

GEOCHEMICAL MODELING OF ALTERATION AND GOLD DEPOSITION AT THE BETZE DEPOSIT, EUREKA COUNTY, NEVADA

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ABSTRACT

This study addresses ore-forming hydrothermal processes via geochemical modeling of the alteration and gold deposition in the Betze gold deposit. This deposit, located along the Carlin trend, is the largest of many Carlin-type deposits in Nevada.

The modeled ore-forming system is considered to be analogous to the natural depositional environment in the Betze gold deposit. This model was constrained by the results of geological, mineralogical, isotope and fluid inclusion studies of the deposit. Computer simulations include interaction of a CO₂-H₂S-NaCl ore fluid with the calcareous host rock, as the ore-forming system cools. The ore fluid transported gold, arsenic, antimony and other components from below the accessible Carlin system.

The major features of the alteration pattern observed in the deposit are produced from the model ore fluid by reaction with limestone of the Popovich Formation. Results indicated that the mineral stability relations in the CaO-MgO-CO₂-Al₂O₃-SiO₂-H₂O system are important and are reflected in the distribution of mineral phases in the alteration pattern. Mass transfer was accompanied by sulfidation of reactive iron in the system resulting in the higher hydrogen, lower aqueous sulfide activity, subsequent destabilization of H₃AsO₃ and Au(HS)₂⁻ complexes, and gold precipitation in association with As-rich pyrite.

The results of modeling provide data on the associated alteration patterns, geochemical controls and gold depositional mechanism in the Betze deposit. This study results in a better understanding of an evolving ore-forming system in the Betze deposit, and also broadens our knowledge of hydrothermal processes in other gold-producing terranes.

INTRODUCTION

Understanding the chemical evolution of metal-bearing hydrothermal fluids and metal-concentrating mechanisms is instrumental to our knowledge of ore formation. Much of the debate over the origin and character of sediment-hosted disseminated gold deposits centers on problems associated with the source(s) of the gold and other ore components, the chemistry of metal-bearing fluid(s) and the depositional mechanism(s), all of which are complicated by multiple

periods of tectonic, hydrothermal and metasomatic activities (Sillitoe and Bonham, 1990; Alvarez and Noble, 1988; Hofstra and others, 1988, 1991; Berry, 1992; Christensen, 1993; Volk and Lauha, 1993; Ilchick and Barton, 1996; Volk and others, 1996; Christensen, 1996). Descriptions can fuel speculation as to the genesis of ore deposits; however, descriptive models by themselves do not provide numerical insight into the geochemical processes that lead to the formation of ore deposits. Descriptive models are further limited because they cannot be tested, nor can they generate alternative models or utilize the nuances of alternative geological environments. The process models and mechanisms responsible for precipitation of gold and the chemical evolution of Carlin-type systems have been discussed by Hofstra and others (1991) and Ilchik and Barton (1996).

The purpose of our study was twofold: (1) to test, *via* numerical modeling, the generalized ore depositional processes outlined by previous researchers, and (2) to provide illustration of the computational methodology and its applications to understanding gold deposition in the Betze deposit. This study focuses on reconstruction of the chemical reactions associated with alteration and ore deposition. At present, our treatment is intended as an introduction to and an overview of the manifold ore depositional problems present in this large and complex deposit.

The modeling procedure presented in this paper represents an extension of the computational methodology developed in studies by Hemley and Woitsekhowskaya (1993), and Woitsekhowskaya and Hemley (1995). Preliminary geochemical modeling of the deposit is based on descriptive studies of the Betze deposit conducted by several workers (Bettles, 1991; Bettles and Lauha, 1991; Berry, 1992; Arehart and others, 1993a; Peters, 1996; Ferdock and others, 1997; Peters and others, 1997).

DESCRIPTION OF THE BETZE GOLD DEPOSIT

The Betze gold deposit is located along the Carlin trend in northeastern Nevada and exhibits mineralogical and alteration features typical for most Carlin-type gold deposits. The deposit is hosted in the upper units of the Devonian and Silurian Roberts Mountains Formation, the Devonian Popovich

Formation, and the lower parts of the Devonian Rodeo Creek unit, all of which are para-autochthonous, and are in contact with the northeast margin of the Jurassic Goldstrike diorite stock (Lauha and Bettles, 1993). The Betze deposit contains over 30 million oz Au representing the largest concentration of gold currently known in the Western Hemisphere (Leonardson and Rahn, 1996).

Previous workers documented the pre-ore and syn-ore stages of hydrothermal activity and the final post-ore and weathering stages that formed the Betze deposit (Arehart and others, 1993; Ferdock and others, 1997). The mineral paragenesis in Betze can be summarized as follows: (1) the main hydrothermal stage of gold mineralization is characterized by the formation of clay minerals (illite, kaolinite, and minor smectite), quartz, pyrite, gold, calcite, dolomite, As-rich pyrite, arsenopyrite and rare native arsenic, and (2) the late paragenetic sequence is characterized by formation of quartz, calcite, realgar, orpiment, stibnite, and barite.

Gold resides predominantly within As-rich overgrowths on pyrite (Arehart and others, 1993a). The intimate association of sub-micron size "invisible" gold with As-rich pyrite is a characteristic feature of Carlin-type deposits, and has been the subject of many studies (Bakken and Einaudi, 1986; Bakken and others, 1991; Arehart and others, 1993a; Sha, 1993; Fleet and Mumin, 1997). Several workers reported that gold in Carlin-type deposits might also be associated with other sulfide minerals including chalcopyrite, sphalerite and cinnabar (Wells and Mullens, 1973; Bakken and Einaudi, 1986), as well as with quartz, carbonate minerals, and clay minerals (Hausen and Kerr, 1968; Drews-Armitage and others, 1996). Understanding the mineral association of hypogene gold in ores in the Betze deposit is crucial, because it helps to constrain fluid chemistry and depositional mechanisms. The most common and economically important minerals in Betze are considered in modeling calculations, although there are many other minor minerals that are found only locally.

A complex interplay between: (1) proximity to the Jurassic Goldstrike stock; (2) degree of fracturing and brecciation that are related to Mesozoic and Tertiary high to low-angle faults; and (3) favorable permeable calcareous stratigraphic units in the Paleozoic host rocks results in variation in the type of gold occurrences, paragenetic interpretations, and alteration patterns in the Betze deposit (Bettles, 1989; Bettles and Lauha, 1991; Lauha and Bettles, 1993; Madeisky, 1993; Peters, 1996; Ferdock and others, 1997). Alteration is similar to that of other sediment-hosted disseminated gold deposits (Radtke, 1985; Bakken and Einaudi, 1986; Kuehn, 1989). It varies from negligible to intense in and between orebodies, and has resulted in decarbonatization, silicification and argillization of individual carbonate beds of the Popovich Formation and the upper Roberts Mountains Formation (Leonardson and Rahn, 1996; Arehart, 1996; Teal and Jackson, 1997).

Temporal and spatial relations between alteration types are poorly understood, although it is well documented that the majority of the ore is present in decarbonatized and weakly to moderately silicified rocks. Most of the gold ore is associated with the decarbonatized host rocks that constitute the most pervasive and intense alteration zones in the Betze deposit. The documented alteration assemblages that sequentially developed during decarbonatization are summarized in the following order (Leonardson and Rahn, 1996; Arehart, 1996; Teal and Jackson, 1997):

fresh carbonate rocks:

calcite+dolomite+kaolinite+pyrite±illite±quartz±carbon;

weak to moderate decalcification:

dolomite+quartz+kaolinite±As-rich

pyrite±illite±calcite±gold±carbon;

intensive decalcification:

kaolinite+pyrite±quartz±dolomite±carbon;

decarbonatization:

kaolinite+pyrite±quartz±carbon.

GEOCHEMICAL CONSTRAINTS ON FLUID CHEMISTRY

The geochemical constraints used herein were based on stable isotope, fluid inclusion, and field studies for Betze and other Carlin-type deposits as documented by previous researchers (Kuehn, 1989; Hofstra and others, 1991; Arehart and others (1993), Kuehn and Rose, 1995; Lamb, 1995, Arehart, 1996; Ilchik and Barton, 1997; Lamb and Cline, 1997). Available fluid inclusion data for the Betze deposit are summarized in table 1. These data suggest that the ore fluid associated with the main stage of gold mineralization contained high density CO₂ (0.86 to 0.78 gm/cm³) and was of moderate to low salinity (10 wt. percent NaCl equivalent). The trapping pressures of the fluid inclusions were 1,000 to 1,425 bars. This mineralization stage took place at minimum temperatures from 210° to 200° C. In contrast, the late stage mineralization resulted in silicification of host rocks and took place at lower temperatures (from 180° to 150° C) and lower salinity. Stable isotope studies by Hofstra and others (1991), and Arehart and others (1993) document a wide range of the stable isotope values [δ³⁴S = -30 to +20 per mil (sulfides); δ¹⁸O values ranging from 0 to +5 per mil (altered rocks) and values of +18 to +24 per mil (unaltered rocks); δD values near -150 per mil; and δ¹³C values -2 to +1 per mil], suggesting that two different fluids were involved in the gold ore-forming episode. The sulfur isotope data for sulfide minerals and barite are evidence for disequilibrium between reduced and oxidized sulfur species in solution. The wide range in sulfur isotopic composition also may reflect compositional variations of sources and variations due to isotopic exchange in the hydrothermal system.

MODELING APPROACH

The alteration mineral assemblages, their paragenetic sequence, and fluid inclusion data (table 1) indicate two major gold mineralization stages, and also indicate that each stage of mineralization took place under different geological conditions. Two sets of modeling calculations were, therefore, required. The first set of calculations involved reaction of ore fluid (table 2) with fresh rock (FR11 on table 3) at the higher temperature and pressure conditions representative of the decarbonatization process and the main stage of mineralization (table 1). The second run of calculations involved reaction of the ore fluid with altered rocks at lower temperature and pressure conditions representative of the silicification process and the later event of hydrothermal activity (table 1). To model the later mineralization stage, the alteration mineral assemblages from the first run were used to simulate reaction with the ore fluid, which was similar to that indicated in table 2.

Field studies indicate that advective transport of chemical components by hydrothermal fluid(s) influenced the chemical processes of gold emplacement in the depositional environment. For example, higher gold grades are often associated with multi-increment deformation such as described by Bettles (1989), exhibiting the intense fluid-rock interactions that enhanced gold removal from the hydrothermal fluid. This study focused on modeling of these fluid-rock interactions as the system cooled, that resulted in mineral precipitation and development of alteration patterns in the Betze deposit. Boiling and fluid mixing were not modeled, because fluid inclusion and mineralogical studies do not provide significant evidence of the boiling process, and because fluid mixing alone cannot account for the observed mineral assemblages and alteration patterns.

The preliminary model of the fluid-rock interaction during cooling is discussed below and emphasizes three important controls on the mineral assemblages produced: (1) temperature, (2) pH, and (3) changes in aqueous silica activity. Although other controls also are important, such as the role of thermochemical sulfate reduction reactions, carbonate dissolution reactions, metal transport concentrations, salinity, and pressure or pH buffered conditions, the selected example

provides adequate illustration of the methodology and its application to understanding of gold deposition during alteration in the Betze deposit.

COMPUTATIONAL PROCEDURE

To model fluid-rock interaction in a geological and geochemical context, a polythermal-polybaric reaction path and thermodynamically open system was required. The modeled system was constructed utilizing a series of chemical “reactors” that simulate chemical mass transfer driven by successive interactions between “flowing” fluid and discrete increments of host rock under temperature gradients. Chemical reactors are the individual parts of the modeled system, which are linked by carrying the dissolved constituent materials from one reactor to each successive reactor with the deposited minerals left behind. Phase relations among hydrothermal minerals in the system are calculated on the basis of the change in the chemical potential of a component and its activity during a geochemical process where ξ is the progress variable for the process (De Donder, 1920; Helgeson, 1968). This methodology implies an examination of geochemical processes in a dynamic open hydrothermal system over a range of environmental constraints. It has been used to model different ore-forming processes (Woitsekhowskaya, 1992; Woitsekhowskaya and others, 1992; Woitsekhowskaya and others, unpublished data, 1997). Some aspects of the “flowing through reactors” computational methodology were developed by Krajnov and others (1988).

The computer software used was the HCh program of Shvarov (1976), which includes the GIBBS code and the UNITHERM database of thermodynamic properties of minerals, aqueous species and gases (see also Krajnov and others, 1988). The GIBBS code is based on the minimization of Gibbs free energy and has been developed for simulation of equilibrium states among gaseous-solid-aqueous phases in homogeneous or heterogeneous systems in the temperature range 0° to 1,000° C and pressure range 1 to 5,000 bars. The GIBBS program treats the overall water-rock-gas interaction as the summary of many simpler processes (dissolution of a single mineral, formation of a single aqueous complex, etc.).

Table 1. Summary of fluid characteristics of two successive stages of gold mineralization in the Betze deposit*

Fluid characteristics	Main gold event	Late gold event
Pressure total (bars)	1,425 - 1,000	1,235 - 750
Salinity (wt.% NaCl equivalent)	≤10.0	3.0 - 0.1
Temperature (°C)	210 - 200	180 - 150
Density of bulk CO ₂ (gm/cm ³)	0.86 - 0.78	0.86 - 0.78

*Value adapted from Lamb, 1995; Kuehn and Rose, 1995; Lamb and Cline, 1997.

The database UNITHERM (Shvarov and others, unpublished data, 1997) is substantially similar to SUPCRT92 (Johnson and others, 1992), but is not cited extensively outside the Russian literature.

Composition of the ore fluid used in simulation

The chemical composition of the ore fluid in the Betze deposit was simulated assuming mutual solubility of pyrite+realgar+stibnite+gold at $T = 250^{\circ}\text{C}$ and $P_{\text{tot}} = 1,200$ bars. The starting temperature used in the calculations was 250°C . This temperature is higher than indicated in table 1 because the fluid inclusion data refer only to a given point of observations and not to the hypothetical initial state of the fluid. Because of a lack of definitive initial state information, multiple calculations were conducted with variable salinity, total Cl was varied from 0.1 to 1.5 molar (maximum value was 7.5 wt. percent NaCl equivalent) and CO_2 at 0.78 g/cm^3 . The activities of O_2 and H_2S , as well as the pH values, were calculated as the functions of a mutual solubility reaction. These parameters are dependent variables in the hypothetical fluid that changed as the equilibrium between the mineral assemblage and fluid chemistry changed. For purposes of sensitivity analysis, several ore fluid compositions were used to react with limestone and altered rock to simulate decarbonatization and silicification processes in Betze. The calculated initial metal concentrations in the ore fluid that was considered to be responsible for formation of the Betze deposit are listed in table 2.

The speciation-solubility calculations demonstrate that

gold was transported mainly as a bisulfide complex $\text{Au}(\text{HS})_2$ -antimony as a H_3SbO_3 complex, arsenic as a H_3AsO_3 complex, and iron as a dichloride complex. The calculated aqueous iron concentration was low, suggesting that the host rocks or underlying rocks, or both, buffered iron in the system. Similarly, sulfide sulfur was relatively low (aH_2S at 10^{-3}). A possible second source for sulfur from reduction of sulfate sulfur is suggested by isotope evidence.

Host rocks used in simulation

Ore in the Betze deposit is hosted, for the most part, by limestone of the Popovich Formation and, therefore, chemical analyses of these rocks were used in the mass transfer calculations. For purposes of sensitivity analysis, different rock types composing the Popovich Formation were utilized and the calculated mineral assemblages were compared. The results of these calculations revealed no significant differences in the calculated depositional patterns, although some deviations in mass abundance of the deposited minerals were considered to be significant. Chemical analyses of representative rocks used in the chemical reaction path calculations are listed in table 3.

RESULTS AND DISCUSSION

The calculations presented below refer to two successive evolutionary phases during alteration and ore deposition. The major compositional characteristics of a natural heterogeneous

Table 2. Initial fluid characteristics used in modeling.

Constituent/parameter	Concentration (in moles)	Source
As*	8.02E-03	calculated from realgar solubility
Au *	3.94E-07	calculated from gold solubility
Cl**	1.01	fluid inclusion (table 1)
Fe *	4.55E-07	calculated from pyrite solubility
K **	0.01	fluid inclusion (table 1)
Na**	1.0	fluid inclusion (table 1)
S *	8.06E-03	calculated from total sulfides solubility
Sb*	2.20E-05	calculated from stibnite solubility
T($^{\circ}\text{C}$)	250**	fluid inclusion (table 1)
pH	4.31*	calculated
log aO ₂	-40*	calculated
log aH ₂	-5*	calculated
CO ₂ (gm/cm ³)	0.78**	fluid inclusion (table 1)
P total (bar)	1,200**	fluid inclusion (table 1)

Note: E is scientific notation = 10^x

*Concentrations determined by modeling mutual solubilities of gold, realgar, stibnite and pyrite in the solution that includes NaCl = 1.0 mole and KCl = 0.01 mole, and that was constrained to be in equilibrium with CO_2 (bulk density of 0.78 gm/cm^3).

** Values are adapted from the study by Lamb and Cline (1997).

Table 3. Host rock lithologies used in modeling.

Sample ID	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	CO ₂	S
FR8 ¹ (wt. %)	13.79	2.89	2.89	0.54	1.52	42.55	0.01	0.49	34.79	0.02
FR11 ² (wt.%)	38.66	5.4	5.4	1.42	8.73	17.73	0.06	1.53	22.95	0.1

¹Dp, Ls, upper unit, limestone of the Popovich Formation ; ²Dp lower unit, limestone of the Popovich Formation (G. Ferdock, unpublished data). Data indicated in this table are those were used in the sets of calculations and, therefore, they do not represent all data in chemical analysis for these samples.

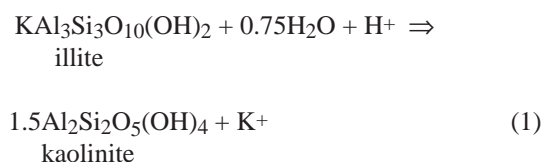
aqueous-solid-gaseous hydrothermal system in Betze is described in terms of 15 components (Al, As, Au, C, Ca, Cl, Fe, H, K, Mg, Na, O, S, Sb, and Si) comprising the modeling set. To mimic fluid-rock reactions during cooling, the solution was constrained to be in equilibrium with specified amounts of the host limestone at a specified temperature, total pressure and partial pressure CO₂. Therefore, each computational step was defined by the following parameters: (1) rock-fluid ratio, (2) temperature, and (3) total pressure. Selection of initial values of these specified parameters required a series of alternative calculations. Results were evaluated on the basis of geological and chemical criteria that included temperature and pressure ranges consistent with the geological context, the mineral phase rule, and the degree of consistency of the calculated mineral assemblage with field observations. Results of other alternative calculations indicated the values of temperature and rock-fluid ratio at each computational step. These values were carefully chosen to ensure the most adequate simulation of the mineral assemblages documented in the field.

Reaction of the ore fluid and limestone

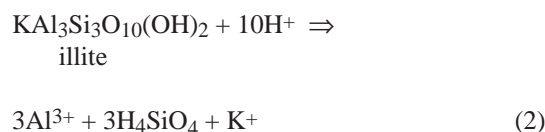
Gold deposition and decarbonatization of the host rock were simulated by a series of fluid-rock reactions between an ore fluid (table 2) and appropriate amounts of relatively fresh limestone (FR-11 from table 3). Small incremental changes of temperature and rock-fluid ratio were utilized while total pressure was maintained approximately at 1,200 bars throughout the entire reaction path. Calculated mineral assemblages, associated chemical reactions, mass transfer, gold deposition interval, pH, temperature, and pressure, corresponding to progressive fluid-rock interaction during decarbonatization, are shown in table 4, figures 1 through 3, and are discussed below.

Modeling results indicated that important chemical reactions occurred during interaction of the ore fluid with limestone and are as follows: (1) dissolution of the clay minerals, silica-leaching and silica-fixation reactions, and (2) carbonate dissolution. Fluid-rock interaction led first to the formation of a kaolinite+pyrite+graphite mineral assemblage, which was accompanied by a relatively low pH value, while the ratio between precipitated solids and dissolved constituents

was small (table 4, reaction step [a]). Overall, the clay minerals in the Betze deposit can be described in the system K₂O- Al₂O₃- SiO₂-H₂O by the general formula K_x(Al₂)(Al_xSi_{4-x})O₁₀(OH)₂ where x is the number of Al³⁺ and interlayer K⁺ ions. It is assumed that when x = 1 the simplified expression between reaction of clay minerals and ore fluid may be written such as follows:



The calculations show that over the first few reaction steps, dissolution reactions produced an aqueous phase in which the Si/Al ratios are higher than those in dissolved limestone (table 4, reaction steps from [a] through [f]). Aqueous silica concentration increased over the entire reaction path and was attributable to alteration of clay minerals in the host rock. Clay minerals (predominantly illite) dissolution (table 4, reaction steps from [a] through [c]) and concurrent precipitation of H₄SiO₄ as quartz (table 4, reactions steps from [d] through [f]), required a reaction such as follows:



Reaction 2 played an important role in the replacement process along the decarbonatization reaction path. In the intermediate zone of alteration, precipitation of quartz from H₄SiO₄ released by hydrolysis proceeded concurrently with clay mineral dissolution (table 4, reaction steps from [c] through [f]).

The pH value is important, but also of significance when the fact that H⁺ was continually consumed as the solution migrated and reacted with host rock as the system cooled. Dissolution of calcite occurred during the first computational steps (table 4, reaction steps from [a] through [c]) expressed by equation (3). Dolomite was stable at slightly higher pH (table 4, reaction step [b], equation (4)). These carbonate

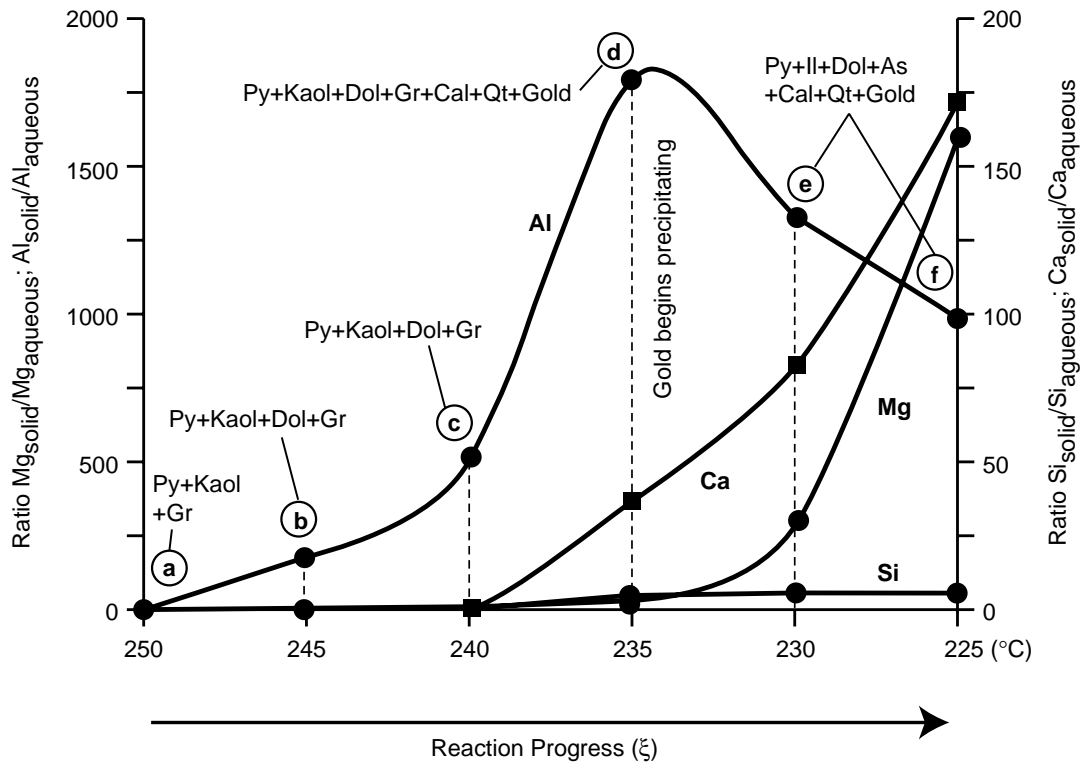
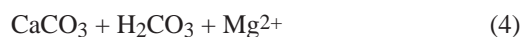
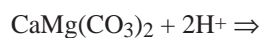
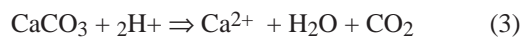


Figure 1. Diagram showing the modeled distribution between solid and aqueous phases for aluminum, magnesium, calcium and silica during main stage reaction steps and decarbonatization processes in the Betze deposit. Gold started to precipitate at 230°C, (1,200 bars, pH = 5.1, and log rock/fluid = -2.5 (reaction step [d], table 4). Note the difference in silica behavior that indicates a more complex control by the system. The letter annotations and dashed lines in the figure refer to sequential events of reaction progress steps (table 4).

dissolution reactions may have contributed to the high CO₂ contents measured in fluid inclusions from Carlin-type deposits.



A significant increase in the pH of the solution was accompanied by the formation of dolomite+calcite+kaolinite+pyrite+gold + quartz + graphite assemblage (reaction step [d], table 4). In this study, the As-rich pyrite formula was interpreted as the sum of native arsenic and pyrite, because of the lack of available petrographic and thermodynamic characteristics for this mineral found in the Betze deposit and other Carlin-type deposits. Arsenic in association with pyrite and gold precipitated in reaction step [e] (table 4). A subsequent reaction path moved along the kaolinite-illite phase

boundary until kaolinite completely gave way to illite (table 4, reaction steps [e] and [f]).

A series of alternative calculations did not reveal significant control by total pressure on the distribution of constituents and, therefore, on gold precipitation, which suggests that neither the stability of solid phases nor the stability of aqueous species varied strongly with pressure under the modeled conditions. In contrast, silica displayed a complex dependence on pressure, temperature, and pH changes in the system. No clear effect of Eh was observed over the pH range calculated in modeled system.

The compositional changes in the aqueous phase during decarbonatization can be outlined in terms of changes in aqueous silica, calcium, magnesium and aluminum activities that occurred in response to the fluid-rock interactions. Distribution of aqueous versus solid phases of the above components also is of interest. Figure 1 is a graphical representation of the distribution of calcium, magnesium, aluminum and silica between solid and aqueous phases during reaction progress in the modeled system (see also table 4 for

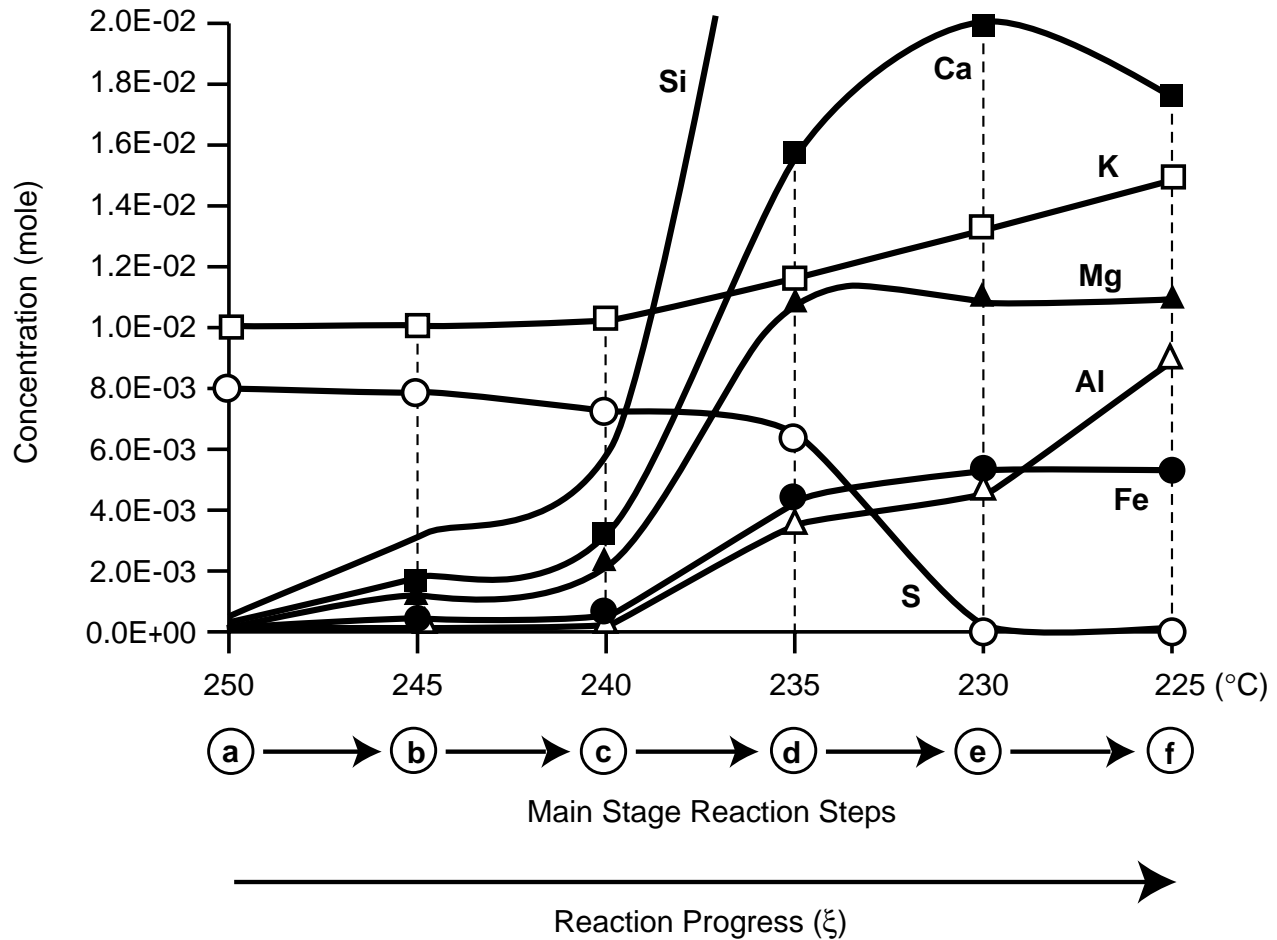


Figure 2. Schematic illustration of the calculated mass transfer of major constituents of the modeled system during the main stage of mineralization in the Betze gold deposit. Mass transfer reflects the mass of minerals produced and destroyed and appears to be a function of reaction progress in the reaction of the ore fluid and limestone. Note the changes in slope of the iron and sulfur curves that depict the calculated reaction path. Sulfur distribution relations demonstrate sulfidation in the modified flow with depletion model, where the total amount of sulfur was deposited and removed, as sulfide mineral precipitated. The letter annotations and dashed lines in the figure refer to sequential events of reaction progress steps (table 4).

more details). Lower ratios correspond to the loss of constituents to the aqueous phase from solid phases and, therefore, the earliest increments of the titrated limestone were almost dissolved. Further acid reduction toward neutral conditions in the system contributed to stabilization of carbonate minerals and illite. The distribution curves for aluminum, calcium and magnesium show that the starting point of gold precipitation corresponded to a degree of destruction of the constituent minerals of the host limestone during rock-fluid interaction. The mass transfer associated with the decarbonatization and hydrolysis reactions discussed above is shown graphically in figure 2. A decrease in the amount of destroyed limestone clearly corresponds to an increase in the

total concentrations of silica, calcium, magnesium, aluminum and potassium as the fluid-rock reaction progressed under cooling conditions. Note an increase in iron and depletion of sulfur that correlate with the onset of gold precipitation. The onset of gold precipitation also corresponds to a decrease in the activity of aqueous sulfur due to sulfidation of the reactive iron in the host rock. Mass transfer demonstrates that gold precipitation was a direct function of the reaction progress variable ξ .

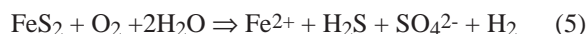
The results of modeling show that gold was complexed as a $\text{Au}(\text{HS})_2^-$ complex and transported in the +1 oxidation state, whereas the dominant arsenic complex was H_3AsO_3 with +3 oxidation state. The calculated association of gold and As-

Table 4. Computed mineral assemblages and associated variables corresponding to the main stage of gold mineralization and decarbonatization process (see text for further discussion).

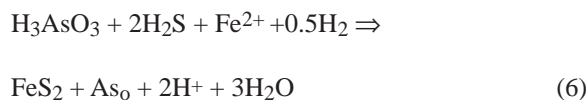
Reaction progress ξ	L o r/f	T (°C)	Mineral assemblages (computed)	pH
[a]	-4.0	250	Py + Kaol + Gr	4.4
[b]	-3.5	245	Py + Kaol + Dol + Gr	4.7
[c]	-3.0	240	Py + Kaol + Dol + Gr	4.7
[d]	-2.5	235	Py + Kaol + Dol + Gr + Cal + Qt + Gold	5.1
[e]	-2.5	230	Py + Il + Dol + Cal + Qt + Gold + Arsenic	7.3
[f]	-2.0	225	Py + Il + Dol + Cal + Qt + Gold + Arsenic	7.5

Minerals computed given in order of reaction progress during interaction of the ore fluid (table 2) with a limestone (table 3). Abbreviations for table: Py = pyrite; Kaol = kaolinite; Gr = graphite; Dol = dolomite; Cal = calcite; Qt = quartz; Il = illite. Ratio r/f = rock-fluid ratio that was used in calculations.

rich pyrite (native arsenic + pyrite) could be attributable to simultaneous reactions that caused precipitation of arsenic, pyrite, a decrease in the sulfur activity, and co-fixation of gold (see equations from (5) through (9)). For example, the oxidation of part of a pyrite grain may lead to low a_{O_2} and high a_{H_2} expressed in the following equation:



The reaction expressed in (5) is coupled with a reaction contributing to the precipitation of As-rich pyrite:

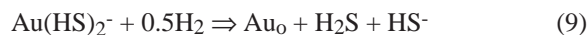


where association of pyrite and arsenic is interpreted as As-rich pyrite.

A decrease in sulfur activity and the presence of hydrogen in the solution, as referred by the following equations (from 7 to 9) contributed to the destabilization of the $Au(HS)_2^-$ complex and gold precipitation:



The resulting equation of the above reactions is as follows:



Reaction of the ore fluid and altered limestone

To model deposition of gold, iron, arsenic, and antimony minerals during the later stage of mineralization, a series of calculations were made between the ore fluid with the alteration mineral assemblages from the previous reaction path calculations (table 4). As before, the equilibrium solution chemistry after each computational step was used as the input ore fluid for the next step. Table 5 summarizes the changes in mineral assemblages deposited and the corresponding incremental changes in pH, temperature and rock-fluid ratio. An alternative series of calculations indicated that, in order to calculate mineral assemblages consistent with those

Table 5. Computed mineral assemblages and associated variables corresponding to the late stage of gold mineralization and silicification (see text for further discussion).

Reaction progress ξ	L o r/f	T (°C)	Mineral assemblages (computed)	pH
[g]	-4.0	220	Py + Realg + Orpm + Kaol + Gold	4.7
[h]	-3.5	215	Py + Dol + Stib + Kaol + Gold + Qt + Gr	4.8
[i]	-3.5	200	Py + Dol + Stib + Kaol + Gold + Qt + Gr	4.7
[j]	-3.0	190	Py + Dol + Kaol + Gold + Qt + Gr	4.8

Minerals computed given in order of reaction progress during interaction of the ore fluid (table 2) with altered limestone (computed mineral assemblages of the altered limestone are listed in table 4, reaction steps from [a] through [c]). Abbreviations for table: Py = pyrite; Kaol = kaolinite; Gr = graphite; Dol = dolomite; Cal = calcite; Qt = quartz; Il = illite; Realg = realgar; Orpm = orpiment; Stib = stibnite. Ratio r/f = rock-fluid ratio that was used in calculations.

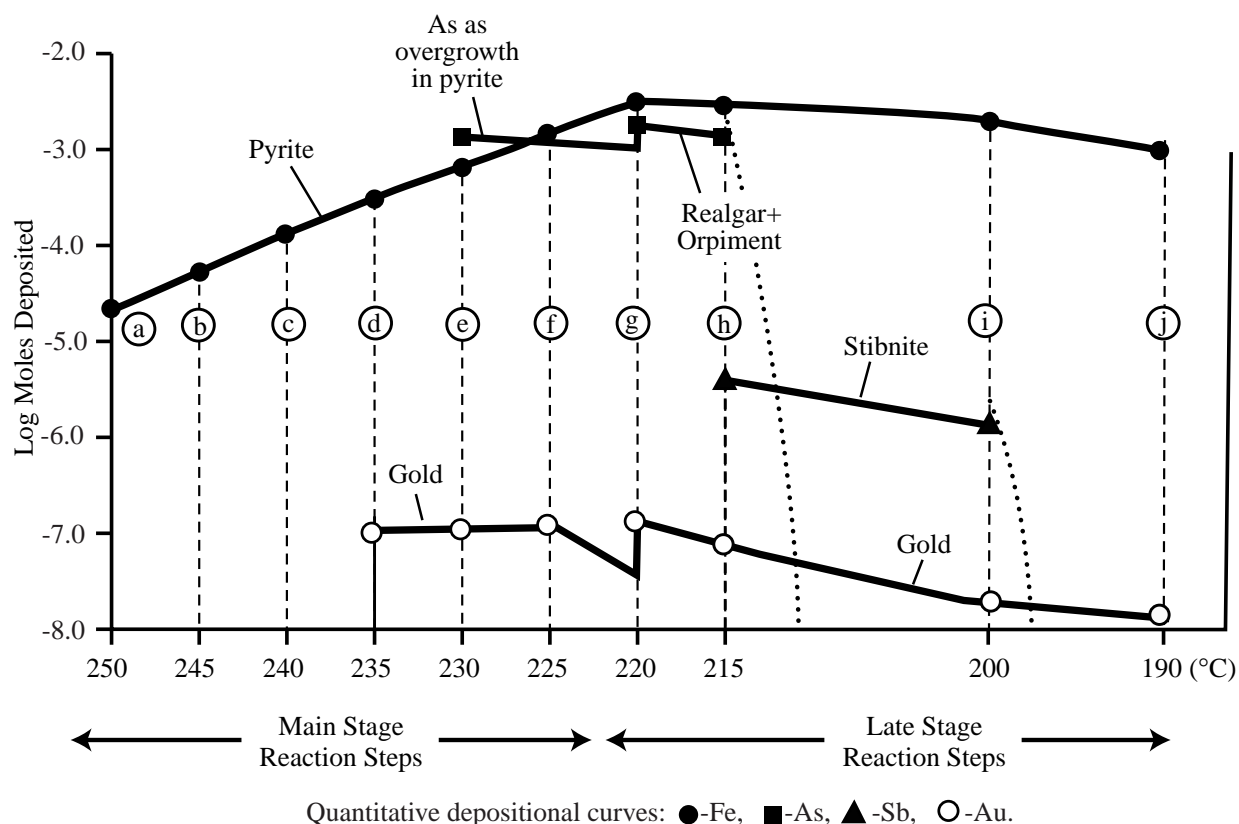


Figure 3. Quantitative depositional curves for sulfide minerals and gold corresponding to the main and late stage of mineralization events in the Betze deposit; quantity of minerals is shown in log moles/kg fluid for each temperature and pressure increment (with 5°C intervals for the main stage calculations; and from 5°C to 15°C intervals for the late stage calculations). Mass of minerals produced is a function of progress in the reaction of the ore fluid (table 2) with limestone (table 3) at temperature and pressure of the process (table 1). The letter annotations in the figure refer to sequential events of reaction progress steps during the main and late mineralization events (see table 4 and table 5).

documented, total pressure should be maintained at about 400 bars, which is relatively lower than indicated in table 1. In addition, relatively high aqueous silica values were assumed to model silicification. A series of alternative calculations also indicated that silica-leaching reactions did not result in saturation of the system with respect to quartz in the first reaction steps, because host limestone is relatively silica-poor (table 3).

As shown in table 5, gold precipitated over the entire reaction path indicating that cooling was important precipitation mechanism during the late gold event (table 5, reaction steps from [g] through [j]). The replacement of calcite by quartz occurred in reaction step [h]. The pH gradient is very small, indicating that leaching reactions were not important during the late stage, and that the mineralizing process was not chemically aggressive, enabling a preservation of textures during the course of replacement.

Calculated quantitative depositional curves for pyrite, native arsenic, realgar, orpiment, gold and stibnite during

alteration are depicted in figure 3. These curves show the relative amounts of minerals precipitated during the reaction steps from [a] through [f] (based on 5° C cooling steps), reaction steps from [h] through [i] (based on 15° C cooling steps), and a 10° C degree cooling increment between reaction steps [I] and [j]. Gold and arsenic were consistently depleted as the system followed the reaction path. Realgar and orpiment precipitated at the lower temperatures of the later stage, and eventually stibnite precipitated due to decrease in sulfur activity and temperature. The geologic expression of these relations is the interplay between changing mineral solubility and depletion of metal in the system.

CHEMICAL MODELING CONSTRAINTS ON BETZE ORE FORMATION

Geologically meaningful results have been obtained by computing reaction paths in the multicomponent and

multiphase system. The modeled system is considered to be analogous to the natural depositional environment in the Betze gold deposit. The modeling results suggest that gold was complexed as a $\text{Au}(\text{HS})_2^-$ whereas the dominant arsenic complex was H_3AsO_3 , and antimony was complexed as a $\text{Sb}(\text{OH})_3$. Gold, arsenic, antimony and other components were transported to the depositional site from below the accessible Carlin system. Geologic evidence suggests that the transported fluids were focused along permeable high- to low-angle faults into favorable conduits in the Popovich Formation.

The major features of the alteration zonation pattern observed in the deposit were simulated by the reaction of the ore fluid with limestone as the system cooled. The mineral stability relations in the $\text{CaO-MgO-CO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system were reflected in the distribution of the mineral phases in the modeled and actual system. Dissolution-precipitation reactions, including carbonate destruction, silica-leaching, silica-fixation, and sulfide mineral precipitation controlled mass transfer in the Betze deposit.

Mass transfer calculations indicate that gold precipitation was associated with sulfidation of reactive iron in the system, and corresponded to a particular reaction progress variable ξ . Sulfidation resulted in higher hydrogen and lower sulfide sulfur activity in the system, which destabilized H_3AsO_3 and $\text{Au}(\text{HS})_2^-$ complexes, and resulted in gold precipitation in association with As-rich pyrite. The results of our modeling study are similar to those of Hofstra and others (1991), and confirm that sulfidation of host rock iron during reaction of the ore fluid with host rock was the primary gold precipitation mechanism in Carlin-type deposits.

The modeling results cannot provide an adequate answer to whether a fluid or a mixture of fluids of various origins entered the depositional environment. Although stable isotope data suggest that the ore fluids mixed with meteoric water, the modeling results indicate that interactions between a single fluid and the host rocks can account for the observed mineral assemblages, suggesting that fluid mixing was not an important depositional control in the Betze deposit.

Research efforts are in progress to better understand geochemical and geological processes controlling gold transport and deposition in Carlin-type gold deposits. Modeling of the origin and character of the ore-forming fluid(s) and its interactions with host rocks in conjunction with field, experimental and laboratory studies will help us to better understand the processes of ore formation in Carlin-type gold deposits.

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REFERENCES CITED

- Alvarez, A.A., and Noble, D.C., 1988, Sedimentary rock-hosted disseminated precious metal mineralization at Purisima Concepcion, Yauricocha District, central Peru: *Economic Geology*, v. 83, p. 1368–1378.
- Arehart, G.B., 1996, Characteristics and origin of sediment-hosted gold deposits: a review: *Ore Geology Reviews*, v. 11, p. 383–403.
- Arehart, G.B., Foland, K.A., Naeser, C.W., and Kesler, S.E., 1993a, $^{40}\text{Ar}/^{39}\text{Ar}$, K/Ar, and fission track geochronology of sediment-hosted disseminated gold deposits at Post Betze, Carlin trend, northeastern Nevada: *Economic Geology*, v. 88, p. 622–646.
- Arehart, G.B., Chryssoulis, S.L., and Kesler, S.E., 1993b, Gold and arsenic in iron sulfides from sediment-hosted disseminated gold deposits: Implications for depositional processes: *Economic Geology*, v. 88, p. 171–185.
- Arehart, G.B., Eldridge, C.S., Chryssoulis, S.L., and Kesler, S.E., 1993c, Ion microprobe determination of sulfur isotope variations in iron sulfides from the Post/Betze sediment-hosted disseminated gold deposit, Nevada, USA: *Geochimica et Cosmochimica Acta*, v. 57, p. 1505–1519.
- Bakken, B.M., and Einaudi, M.T., 1986, Spatial and temporal relations between wall-rock and gold mineralization, main pit, Carlin gold mine, Nevada, in MacDonald, A.J., *Gold'86: Willowdale, Ontario*, Konsult International Inc., p. 388–403.
- Bakken, B.M., Fleming R.H., and Hochella M.F., 1991, High-resolution microscopy of auriferous pyrite from the Post deposit, Carlin District, Nevada, in Hausen, D.M., Petruk, W., Hagni, R.D., and Vassiliou A., eds., *Process Mineralogy XI-Characterization of Metallurgical and Recyclable Products: The Minerals, Metals and Materials Society*, p. 13 - 23.
- Berry, A.R., 1992, A geological study of the Betze gold deposit, Eureka County, Nevada: University of Nevada, Reno, M.S. Thesis, 173 p.
- Bettles, K.H., 1989, Gold deposits of the Goldstrike Mine, Carlin Trend, Nevada: *Society of Mining Engineers Preprint*, 89–158, p. 14.
- Bettles, K.H., and Lauha, E.A., 1991, Gold deposits of the Carlin Trend, Nevada: *World Gold '91, Forum on Technology and Practice: Second Australian Institute of Mining and Metallurgy Society of Mining and Metallurgy Joint Conference*, 21–26 April, Cairns, Australia, p. 251–257.
- Christensen, O. D., 1993, Carlin trend geologic overview, in Christensen, O.D., ed., *Gold Deposits of the Carlin Trend, Nevada: Society of Economic Geologists Guidebook Series*, v. 18, p. 326.
- 1996, Carlin trend geologic overview, in Green, S.M., and

- Strusacker, E., eds., *Geology and ore deposits of the American Cordillera Road Trip B, Structural Geology of the Carlin Trend: Geological Society of Nevada Field Trip Guidebook Compendium*, 1995, Reno/Sparks, Nevada, p. 147–156.
- De Donder, T., 1920, *Leçons de Thermodynamique et de Chimie Physique*: Paris, Gauthier Villars, 210 p.
- Drews-Armitage, S.P., Romberger, S.B., and Whitney, C.G., 1996, Clay alteration and gold deposition in the Genesis and Blue Star deposits, Eureka County, Nevada: *Economic Geology*, v. 91, p. 1383–1393.
- Ferdock, G.C., Castor, S.B., Leonardson, R.W., and Collins, T., 1997, Mineralogy and paragenesis of ore stage mineralization in the Betze gold deposit, Goldstrike Mine, Eureka County, Nevada, in Vikre, P., Thompson, T.B., Bettles, K., Christensen, O., and Parratt, R., eds., *Carlin-type Gold Deposits Field Conference: Society of Economic Geologists Guidebook Series*, v. 28, p. 75–87.
- Fleet, M. E., and Mumin A. H., 1997, Gold-bearing arsenian pyrite and marcasite and arsenopyrite from Carlin Trend gold deposits and laboratory synthesis: *American Mineralogist*, v. 82, p. 182–193.
- Hausen, D. M., and Kerr, P. F., 1968, Fine gold occurrence at Carlin, Nevada, in Ridge, J.D., ed., *Ore Deposits of the United States: American Institute Mining Metallurgy and Petroleum Engineers*, New York, p. 908–940.
- Helgeson, H.C., 1979, Mass transfer among minerals and hydrothermal solutions, in Barnes, H.L., ed., *Geochemistry of Hydrothermal Ore Deposits*: New York, Holt, Rhinehart, and Winston, p. 568–610.
- , 1968, Evaluation of irreversible reactions in geochemical processes involving minerals and aqueous solutions: I. Thermodynamic relations: *Geochimica and Cosmochimica Acta*, v. 32, p. 853–877.
- Hemley, J.J., and Voitsekhowskaya, M., 1993, Modeling ore metal transport and deposition in hydrothermal systems: *Geological Society of America, Abstract with Programs*, v. 25, p. A401.
- Hofstra, A.H., Northrop, H.R., Rye, R.O., Landis, G.P., and Birak, D.J., 1988, Origin of sediment-hosted disseminated gold deposits by fluid mixing: Evidence from jasperoids in the Jerritt Canyon gold district, Nevada, USA, in Goode, A.D.T., and Bosma, L.I., eds., *Geological Society of Australia, Proceedings of Bicentennial Gold' 88: Economic Geology, Abstract Series* no. 22, p. 284–289.
- Hofstra, A.H., Leventhal, J.S., Northrop, H.R., Landis, G. P., Rye, R.O., Birak, D.J., and Dahl, A. R., 1991, Genesis of sediment-hosted disseminated gold deposits by fluid mixing and sulfidation: chemical reaction path modeling of ore depositional processes documented in the Jerritt Canyon District, Nevada: *Geology*, v. 19, no. 1, p. 36–40.
- Ilchik, R.P., and Barton, M.D., 1996, Physical and chemical constraints for an amagmatic origin of Carlin-type gold deposits, a source-sink approach, in Coyner, A.R., and Fahey, P.L., eds., *Geology and Ore deposits of the American Cordillera: Geological Society of Nevada Symposium Proceedings*, v. 2, p. 687–708.
- Johnson, J.W., Oelkers, E.H., and Helgeson, H.C., 1992, SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species and reactions from 1 to 5,000 bars and 0 to 1,000° C: *Computers and Geosciences*, v. 18, p. 899–947.
- Krajnov, S.R., Shvarov, Y.V., and Grichuk, D.V., 1988, *Methods of thermodynamic modeling and forecasting in hydrogeology*: Nedra Press, Moscow, 203 p., (in Russian).
- Kuehn, C.A., 1989, *Studies of disseminated gold deposits near Carlin, Nevada: Evidence for a deep geologic setting of ore formation*: Pennsylvania State University, Ph.D. dissertation, 395 p.
- Kuehn, C.A., and Rose, A.W., 1995, Carlin gold deposits, Nevada: Origin in a deep zone of mixing between normally pressured and over pressured fluids: *Economic Geology*, v. 90, p. 17–36.
- Lamb, J.B., 1995, *A petrographic and fluid inclusion study of the Purple Vein and Post-Betze orebodies, Carlin, Nevada*: University of Nevada, Las Vegas, M.S. Thesis, 161 p.
- Lamb, J.B., and Cline, J.M., 1997, Depth of formation of the Meikle and Betze/Post deposits, in Vikre, P., Thompson, T.B., Bettles, K., Christensen, O., and Parratt, R., eds., *Carlin-type Gold Deposits Field Conference: Society of Economic Geologists Guidebook Series*, v. 28, p. 101–108.
- Lauha, E.A., and Bettles, K.H., 1993, A geologic comparison of the Post/Betze and Purple vein deposits of the Goldstrike and Meikle Mines, Nevada: *Society for Mining, Metallurgy, and Exploration, Preprint* 93–170, 20 p.
- Leonardson, R.W., and Rahn, J.E., 1996, Geology of the Betze-Post gold deposits, Eureka County, Nevada, in Coyner, A.R., and Fahey, eds., *Geology and Ore Deposits of the American Cordillera: Geological Society of Nevada, Symposium Proceedings*, Reno/Sparks, Nevada, April, 1995, p. 61–94.
- Madeisky, H.E., 1993, Pearce element ratio analysis: applications in lithogeochemical exploration, in Coyner, A.R., and Fahey, P.L., *Geology and Ore Deposits of the American Cordillera: Geological Society of Nevada Symposium Proceedings*, Reno/Sparks, Nevada, April, 1995, p. 709–732.
- Peters, S.G., 1996, Definition of Carlin trend using orientation of fold axes and applications to ore control and zoning in the central Betze orebody, Betze/Post Mine, in Green, S.M., and Struhsacker, E., eds., *Geology and Ore Deposits of the American Cordillera, Trip B-Structural Geology of the Carlin Trend, Field Trip Guidebook Compendium*, 1995: Geological Society of Nevada, Reno/Sparks, Nevada, p. 59–95.
- Peters, S.G., Leonardson, R.W., Ferdock, G.C., and Lauha, E.A., 1997, Breccia types in the Betze orebody, Goldstrike Mine, Eureka County, Nevada, in Vikre, P., Thompson, T.B., Bettles, K., Christensen, O., and Parratt, R., eds., *Carlin-type Gold Deposits Field Conference: Society of Economic Geologists Guidebook Series*, v. 28, p. 87–101.
- Radtke, A.S., 1985, *Geology of the Carlin gold deposit, Nevada*: U.S. Geological Survey Professional paper 1267, 124 p.
- Sillitoe, R.H., and Bonham, H.F., 1990, Sediment-hosted gold deposits: Distal products of magmatic-hydrothermal systems: *Geology*, 18, p. 157–161.
- Sha, P., 1993, *Geochemistry and genesis of sediment-hosted disseminated gold mineralization at the Gold Quarry Mine, Nevada*: Ph.D. Thesis, University of Alabama, 254 p.
- Shvarov, Y.V., 1976, Calculation of equilibrium composition in a multicomponent heterogeneous system: *Academia Nauk SSSR Doklady*, v. 229, no. 6, p. 223–225 (in Russian).
- Teal L., and Jackson M., 1997, Geologic overview of the Carlin trend gold deposits and description of recent deep discoveries, in Vikre, P., Thompson, T.B., Bettles, K., Christensen, O., and Parratt, R., eds., *Carlin-type Gold Deposits Field Conference*:

- Society of Economic Geologists Guidebook Series, v. 28 , p. 3-37.
- Volk, J.A., and Lauha, E.A., 1993, Structural controls on mineralization at the Goldstrike property, Elko and Eureka counties: Geological Society of America Abstracts with Programs, v. 23, no. 2, p. 106.
- Volk, J.A., Lauha, E., Leonardson, R.W., and Rahn, J.E., 1996, Structural geology of the Betze Post and Meikle deposits, Elko and Eureka Counties, *in* Green, S.M., and Struhsacker, E., eds., Geology and Ore Deposits of the American Cordillera, Trip B, Structural Geology of the Carlin Trend, Field Trip Guidebook Compendium, 1995: Geological Society of Nevada, Reno/Sparks, Nevada, p. 180-194.
- Wells, J.D., and Mullens, T.E., 1973, Gold-bearing arsenian pyrite determined in microprobe analysis, Cortez and Carlin gold mines, Nevada: Economic Geology, v. 65, p. 187-201.
- Woitsekhowskaya, M., 1992, A modeling study of alteration process sequences in response to Au-mineralization associated with volcanic rocks: International Conference on Mineral Deposit Modeling in Relation to Crustal Reservoirs of the Ore-forming Elements, Nottingham, United Kingdom, (unpaginated).
- Woitsekhowskaya, M. B., and Hemley, J.J., 1995, Modeling metal transport and deposition in Butte-type hydrothermal systems: Economic Geology, v. 90, p. 1329-1337.
- Woitsekhowskaya, M., McArdle, P., and O'Connor, P., 1992, Chemical modeling of the Au-Cu Avoca deposit, SE Ireland: 2nd Symposium on Thermodynamics of Natural Processes, Novosibirsk, Russia, (unpaginated).