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Chapter 13

Gold in Sedex Deposits

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Abstract

Newly recognized gold-rich sedimentary-exhalative (sedex) mineralization in Nevada, with an average gold grade of 14 g/tonne (t), and the occurrence of significant amounts of gold in classic sedex deposits like Rammelsberg, Germany (30 Mt at 1 g/t), Anvil, Canada (120 Mt at 0.7 g/t), and Triumph, Idaho (? at 2.2 g/t) demonstrate that basin brines can form gold ore. The sedex Au mineralization in Nevada represents a previously unrecognized end member in a spectrum of sedex deposits that also includes large Zn-Pb, intermediate Zn-Pb-Ba ± Au, and barite deposits. Study of ore deposits, modern brines, and chemical modeling indicates that variation in metal ratios and their abundance in sedex deposits are dominantly controlled by the concentration and redox state of sulfur in brines. For example, Au and Ba solubilities are highest in H_2S-rich, SO_4-poor fluids, whereas base metal solubilities are highest when H_2S is not present. Chemical modeling indicates a typical reduced brine (15 wt % NaCl equiv, pH = 5.5, H_2S = 0.01 m) at 200°C is capable of transporting as much as 1 ppm Au in solution.

The H_2S content in brines is controlled by the rate of its production through thermochemical reduction of sulfate by organic matter and the rate of its removal from the fluid through the sulfidation of reactive Fe in the sediments. Thus, sedimentary basins with high organic carbon and sulfate in rocks low in reactive Fe, such as carbonates and shales, are most likely to produce H_2S-rich brines that may form gold-rich sedex deposits. Because of the tremendous scale of sedex hydrothermal systems, evidence that basin fluids can transport gold identifies a new mechanism for concentrating gold in sedimentary basins and opens extensive areas to further gold exploration.

Introduction

HISTORICALLY, gold has been considered unimportant in sedimentary exhalative (sedex) Zn-Pb and barite deposits. However, recent work in Nevada has demonstrated that the host rocks of mid-Tertiary Carlin-type gold deposits also contain Devonian sedex mineralization, which is significant because these deposits will be mined for gold and not Zn-Pb or barite (Emsbo et al., 1997, 1999). This work also demonstrates that the transport of gold by basinal fluids, and its subsequent deposition in the sedex environment, can produce gold ore. In light of these new findings, a review of the literature shows that several classic sedex deposits actually contain significant gold. Although very limited, there has been suggestion of Au transport and deposition in this hydrothermal environment by previous workers. For example, based on a conceptual model for the formation of sedex barite deposits, Lydon et al. (1985) speculated that Au might be mobile in the reduced basin brines that formed these deposits. Based on the characteristics of sedex Au occurrences on the Carlin trend and results of geochemical modeling, Emsbo et al. (1997, 1999) proposed that Au is mobile in reduced H_2S-rich brines. Also, recent geochemical modeling by Cooke et al. (2000) demonstrated that Au can be soluble in reduced basin brines.

The objective of this paper is to show that gold can be significantly concentrated in the sedex environment, and that the Nevada sedex Au occurrences represent a previously unrecognized end member in a spectrum of sedex deposits that includes enormous gold-poor Zn-Pb deposits, smaller Zn-Pb-Ba ± Au deposits, and barite deposits. Evidence is presented that the gold, base metal, and barite contents of sedex deposits are dominantly controlled by the concentration and redox state of sulfur in basin brines. For example, while H_2S dramatically enhances gold solubility, it significantly curtails base metal contents of a brine; sulfate concentrations, on the other hand, have little effect on these metals, but strongly limit the solubility of barium. Because of these interrelationships, the chemistry of Au is discussed in the context of the full spectrum of sedex deposits with a focus on processes in hydrothermal source regions of sedimentary basins that control the concentrations and redox state of sulfur.

Sedex versus Volcanic-Hosted Massive Sulfide Deposits

Sedex deposits are distinct from the volcanic-hosted massive sulfide deposits described by Huston (2000). Although these two types of deposits have some similarities, particularly ore deposition on or just below the sea floor, sedex deposits differ in that they occur in sedimentary basins formed in intracratonic and epicratonic rift systems

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(Large, 1980), are sediment-hosted, and formed by basin brines derived from their host basins (Badham, 1981; Lydon, 1983). Linkage between the two deposit types has been suggested based on modern sediment-hosted deposits like Middle Valley, Escanaba, and Guaymas basin located in sediment-covered spreading centers (Goodfellow et al, 1993). However, volcanic-hosted massive sulfide deposits are excluded here from the sedex class because they formed from seawater modified during hydrothermal convection in a volcanic-dominated ore system and not from a brine derived from a sedimentary basin.

Spectrum of Sedex Deposits

Based on their size and relative proportions of base metals, barite, and gold, the spectrum of "classic" sedex deposits can be divided into three general types. Very large Zn-Pb deposits like the HYC, Century, and Mount Isa deposits in the MacArthur River basin, the Sullivan deposit in Canada, the Red Dog deposit in Alaska, and the Howards Pass deposit in the Selwyn basin represent the base metal-rich end member of sedex deposits. They are enormous, with typically >100 and up to 550 Mt of ore, generally high grade, have gold contents near crustal abundance, and except for Red Dog, contain very little barite. Intermediate Zn-Pb-Ba ± Au deposits like Rammelsberg in Germany, the Tom and Jason deposits, and those of the Anvil district in the Selwyn basin are generally smaller with <50 Mt, of slightly lower Zn-Pb grades, have associated high-grade barite, and can contain significant gold grades. Finally, barite deposits that are common in both the Selwyn basin and Nevada contain up to 90 percent barite with little base metal sulfide. The gold contents of these barite deposits are, unfortunately, poorly known. The only recorded information is from the Tea deposit, which contains only slightly anomalous gold (up to 11 ppb; Lydon et al., 1985). Although characteristics of the intermediate Zn-Pb-Ba ± Au deposits resemble the Nevada sedex Au occurrences, no other well-documented sedex Au deposits of this fourth sedex-type are described in the literature.

This spectrum of metal endowments in sedex-type deposits has been ascribed to a spectrum of differing fluid compositions generated in sedimentary basins that reflect basin-wide lithologic differences in hydrothermal source regions (Lydon, 1983; Lydon et al., 1985; Large et al., 1998; Emsbo et al., 1999; Cooke et al., 2000). Although this generalization is broadly applicable, there are significant exceptions. For example, the Selwyn basin hosts the entire spectrum of deposits, including Howards Pass, the world's largest Zn-Pb deposit, the intermediate Tom, Jason, and Anvil Zn-Pb-Ba ± Au deposits as well as many barite deposits like the Tea deposit. Lydon (1983) and Lydon et al. (1985) interpret the occurrence of these differing deposits in the same sedimentary basin, some formed during the same time, as evidence for the venting of differing basinal fluids from reservoirs of vastly different lithologic characteristics and temperatures.

Gold in Sedex Zn-Pb-Ba ± Au Deposits

Although gold content is typically very low in sedex Zn-Pb deposits, it is often present in Zn-Pb-Ba ± Au deposits (Table 1). Unfortunately, gold analyses are not routinely reported for many sedex deposits, reflecting the prevalent view of many workers that gold is absent in sedex systems. All of the classic sedex deposits described below, for example, have been referenced in the literature as not containing Au.

Rammelsberg deposit

The Rammelsberg deposit, one of the most important massive sulfide deposits in the Variscan belt of central Europe, is hosted in the Middle Devonian Wissenbach Shale. Abrupt facies transitions in underlying fossiliferous calcareous shales, and the presence of more than 20 thin felsic tuff horizons, indicate a sudden change in the sedimentary and tectonic environment (Fig. 1; Large, 1980). This stratigraphic sequence has been interpreted as a block-faulted continental margin bordering rift-generated basins (Large, 1980; Werner, 1988).

During the long mining history at Rammelsberg, about 30 Mt of ore were mined with an average grade of 14 percent Zn, 6 percent Pb, 2 percent Cu, 140 g/t Ag, 1g/t Au and 20 percent barite (Large and Walcher, 1999). This ore was assigned to four general types (Fig. 1). Massive ore averaged 24 percent combined Zn-Pb-Cu, was internally laminated and was composed of pyrite, sphalerite, galena, and chalcopyrite with 22 percent barite and 10 percent carbonate. Lenses of massive ore are interbedded with banded ore that averages 10 percent Zn and 4 percent Pb and consists of rhythmic, millimeter-scaled laminations of ankeritic dolomite, pyrite, sphalerite, and galena with interlaminated pyritic shales. Gray ore stratigraphically overlies the other ore and consists primarily (about 80%) of fine-grained, laminated barite, intergrown with sphalerite and galena, with grades of about 4 percent combined Zn-Pb-Cu. In addition, discordant kniest mineralization occurs in the footwall of the deposit and is composed of pyrite, sphalerite, galena, and chalcopyrite accompanied by quartz, ankerite, calcite, and chlorite. Grades average 3 percent Zn, 1.3 percent Cu, and 1.4 percent Pb, but this ore type has not been extensively mined (Large and Walcher, 1999).

Gold values in the Old Orebody, which is primarily composed of massive and banded ore, are generally between 1 and 2.8 g/t (Fig. 1). Gold occurs as both native grains and electrum, associated with galena and tetrahedrite. The ore also averages 800 ppm Sb, 500 ppm As, 150 ppm Co, and 50 ppm Sn. Peripheral to the orebody, the ore-bearing horizon is characterized by a distinctive 8- to 19-m-thick, finely laminated shale with light gray, pyrite dolomite partings (pinstripe pyrite) that is slightly enriched in Zn, Pb, Hg, Ag, Sb, As, and Bi (Large and Walcher, 1999). The reported gold grades and tons mined indicate that this sedex deposit hosted nearly 1 Moz of Au at 1 g/t.

Anvil district

The Anvil district contains five classic Zn-Pb-Ba sedex deposits, the Faro, Grum, Vangorda, Dy, and Swim, which have been extensively studied by Jennings and Jilson (1986). These deposits contain a combined total of 120 Mt of ore that average 5.6 percent Zn, 3.7 percent Pb, 45 to 50g/t Ag.

TABLE 1. Gold in Sedex Deposits

Deposit	Size (Mt)	Au (g/t)	Range of Au (g/t)	Zn (%)	Pb (%)	Ba	Estimated total Au (t)	References
Ramelsberg	30	1.0	1.0-2.8	14	6	Yes	30	Large and Walcher, 1999
Triumph mine	na	2.2	0.7-6.2	6.57	4.02	Minor	na	Turner and Otto, 1995
Anvil district (Total)	120	0.7		5.6	3.7	Yes	83	Jennings and Jilson, 1983
Dy	21.1	1.0		6.7	5.5	Yes	21	Jennings and Jilson, 1983
Grum	30.8	0.8		4.9	3.1	Yes	25	Jennings and Jilson, 1983
Vangorda	7.1	0.8		4.3	3.4	Yes	6	Jennings and Jilson, 1983
Faro[1]	57.6	0.5		5.7	3.4	Yes	29	Jennings and Jilson, 1983
Swim	4.3	0.7		4.7	3.8	Yes	3	Jennings and Jilson, 1983
Remaining in Dy+ Vangorda+Grum	37.7	0.7		Zn + Pb = 8.34		Yes	26	Burk, 1996
Red Sea	90	0.5	0.5-21.3	2	0.1	Yes	45	Hannington et al., 1991
Rodeo	na	14.0	.01-68.0	1	0.05	Yes	na	Emsbo et al., 1999

[1] Gold content estimated from Jennings and Jilson, 1983

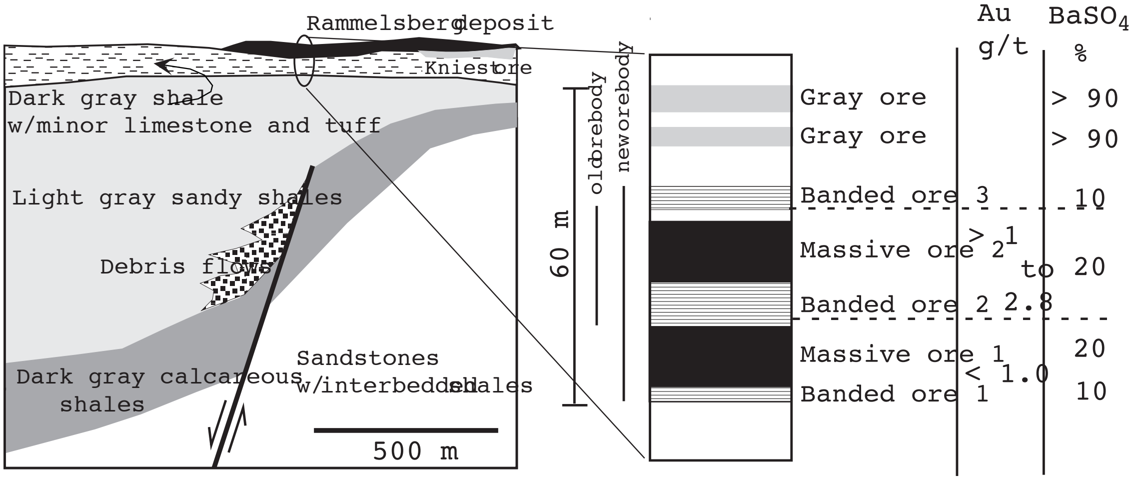

FIG. 1. Schematic cross section showing changes in both the thickness and facies of the Wissenbach shale during deposition of the Rammelsberg deposit with expanded view of ore zone showing different ore types and the distribution of gold and barite. Modified from Large and Walcher (1999).

They occur in an anomalously thick (150 m) section of graphitic phyllites that straddle the Cambrian Mount Mye and Vangorda Formations (Fig. 2). These deposits formed in the shale-rich, distal portion of the Late Proterozoic-early Paleozoic North American miogeocline. They are thought to be aligned along synsedimentary faults that formed in an evolving extensional rift basin. Although minor volcanic rocks occur in laterally equivalent strata, most of the alkali basaltic rocks related to this intracontinental rift occur above the 1-km-thick Vangorda Formation in the Upper Cambrian to Lower Ordovician Menzie Creek Formation.

Typically, these five stratiform, pyritic Zn-Pb-Ba deposits have banded to massive pyrite-sphalerite-galena ore, with accessory pyrrhotite, chalcopyrite, arsenopyrite, magnetite, and marcasite (Fig. 2). Sulfide content in these ores is 60 to 100 percent with varying proportions of quartz-barite-calcite-dolomite-ankerite gangue. These ores grade upward and outward into thinly banded sulfide-barite ore that contains pyrite, galena, honey-colored sphalerite, and magnetite, along with barite and lesser calcite, dolomite, ankerite, and witherite. Barite contents vary, but commonly are as high as 50 percent. The distribution of gold is not known in detail, but it is weakly associated with anomalous Cu in the massive ore. Gold content also increases upward, along with Ag, in some deposits and coincides with the thickest development of baritic ore (Fig. 2).

A recent calculation estimates that 37.7 Mt of ore with an average grade of 8.34 percent combined Pb and Zn, 52.6 g/t Ag and 0.70 g/t Au remains in the Vangorda, Grum, and Dy deposits, indicating a reserve of about 850,000 oz of gold (Burke, 1996). If these grades are applied to the entire district, it may have contained in excess of 3 Moz of Au.

Triumph deposit

Ore in the Triumph deposit in Idaho is hosted in the Devonian Milligan Formation and has been studied by Turner and Otto (1995). Its age, geologic setting, mineralogy,

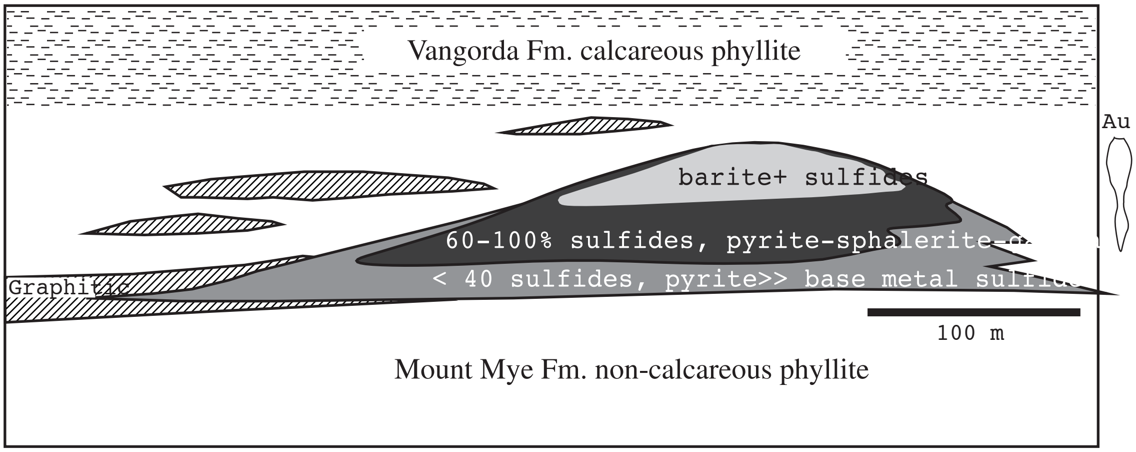

FIG. 2. Idealized cross section of the five deposits in the Anvil district showing general distribution of ore types and Au. Modified from Jennings and Jilson (1986).

and geochemistry are similar to those of sedex gold occurrences in correlative rocks to the south in Nevada. The ore horizon occurs in carbonaceous argillites, cherts, and phyllitic shales above a series of debris flows that rest on a local thick-bedded, carbonaceous micritic limestone. Several very thin (<3 cm) tuff horizons and a few mafic dikes have been identified in rocks correlative to those that host ore. The facies changes and the thick section of debris flows directly under the ore body have been interpreted as evidence of a synsedimentary fault that focused flow of the ore fluids.

The ore consists of sphalerite, pyrite, galena, boulangerite, and ferroan carbonate-quartz laminae hosted in a series of carbonaceous siltstones that commonly contain between 0.7 and 1.6 g/t and locally up to 6.2 g/t Au (Emsbo unpub. data; Turner and Otto, 1995). Although barite is only a minor component of the ore, barite-dominated deposits occur locally in the district. Unfortunately, production records are incomplete, but the mine operated from 1927 to 1957, and between 1936 and 1948 produced about 1.06 Mt of ore and was the largest silver producer in Idaho. Between 1941 and 1948 production grades averaged 6.57 percent Zn, 4.02 percent Pb, 243 g/t Ag, and 2.2 g/t Au (Turner and Otto, 1995).

Red Sea

The Atlantis II Deep in the Red Sea is considered the closest modern analogue to a sedex hydrothermal system (Goodfellow et al., 1993). Although some have considered this a volcanic-hosted massive sulfide deposit because of the occurrence of spreading ridge basalts, the generative fluid is clearly a basin brine; thus, more akin to that of a sedex system. Sediment samples throughout the 17 × 4 km basin average nearly 0.6 g/t Au and range up to 5.6 g/t (Hendricks et al., 1969). More than 50 analyses of six cores from sulfide-rich sediments in the southwest corner of the Deep yield an average of 2.4 g/t Au, with one sample containing 21.3 g/t (Oudin, 1987). A conservative estimate of recoverable byproduct gold from a calculated base metal "resource" of 90 Mt is 1.4 Moz (Hannington et al., 1991). This estimate is significantly low for the basin because large areas with low base metal but significant gold content were excluded from the calculation, and based on assay data (Hendricks et al., 1969; Oudin, 1987), the gold content was underestimated.

Nevada Sedex Au Occurrences

Sedex-type gold occurrences, which are clearly distinct from classic Carlin-type gold ore, have recently been identified in the northern Carlin trend, north-central Nevada (Emsbo et al., 1997, 1999). These occurrences are hosted in the Silurian-Devonian Roberts Mountains and Devonian Popovich Formations that also host the mid-Tertiary, Carlin-type gold deposits. They are interpreted to be of sedex origin because they are stratiform and the mineralization predates compaction and lithification of their unaltered Devonian host rocks. The most significant of these occurrences contains ore grades (up to 68 g/t), which will be mined underground, along with Carlin-type ore, as part of the Barrick Goldstrike Rodeo deposit (Emsbo et al., 1999). The term "occurrence" rather than "deposit" is used because it is not yet known whether Rodeo would be economic to mine if Carlin-type ore was not also present. Locally, the rocks of the Devonian stratigraphic sequence contain abrupt lateral and vertical facies changes, thick sequences of debris flows, and synsedimentary slump structures that reflect foundering of the carbonate platform and synsedimentary extensional faulting (Emsbo et al., 1997; Griffin, 2000). This is consistent with a fault-controlled, restricted basinal setting (Fig. 3A; Emsbo et al., 1997; Griffin, 2000). This structural interpretation is supported by the presence of alkali basalts and evidence of rifting in correlative rocks of the marginal basin farther west (Miller et al., 1992).

The stratiform mineralization is hosted in the Popovich Formation and ranges from nearly pure, bedded barite to disseminated barite containing base metal sulfides (Fig. 3B). Lenses of barite as much as 12 m thick are white to light gray, saccharoidal, fine-grained barite, and contain disseminations of honey-colored sphalerite, boulangerite, galena,

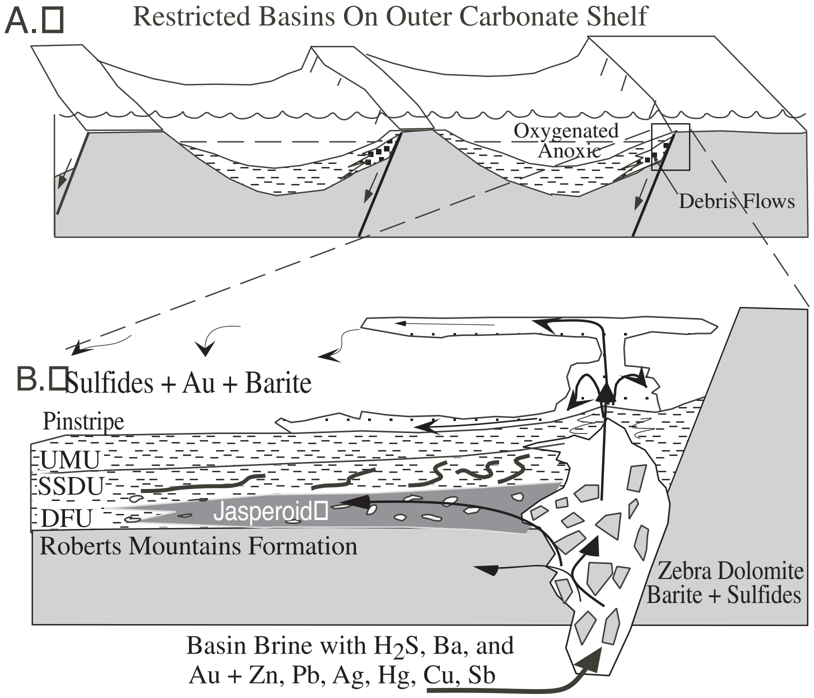

FIG. 3. A. Schematic cross sections of western United States continental margin showing restricted anoxic basins of outermost carbonate shelf during Middle Devonian time and inferred faulting. B. Schematic geologic model for Devonian sedex mineralization in the Rodeo deposit. DFU = debris flow unit; LMU = laminated mudstone unit; SSDU = soft-sediment deformation unit; UMU = upper mudstone unit of the Popovich Formation. Modified from Emsbo et al. (1999).

and tetrahedrite. Mudstones also contain pinstripe pyrite that consists of thin, concordant laminae of sulfide, typically 1 to 4 mm thick, mainly pyrite, but with minor sphalerite, tetrahedrite, and chalcopyrite (Fig. 3B). Pinstripe pyrite also contains barite in beds as much as 4 cm thick and as barite nodules and rosettes. Pinstripe pyrite has been found over an area of 8 square miles where it consists mainly of pyrite and minor barite. Small lenses of massive sulfide with barite also occur in this rock and are as thick as 0.5 m.

The habit of native gold in these rocks indicates that it formed contemporaneously with the barite and base-metal sulfide assemblage. Grains of native gold, generally less than 1 mm in diameter, occur in ore-grade mudstones as inclusions in tetrahedrite, chalcopyrite, pyrite, and barite, as free grains in the mudstone, and overgrown by diagenetic barite nodules. Sulfides lacking microscopically visible inclusions of native gold were also analyzed using an electron microprobe and laser ablation-inductively coupled plasma-mass spectrometry. Gold contents of as much as 500 ppm were measured in sphalerite and pyrite while chalcopyrite and tetrahedrite contained as much as 2,200 ppm Au. Auriferous pyrite, interpreted as an early diagenetic phase, has also been reported at the Gold Quarry mine on the southern Carlin trend (Sha, 1993).

Discordant footwall stockworks below stratiform mineralization in laminated mudstones of the Popovich Formation consist of thin veinlets of sphalerite, barite, boulangerite, and galena. Footwall limestones in the underlying Roberts Mountains Formation are pervasively dolomitized adjacent to vertical faults (Fig. 3B). The resulting dolostone exhibits “zebra” texture characterized by alternating bands of light and dark sparry dolomite that contain disseminations and veins of barite, sphalerite, boulangerite, pyrite, galena, tetrahedrite, and chalcopyrite. Fluid inclusion measurements from discordant mineralization indicate salinities of 9 to 20 wt percent NaCl equiv in sphalerite and barite, and homogenization temperatures of 200° to 265°C in sphalerite (Lamb, 1995).

These sedex Au occurrences predate compaction and lithification of their unaltered Devonian host rocks. They contain barite that exhibits $\delta^{34}S$ and $\delta^{18}O$ values identical to sulfate in Devonian seawater and other sedex-type barite deposits of similar age in Nevada. Abrupt facies changes in their host rocks strongly suggest synsedimentary faulting before and during mineralization, as is characteristic of sedex deposits. The absence of alteration and lack of $\delta^{13}C$ and $\delta^{18}O$ isotopic shift of primary carbonates in these rocks is strong evidence that this gold was not introduced with classic Carlin-type mineralization that is characterized by large negative isotopic shifts. Collectively, these features show that the Devonian strata were significantly enriched in gold at least 300 m.y. prior to formation of the mid-Tertiary Carlin-type deposits.

Fluid Chemistry and Controls on Metal Solubility

Over the last 30 yr, ore deposit research, in tandem with geochemical studies of modern brines and geochemical modeling, has contributed tremendous insights into the source, transport, and deposition of metals in sedimentary basins. However, most studies have focused on Zn and Pb transport in oxidized basin brines, while the other metals, such as Au, and reduced brines have received little attention. Nonetheless, these studies place important constraints on temperature, salinity, pH, and chemical characteristics that are necessary to model Au in basin brines.

Brines chemistry

Although it is clear that sedex deposits are formed by basin brines, the chemical composition of the brines are poorly known because of the lack of systematic study of fluid inclusions (Goodfellow et al., 1993). The fluid inclusion data, mineral assemblages, and isotopic data that are available, however, indicate the deposits formed at 50° to 260°C from fluids with neutral to moderately acidic pH and salinities that range from 8 to 28 wt percent NaCl equiv (Goodfellow et al., 1993; Lydon, 1996). Although these studies have been valuable, much of our understanding of basin brines is derived from comparison with modern-day brines, constraints from thermodynamic calculations, and fluid inclusion data from Mississippi Valley-type deposits.

Analyses of modern brines from the Gulf Coast region of the United States have significantly contributed to our understanding of the geochemical processes involved in brine generation. These studies have demonstrated that basin brines have salinities as high as 35 percent total dissolved solids. Anion/cation ratios and isotopic compositions are generally consistent with residual bittern brines that result from subaerially-evaporated sea water (Carpenter, 1978; Kharaka et al., 1987; Moldovanyi and Walter, 1992). However, as demonstrated around salt domes in Louisiana, some brines also obtain their salinity directly from the dissolution of evaporites (Hanor, 1994). Gulf Coast brines range from 50° to 160°C and are generally neutral to moderately acidic. Measured pH values tend to decrease with increasing salinity, but generally range from ca. 4.5 to 8 and average 5.5. Rarely do pH values fall below 4, and then only in brines that have >30 wt percent total dissolved solids (Hanor, 1994). It is important to note that these pH values are field measurements of brines at the surface and are uncorrected for reservoir conditions. The true in situ pH values are not known, but chemical modeling of these brines indicate pH values generally between 4.5 and 6.5 under most conditions (Kharaka et al., 1987; Moldovanyi and Walter, 1992; Plumlee et al., 1994).

The sulfur geochemistry and redox state of most basinal waters are not known in detail, but are significant to metal solubilities. Unlike major cations and alkalinity, there does not appear to be a correlation between concentration of dissolved sulfate and salinity. Sulfate concentrations typically do not exceed 0.02 m (Hanor, 1994). Variations in sulfate concentrations are thought to reflect rate-controlled processes involving release of sulfate through dissolution of anhydrite, and removal via reduction to sulfide (H_2S) by biogenic sulfate reduction and thermochemical sulfate reduction. The latter is ultimately controlled by the reduction of sulfate through its reaction with organic matter to produce H_2S (McManus and Hanor, 1993)

Significant concentrations of H2S in brines have been recorded in many sedimentary basins with concentrations up to ca. 0.03 m (Wade et al., 1989; Moldovanyi and Walter, 1992). It is important to note that these analyses represent minimum values as they are sampled at well heads, where significant loss of H_2S is unavoidable (Moldovanyi and Walter, 1992). The upper limit of H_2S concentration is constrained by condensation of liquid sulfur, but this does not occur for reduced, near neutral solutions until about 1.0 m (Gammons, 1997).

Most modern H_2S-rich brines also typically contain significant sulfate (Kharaka et al., 1987; Moldovanyi and Walter, 1992; Hanor, 1997) suggesting that sulfate persists in reduced brines in a metastable state. This is further supported by laboratory studies that indicate oxidation of H_2S by O_2 occurs easily even at ambient temperatures, but the reduction of SO_4 is kinetically inhibited below 350°C (Ohmoto and Goldhaber, 1997). These relationships suggest that, in the absence of thermochemical sulfate reduction or biogenic sulfate reduction, SO_4 can persist at significant levels even in reduced brines.

Hydrothermal brines that form Mississippi Valley-type deposits, although perhaps having different crustal migration mechanisms, have a similar origin to those that formed sedex deposits (Hutchinson, 1980; Badham, 1981; Sangster, 1990). Fluid inclusions from Mississippi Valley-type deposits deposits have been extensively studied and yield temperatures of 75° to 200°C and salinities between 10 and 30 wt percent (Leach and Sangster, 1993; Plumlee et al., 1994). Analyses of fluid inclusions from 14 major Mississippi Valley-type deposits districts indicate the ores formed from fluids that are essentially the same as modern-day bittern brines (Viets et al., 1996). These data also indicate that SO_4 concentrations are typically low and primarily controlled by the precipitation of gypsum or anhydrite. Although there is minor evidence for thermochemical sulfate reduction, base metal-transporting fluids in Mississippi Valley-type deposits deposits contain only 10^{-3} and 10^{-5} m H_2S at pH values of 4.3 to 5.0 (Plumlee et al., 1994).

Metal solubility in brines

Although this paper highlights gold in sedex deposits, the controls on the solubility of Zn-Pb and Ba in basin brines are also discussed to illustrate the place of Au in the spectrum of sedex deposits. The solubilities of Zn, Pb, Ba, and Au are all dominantly controlled by the concentration and redox state of sulfur in the brine. Thus, the relative proportion of these elements provides insight into processes that control Au solubility in basin brines and also explains many chemical variations in resulting ores.

Analysis of modern brines and chemical modeling have demonstrated that, although variables like temperature and pH have some effect, high Zn and Pb solubilities result primarily from a combination of high salinity and low H2S concentration (Kharaka et al., 1987; Moldovanyi and Walter, 1992; Hanor, 1997). As these metals are dominantly transported as chloride complexes, salinity (chlorinity) is a primary control on their solubilities. Empirical data and modeling indicate a dramatic increase in solubilities of Zn and Pb above a threshold of about 10 percent total dissolved solids where Zn/Pb ratios are consistently about 5:1 (Hanor, 1997). Although laboratory studies indicate temperature has a significant effect on the solubility of these metals, data from modern brines demonstrate no correlation between metal concentration and temperature between 50° and 150°C. Solubilities of base metals, however, show a dramatic inverse relationship to H_2S contents, with Zn and Pb concentrations in brines decreasing by several orders of magnitude in the presence of even moderate contents of H_2S (Kharaka et al., 1987; Moldovanyi and Walter, 1992; Hanor, 1997).

Although the solubility of Ba is also controlled by salinity, temperature, and pH, its dominant control in basin brines is the concentration of SO_4 in the fluids, as Ba solubilities are extremely low in the presence of sulfate (Lydon, 1983; Cooke et al., 2000). This is evident from analyses of modern brines where salinity, pH, and H_2S concentrations display no discernible correlation to Ba concentration, while there is a dramatic inverse correlation to SO_4 contents (Moldovanyi and Walter, 1992; Hanor, 1994).

Conversely, Au solubilities are relatively unaffected by salinity at temperatures <300°C and pH > 4, because Au is not significantly soluble as a Cl complex (Seward, 1973). Gold is, however, very soluble as bisulfide complexes at temperatures between 150° and 300°C (Seward, 1973; Shenberger and Barnes, 1989; Gilbert et al., 1998), which led Lydon et al. (1985) to suggest that Au could be soluble in basin fluids. They tested this model by sampling the Tea barite deposit in the Selwyn basin and found that the barite horizons were only slightly elevated in Au relative to the surrounding host rocks. Detailed study of the sedex Au occurrences on the Carlin trend caused Emsbo et al. (1997, 1999) to also propose that Au is mobile in H_2S-rich brines. More recently, Cooke et al. (2000) modeled Au solubilities for basin brines at 150° and 250°C and calculated that at 150°C, 25 wt percent NaCl equiv, and $H_2S = \sum S = 0.001\ m$, the solubility of Au is >10 ppb at pH ranges between 4.6 to 7.3. Although this gold solubility is very significant, the sulfur content used in this model is more than an order of magnitude lower than those observed in many modern brines (Moldovanyi and Walter, 1992; Wade et al., 1989). This is particularly relevant for reservoirs where sulfur occurs as H_2S, because the calculation significantly underestimates the solubility of Au. For example, a one order of magnitude increase in α_{H_2S} will increase the solubility of Au by more than two orders of magnitude (Gammons, 1997).

The antithetical relationship between base metals on the one hand, and gold and barium on the other, as a function of the redox state of sulfur is demonstrated in Figure 4. Chosen parameters such as salinity (15 wt %), pH (5.5), and total sulfur (0.01 *m*) contents all remain consistent with values measured in modern brines. Similarly, the selected temperature of 200°C is consistent with temperatures reported for ore deposition in many sedex deposits. The only variable in this model that changes is the ratio of the activity of SO_4 and H_2S that together comprise the total sulfur in the brine. Under these conditions, base metals are very soluble as chloride complexes in hydrothermal fluids with a low activity of reduced sulfur. Conversely, the solubility of gold as bisulfide complexes at low α_{H_2S} is insignificant. However, as the H_2S increases by the reduction of sulfate, gold solubility increases dramatically. Similarly, the reduction of sulfate to sulfide also greatly enhances Ba solubility, which is inversely controlled by sulfate content.

Generation of H_2S-Rich Brines

Because of its dominant control on Au solubility, it is important to understand basinal processes that govern the H_2S content of brines. Below surficial and shallow conditions, hydrogen sulfide is generated in sedimentary basins by thermochemical sulfate reduction, as well as by thermal decomposition of kerogen, coal, and high sulfur oils (Hunt, 1996). It is significant that all of these processes involve organic carbon and are consistent with the observations of Le Tran (1972) that indicate the amount of H_2S in deep drill holes correlates with the content of organic matter in surrounding rocks. All of these mechanisms of H_2S generation are strongly controlled by temperature. Empirical evidence from sedimentary basins indicates that the generation of H_2S significantly increases with depth and temperatures greater than 170°C and is consistent with the restricted occurrence of H_2S-dominated gas reservoirs to the hottest and deepest parts of sedimentary basins (Le Tran, 1972). Isotopic and chemical constraints clearly indicate that H_2S generation in these areas is dominantly controlled by thermochemical sulfate reduction (Orr, 1974), which is further supported by the observed association of the most H_2S-rich reservoirs with rocks rich in evaporitic sulfate minerals (Hunt, 1996; McManus and Hanor, 1993). The strong temperature dependence of H_2S is also consistent with experimental and fluid inclusion data from sour gas fields which indicate that at temperatures below ca. 140°C thermochemical sulfate reduction are kinetically inhibited and capable of generating only insignificant amounts of H_2S sulfide (Machel et al., 1995).

In addition to the generation of H_2S, a fundamental control on H_2S concentration is its removal by the sulfidation of reactive Fe to form pyrite in the reservoir. The highest H_2S concentrations observed in sedimentary basins are in rocks with low contents of reactive Fe (i.e., carbonates; Hunt, 1996). Thus, the amount of H_2S generated in a sedimentary basin is ultimately controlled by the rate of its production through thermochemical sulfate reduction, balanced by the extent of its removal through the sulfidation of reactive Fe.

Discussion

Study of basin brines combined with chemical modeling indicate that although salinity, temperature, and pH significantly control metal solubility, the concentration and redox state of sulfur is a first order control on the solubility of base metals, gold, and barium in basin brines. Barium and Au solubilities are highest in H_2S-rich, SO_4-poor fluids, whereas base metal solubilities are highest when H_2S is not present.

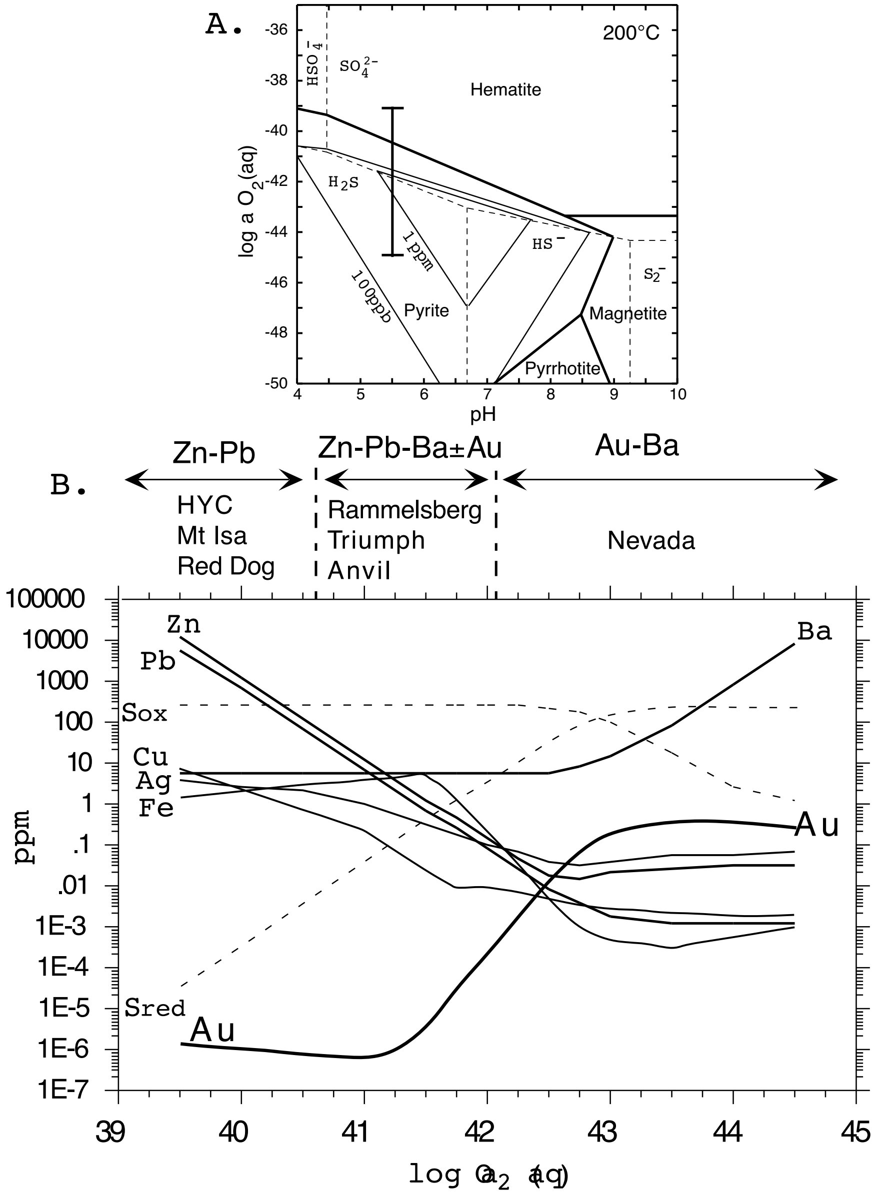

FIG. 4. A. Log $\alpha_{O2(aq)}$ –pH diagram showing stability fields of Fe-minerals, sulfur species, and Au solubility contours (100 ppb and 1 ppm) of a typical brine with a salinity of 15 wt % NaCl equiv and $\sum S = 0.01$ *m* at 200°C. Vertical line shows range of conditions for (B). B. Solubility of metals and activities of reduced (S_{red}) and oxidized (S_{ox}) sulfur species at pH 5.5 between log $\alpha_{O2(aq)}$ 39.5 and 44.5. Note significant and antithetical relationship of gold, base metals, and barite as a function of the redox state of sulfur and its relationship to metals in sedex deposits. Modeling by A. Hofstra using data from Bethke (1998).

Although many factors cause differences in metal ratios and the size of deposits, the sulfur chemistry of the ore fluids is most important.

For example, the large Zn-Pb sedex deposits in the McArthur River basin of Australia commonly contain >100 Mt of ore, almost no barite, and have Au contents that are the same or less than those of surrounding unmineralized rocks. These characteristics indicate that they formed from oxidized brines, which contained very little, if any, reduced sulfur (Fig. 4; Large et al., 1998; Cooke et al., 2000). Conversely, intermediate Zn-Pb-Ba ± Au sedex deposits are generally barite-rich, have slightly lower base metal grades, and are typically significantly smaller (<50 Mt). These characteristics indicate that they formed from fluids that contained enough H_2S to transport some gold, yet at levels still low enough to form base metal deposits (Fig. 4). The sedex Au occurrences on the Carlin trend, with high contents of barite but low base-metal sulfides, suggest that they were deposited from H_2S-rich and SO_4-poor fluids at the other end of the spectrum of sedex deposits (Emsbo et al., 1999; Fig. 4). The high H_2S content of the fluids suppressed the solubility of base metals, precluding formation of large, more characteristic Zn-Pb sedex deposits.

Although the concentration and redox state of sulfur in the generative ore fluid explains many differences in the metal endowment of sedex deposits, there are some deviations from the general pattern outlined above. For example, the Triumph deposit is relatively small and very rich in gold, yet contains very little barite. There are several possible explanations for the rarity of barite:

1. The ore fluid contained enough sulfide to move gold and limit the Zn-Pb content of the deposit, yet also contained significant metastable sulfate to limit the solubility of barite.
2. The pH of the ore fluid or the pCO_2 may have been sufficiently high to limit the solubility of Ba by its precipitation in witherite in the source region (Cooke et al., 2000). A higher pH would also have had the added affect of increasing the solubility of Au.
3. Ore deposition may have occurred by mixing of the metalliferous brines with anoxic SO_4-poor seawater, inhibiting precipitation of barite and allowing its dispersal over a wide area. This is consistent with the very carbonaceous host rocks that testify to anoxic conditions during ore deposition.

Conversely, Red Dog is an enormous, gold-poor Zn-Pb deposit, but also contains very significant amounts of barite. However, barite is not temporally coincident with most of the sulfide mineralization as it is replaced by, and thus older than, the Zn-Pb sulfides (Young, 1989). The difference in timing may explain the apparent contradiction in fluid chemistry. For example, it may indicate chemical variations within the fluid reservoir or, more likely, that different brine reservoirs vented in the same area. The latter also agrees with the general lack of spatial correlation between Ba and Zn-Pb in the rest of the western Brooks Range. It is common for sedimentary basins to contain multiple brine reservoirs with vastly different chemical characteristics, which may explain the different types of sedex mineralization of similar age in the same basin (Lydon et al., 1985). In fact, mixing of a base metal-rich brine with a H_2S-rich brine, generated in a different reservoir or horizon, is a favored ore depositional mechanism for base metals in Mississippi Valley-type deposits (Anderson, 1975; Badham, 1981; Leach and Sangster, 1993).

Controls on Au solubility

The temperature, pH, and H_2S concentration of reduced brines in sedimentary basins suggest that they can be ideal gold ore fluids. This potential is clearly controlled by the amount of sulfide in the fluid, which is primarily governed by the balance between its generation through thermochemical sulfate reduction and its removal by sulfidation of reactive Fe. Thus, the ideal reservoir rocks for generation of a gold-bearing brine are those that are rich in both organic carbon and sulfate while containing low reactive Fe such as carbonates and black shales. Temperature is also an extremely important control on the potential of a brine as a gold ore fluid for two reasons. First, the chemical reaction for thermochemical sulfate reduction is very temperature dependent and greatest at temperatures >170°C. Secondly, gold solubilities increase dramatically with temperature and are highest between 150° and 250° C.

In addition to production of vast quantities of H_2S at higher temperatures, thermochemical sulfate reduction also increases the pH of the solution further maximizing the solubility of gold as a bisulfide complex (Gammons, 1997). Such a fluid has the potential to transport tremendous amounts of Au and, if vented into seawater, would deposit gold-rich, but base metal-poor, mineralization like that observed in Nevada.

Source of Au

Contents of Pb, Zn, and Ag in sedex ores indicate that they have all undergone concentration of 10^3 to 10^4 times their average crustal abundances (Fig. 2). Average trace elements contents reported from these ores, such as As (>1,000 ppm) and Sb (>250 ppm) (Goodfellow and Rhodes, 1990; Large and Walcher, 1999), are also enriched > 10^3 times. Similar enrichments for gold would be from 3 ppb to between 3 and 30 g/t.

Gold grades in the large sedex Zn-Pb deposits are remarkably low with values similar to the average crustal abundance (Fig. 5), confirming that gold was extremely insoluble in ore fluids that formed these deposits. Although significant, average gold grades in the auriferous sedex Zn-Pb-Ba deposits range from 0.7 to 2.2 g/t, thus, are not as strongly concentrated as the other metals in these deposits. This indicates that their generative brines were capable of, but not ideal for, leaching and transporting Au. Conversely, the gold content of sedex mineralization in the Rodeo deposit, which averages 14 g/t, is significantly more concentrated compared with the content of the other elements (Fig. 5). However, these extra-

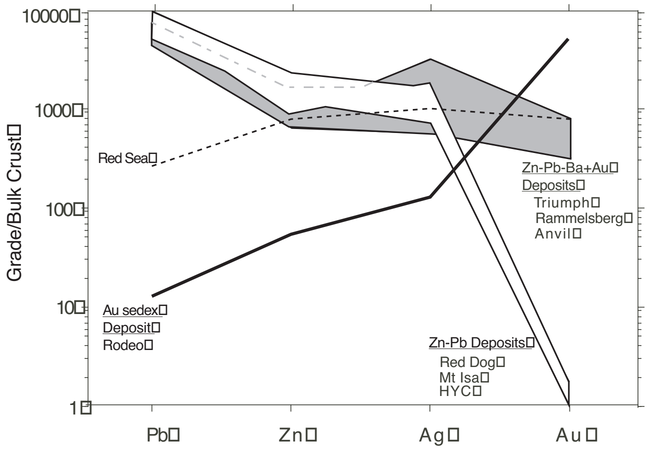

FIG. 5. Average metal grades from sedex ores normalized to those of bulk continental crust. Metal grades from Table 1 and from Lydon et al. (1996) and (McGoldrick et al., 1996) for Zn-Pb deposits. Bulk continental crust Zn (80 ppm), Pb (8 ppm), Ag (80 ppb), and Au (3 ppb) from Taylor and McLennan (1985).

ordinary gold grades correspond to enrichment factors similar to those of Zn and Pb in many sedex Zn-Pb deposits. The very high Au solubility indicated for some brines suggests that their gold contents are not limited by gold's solubility in the fluid, but rather the fluid/rock ratio during fluid movement.

The amount of contained metal in large sedex deposits, 20 and 6 Mt of contained Zn and Pb respectively, testifies to the enormous scale of these hydrothermal systems. Assuming proportionately similar and uniform crustal abundance of gold in source regions and similar efficiency of its leaching, transport, and deposition in a H_2S-rich brine, there is a potential for the transport and concentration of 1000 t of gold. These parameters indicate that world-class Au deposits can, theoretically, be formed by basin brines.

Conclusion

Examples of Au-rich sedex deposits demonstrate that, contrary to general opinion, significant amounts of gold are transported, concentrated, and deposited by sedex hydrothermal systems. The newly recognized sedex gold occurrences in Nevada, which are supported by chemical analyses and modeling of modern brines, further demonstrate that reduced brines can be ideal fluids for the transport of gold. Moreover, the scale of these hydrothermal systems combined with their temperature, pH, and unbuffered sulfide contents suggest they are capable of transporting huge amounts of gold.

The sedex Au occurrences in Nevada are the best known examples of deposits formed by a H_2S-rich brine end member of a spectrum of sedex deposit-forming hydrothermal systems. These occurrences are significant because their gold may have been a partial, perhaps even major, source of gold for the younger Carlin-type deposits. If so, this would aid in explaining the genesis of the remarkably gold-rich Carlin-type deposits and would also be of great practical importance to exploration for gold in Nevada. Most important, however, evidence that basinal fluids can transport gold identifies a potential, but previously unrecognized, mechanism for concentrating gold in geological terranes previously considered to have low gold potential which opens extensive areas of the world to gold exploration.

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