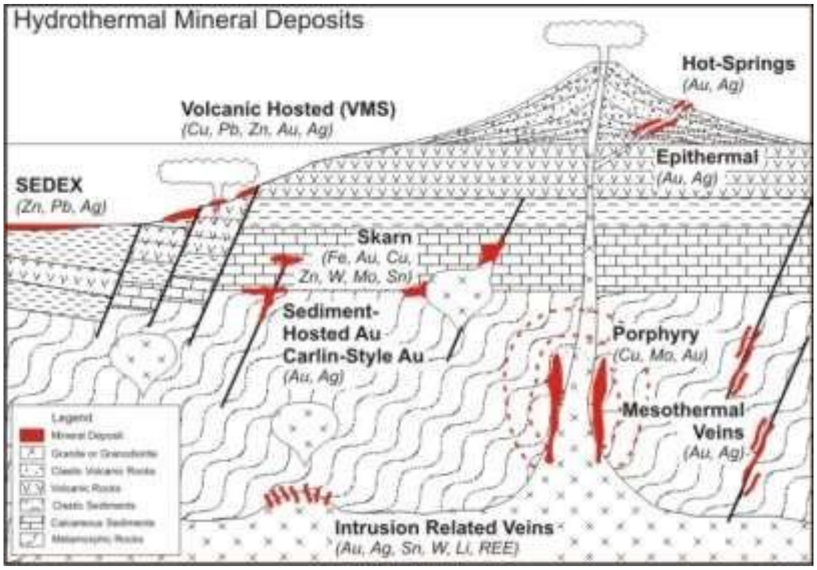

Fig. 1.: Model large group of mineral deposits formed from hydrothermal fluids according to Edwards and Atkinson (1985).

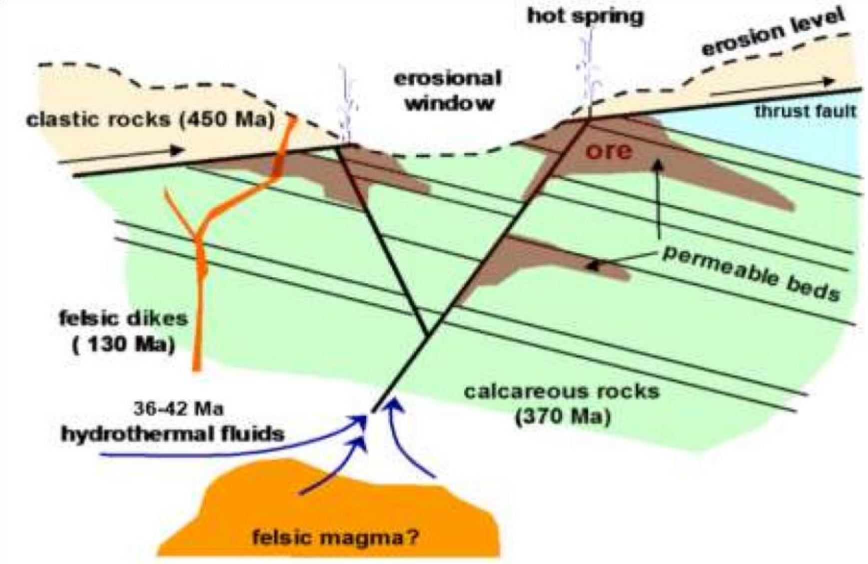

Fig. 2: Model of migration of hydrothermal fluid according to Edwards and Atkinson (1985).

4. Mineralogy and Geochemistry of the hydrothermal gold deposit

Many writers have explored the chemistry associated with a wide range of hydrothermal ore deposits (e.g., Phillips 1986; Robert and Brown 1986; Bierlein et al. 1998; Deksissa and Koeberl 2004; Henley and Berger 2011; Zhu et al. 2011; Cepedal et al. 2013; Zachariá et al. 2013). Both types of alteration textures range from minor alteration of only parts of the minerals or matrix in the host rocks, providing a punky or earthy appearance to the overall rock, to partially changed phenocrysts. Rocks can be pervasively altered at high alteration intensities, with nearly all fundamental phases in the rock being converted to new hydrothermal minerals (Shanks, 2012). Concerning gold mineralization connected with the hydrothermal system, gold may substitute into refractory sulfides such as pyrite and arsenopyrite, hindering mineral processing. As a result, as magmas fractionally crystallize, gold gets concentrated due to sulfide segregations that scavenge gold from the silicate residue. The typical Au contents in natural ore-forming hydrothermal fluids, as well as the time scale of deposit formation, are the subject of scholarly discussion. Based on direct study of active geothermal fluids, Simmons and Brown (2006) proposed that average Au concentrations in the ore-forming fluids of the enormous Ladolam Au deposit were no more than 15 ng/g. Microanalyses of fluid inclusions in various magmatic-hydrothermal ore deposits, on the other hand, show 100e1000 times greater Au concentrations (Ulrich et al., 1999; Pudack et al., 2009; Seo et al., 2009), signifying considerably faster and more effective metal enrichment. Magma emplacement causes and controls the circulation of hydrothermal fluids, which can deliver ore-forming components to economically valuable deposits.

In general, hydrothermal deposits are classified based on their depth and temperature of formation. At vast depths and high temperatures, hypothermal deposits form; at intermediate depths and temperatures, mesothermal deposits form; and at the shallowest depths and lowest temperatures, epithermal deposits occur. Some mineral species only crystallize at specific temperatures and pressures. Because the temperatures and pressures in each type of hydrothermal deposit change, each has a distinct group of related minerals.

- *Geochemical associations in epithermal gold deposits*

Waldemar Lindgren, a prominent American geologist, invented the term epithermal in 1933, with epi meaning shallow and thermal referring to the heated fluid. Epithermal gold deposits are among the world's richest gold resources, with some bonanza-grade ore shoots holding more than 1000 g/t goldequivalent, or a kilogram of gold for every tone of rock mined. Epithermal gold deposits are a type of lode mineral deposit that contains economically significant amounts of Au, Ag, and base metals. These deposits develop from ascending hydrothermal fluids in a variety of host rocks, primarily through replacement and/or open-space filling (Kamina,2012). Because alteration zones in epithermal systems are typically larger than the associated ore deposit, recognizing mineralogical and geochemical zonation within the area of alteration may provide a basis for developing vectors to the ore deposits, which is critical for mineral exploration. Temperature, pressure, rock type, nature of circulating fluids (such as pH, CO_2, H_2S activity), and water/rock ratios all influence the formation of hydrothermal mineral phases in epithermal systems. The interplay of (1) acidic fluids, (2) near-neutral chloride fluids, and (3) alkaline fluids can be used to explain hydrothermal change in epithermal systems. Mineral assemblage recognition is critical in separating low-sulphidation from high-sulphidation (Hedenquist and Lowenstern, 1994; Pirajno, 2008; Kamina, 2012). Gold in an intrusion-related IOCG environment is mostly associated with the most recent epithermal event or overprint and is found in pyrite or specular hematite, but at least two other types of gold, magnetite, and chalcopyrite-related gold have been described in Chilean IOCG deposits (Filip and Orlandea, 2016).

Table 1: Geochemical associations of epithermal gold deposits (Kamina,2012).

	Low Sulphidation	High Sulphidation
Anomalously high	Au, Ag, As ,Sb ,Hg ,Zn ,Pb ,Se ,K, Ag/Au	Au,Ag,As,Cu,Sb,Bi,Hg,Te,Sn,Pb, Mo , Te/Se
Anomalously low	Cu,Te/Se	K, Zn, Ag/Au

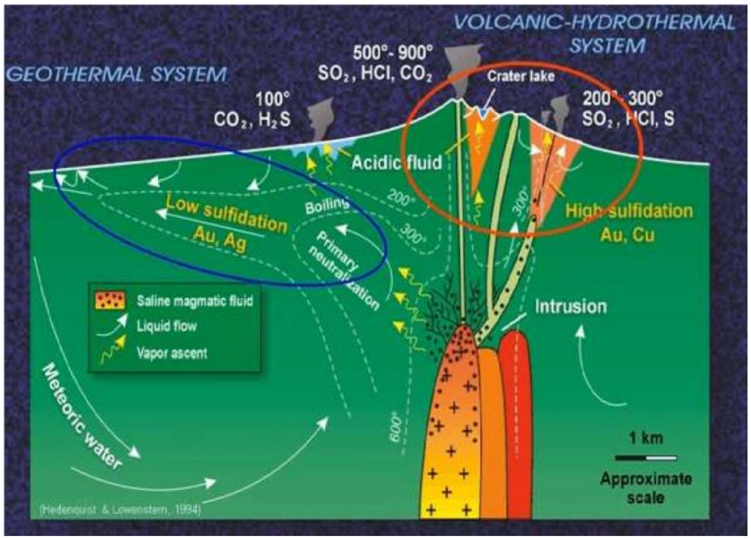

Figure 3: Model of Epithermal deposit (High-intermediate-low sulfidation) (Hedenquist and Lowenstern,1994).

The amount and degree of interaction between magmatic fluid, groundwater, and host rocks is the fundamental distinction between high and low sulfidation epithermal deposits. Some writers attempted to create a third zone of sulphidation known as Intermediate Sulfidation Epithermal. As the name implies, it is located halfway between high and low sulfidation settings, with some dilution by groundwater but not to the same extent as a low sulfidation system. This zone lacks distinctive mineralogy when compared to the high and low sulfidation zones, however it does include alunites, which are found in high sulfidation epithermals. In addition to gold, the intermediate sulfidation epithermal zone typically contains considerable amounts of silver, galena, and zinc in the form of sphalerite (Andrew, 2013).

- ***Geochemical associations in mesothermal gold deposit***

Due to the circulation of deep crustal fluids (750-3000m) at the contact with or surrounding subvolcanic to hypabyssal-plutonic intrusive, gold rich mesothermal and skarn deposits linked with dominant magmatic fluids exist. Stockwork to irregular bodies, lode-vein structures, and replacement-lens shaped bodies are all part of the geometry of ore. The majority of mesothermal lode structures are located in major shear zones, and a metamorphic fluid component is occasionally mixed with dominant magmatic-hydrothermal fluids; ore-forming minerals occur at moderate temperature-pressure, and remobilization of some metals (Cu, Au) during shear zone evolution is possible when associated with retrograde evolution of the alteration-mineralization system. Associations of chlorite/epidote-garnet-wollastonite imply a deeper mesothermal to skarn mineralized deposit. Many mesothermal gold bearing formations have shearing fractures or tabular shear zones (lodes), implying a metamorphic fluid component or metal remobilization from preexisting sources. In general, the mesothermal gold deposit may contain native gold (Au) and the sulfides galena (PbS), sphalerite (ZnS), chalcopyrite ($CuFeS_2$), pyrite (FeS_2), bornite (Cu_5FeS_4), arsenopyrite (FeAsS), and tetrahedrite ($(Cu,Ag)_{12}Sb_4S_{13}$). Mined metals include copper (Cu), zinc (Zn), silver (Ag), gold (Au), and lead (Pb).

- ***Geochemical associations in hypothermal gold deposits***

Hypothermal deposits arise at extreme depths, pressures, and temperatures. Temperatures during the production of such deposits might vary from 300° to 500° Celsius. Mineral associations that can occur in hypothermal deposits include cassiterite, wolframite, and molybdenum veins, goldquartz veins, copper-tourmaline veins, and lead-tourmaline veins. Quartz, fluorite, tourmaline, and topaz are minerals found in hypothermal veins. Ore minerals found may include native gold (Au); the sulfides galena (PbS), chalcopyrite ($CuFeS_2$), pyrite (FeS_2), molybdenite (MoS_2), bismuthinite (Bi_2S_3), and arsenopyrite (FeAsS); the oxides uraninite (UO_2), cassiterite (SnO_2), and magnetite (Fe_3O_4); and the tungstates wolframite ($(Fe,Mn)WO_4$) and scheelite ($CaWO_4$). Copper (Cu), molybdenum (Mo), tin (Sn), tungsten (W), gold (Au), and lead (Pb) are some of the metals that can be mined from hypothermal deposits (Edwards and Atkinson,1986).

5. Conclusion

Hydrothermal alteration is a geological process in which hot, mineral-rich fluids interact with rocks and minerals, altering their physical and chemical properties. This interaction can result in the development of new minerals as well as the alteration of existing minerals, resulting in the formation of mineral deposits including metals such as copper, gold, and silver. Hydrothermal alteration assemblages exhibit zonal patterns that represent progressive rock buffering from the ore zone to the least changed host rock. Quartz, calcite, ankerite, albite, and sericite are mineralized veins' proximal hydrothermal alteration zones.

The geochemistry of gold in hydrothermal deposits is impacted by the source of transporting solutions, metal source, transport methods, and ore deposition mechanisms. Depending on the deposit type, the solutions may be produced from a magmatic source or from any of the following: sea water, connate water, meteoric water, or water evolved during metamorphism. Gold tends to be concentrated in the vapor phase of fluids at high temperatures and pressures in terms of mineralization. In gold deposits, Au-As and Au-Sb relationships are prevalent. Native antimony and/or arsenic - native gold assemblages may precipitate from low sulfur fugacity hydrothermal fluids. The composition of the solutions in hydrothermal systems where gold may be accompanied by pyrite and other arsenic sulfides required to be such that the gold was transported as bisulfide complexes. Some of the specific mineralogical assemblages will alter depending on the kind of hydrothermal deposit, which can range from hypothermal to mesothermal to epithermal. Only in a few systems dominated by hematite or other oxides, or at temperatures greater than those determined for typical epithermal deposits, would gold chloride complexes predominate.

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