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Arsenic evolution as a tool for understanding formation of pyritic gold ores

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ABSTRACT

Arsenic (As) and gold (Au) are closely associated in many gold deposits, both being hosted in Fe-sulfide minerals (pyrite, marcasite, and arsenopyrite), partly because As geochemistry controls Au accumulation. Yet, the partitioning behavior of As between pyrite, arsenopyrite, and hydrothermal fluids remains poorly understood. Here, we introduce solid-solution models for As in pyrite and As in arsenopyrite into a thermochemical model of fluid-rock interaction, and use it to evaluate the effects of temperature, redox state, and fluid-flow dynamics on As and Au by association—partitioning. We find that As concentrations in pyrite decrease with increasing temperature, despite the widening of the solid-solution composition range. This is related to the preferential partitioning of As into fluids at higher temperatures. Simulations of infiltration of rock-buffered H_2O-CO_2 -As fluids into low-As pyrite (As:S = 0.01) ores reveal a continuous enrichment of As in pyrite with increasing fluid:rock ratio. The modeling suggests that upgrading of early-formed low-grade ores by multistage hydrothermal events can generate large gold deposits. In this scenario, an anomalously Au-rich fluid is not needed, but instead, prolonged fluid-rock interaction enriches pyrite in As, which promotes gold sequestration.

INTRODUCTION

The association between Au and As in Fe(-As) sulfides (pyrite [FeS₂], marcasite [FeS₂], and arsenopyrite [FeAsS]) is a well-recognized characteristic of most Au deposits. Hence, the correlation between Au and As makes As in pyrite a good proxy for Au mineralization. This As-Au coupling also may reflect a partial control of Au accumulation by As geochemistry in hydrothermal gold systems (Deditius et al., 2014). Yet, the behavior of As in fluid-rock systems remains poorly understood, due to limited understanding of the solid solution of As in iron-sulfide minerals (Reich and Becker, 2006).

Thermodynamic reactive transport modeling is an important tool for understanding complex fluid-rock interactions, element mass transfer, and the potential of fluids to carry economic amounts of metals (Seward and Barnes, 1997). To date, our capacity to model As mobility under hydrothermal conditions has been severely limited by the absence of a thermodynamic model for As-in-pyrite and As-in-arsenopyrite solid solutions. Consequently, most available models overestimate As mobility in hydrothermal fluids, because As remains in solution until an As-dominant mineral such as arsenopyrite or löllingite precipitates (Zhong et al., 2015).

Here, we build a model of As solid solution in pyrite-marcasite and in arsenopyrite, and use it to calculate the partitioning of As between pyrite-marcasite, arsenopyrite, and fluids under conditions typical for Au deposition (Phillips and Evans, 2004). We find that the model provides important insights into the role of fluidrock interaction in Au mineralization. We show that the empirically well-established retrograde As solubility in pyrite with increasing temperature, T (Deditius et al., 2014), is a result of prograde As solubility in fluids. We further show that recurring fluid flow can enrich As in pyrite and arsenopyrite through extensive fluid-mineral interactions, which results in gold incorporation, generating high-grade gold resources.

THERMODYNAMIC MODELING OF THE FeS₂-FeAs₂ BINARY

The FeS_2 - $FeAs_2$ binary (Fig. 1) is modelled using three phases: pyrite-marcasite solid solution [$Fe(S,As)_2$], arsenopyrite solid solution (FeAs_{1-x}S_{1-x}), and löllingite (FeAs₂). Löllingite is assumed to be stoichiometric, in view of the limited S solubility in this mineral (Fleet and Mumin, 1997; Reich and Becker, 2006).

Arsenopyrite is modeled as a solid solution between the fictional end members $FeS_{1,2}As_{0,8}$ and $FeS_{0.8}As_{1.2}$. Pyrite-marcasite is described as a solid solution between marcasite (FeS₂) and a fictional (fic) löllingite (Lö, FeAs₂), which is defined such that $\Delta_f G_{Lo}^{fic} = \Delta_f G_{Lo} + 10 \text{ kJ/mol}$ (where $\Delta_{\rm f} G$ is the Gibbs free energy of formation from the elements to the subscripted species) so that löllingite is the stable mineral on the As-rich side of the diagram. This pyrite-marcasite model assumes that As1- is substituting for sulfur in the disulfide anion, S_2^{2-} , which is the predominant substitution mechanism in pyrite-marcasite (Qian et al., 2013). Due to the nature of As-S interactions, non-ideal contributions need to be incorporated for realistic modeling of the FeS2-FeAs₂ binary (Reich and Becker, 2006). Because of experimental difficulties (non-homogenous As distributions and nanoscale inclusions of As-rich phases), we use the theoretical energies of mixing derived from first principles by Reich and Becker (2006) to calibrate the excess free-energy models for pyrite-marcasite and arsenopyrite (Redlich-Kister formalism; Redlich and Kister, 1948). Reich and Becker (2006)'s calculations indicate that pyrite-marcasite can hold a maximum of ~6 wt% As in solid solution (Fig. 1); natural pyrite contains up to 19 wt% As, but many such As-rich pyrites have been shown to contain nanometer-size inclusions of As-rich phases (Deditius et al., 2014; Reich and Becker, 2006).

Thermodynamic calculations were conducted using the HCh software (http://www1 .geol.msu.ru/deps/geochems/soft/index_e.html), which employs a Gibbs free-energy minimization algorithm (Shvarov, 1999, 2008). Figure 1 illustrates the good agreement between the HCh model and the theoretical phase

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Figure 1. FeS₂-FeAs₂ phase diagram. Crosses represent theoretical diagram derived by Reich and Becker (2006) on basis of firstprinciple quantum mechanical computations, and colored fields are phase diagram predicted from thermodynamic data derived in this study.

diagram. Details of the calculation procedure and thermodynamic properties are provided in GSA Data Repository¹.

ARSENIC SOLUBILITY IN PYRITE-MARCASITE AND ARSENOPYRITE

Fluid-rock equilibria are calculated in the Fe-As-S-Na-Cl-K-Al-Si-H-O system (25-600 °C, fixed pressure of 200 MPa) for two conditions: an oxidized system buffered by pyrite + hematite, and a reduced system buffered by pyrite + pyrrhotite + magnetite. Fluid pH is buffered by K-feldspar + muscovite + quartz. Under these rock-buffered conditions, aqueous As concentrations increase with increasing temperaturefrom parts per billion to thousands of parts per million in the case of hematite-bearing assemblages (Fig. 2A). In arsenopyrite-absent assemblages, for a given As content of the simulated system, pyrite composition is largely temperature independent up to ~200 °C for the oxidized system, and 400 °C for the reduced system (Figs. 2C and 2D). Then As concentrations in pyrite decrease rapidly with increasing temperature, despite the fact that in the water-free system As solubility in pyrite increases slightly with temperature (Fig. 1).

The model predictions tally with the empirical observations that As contents of pyrite decrease as a function of increasing ore-formation

temperature, from ~200 to ~500 °C (Deditius et al., 2014). To understand the cause of the retrograde As contents of hydrothermal pyrite, it is useful to express the equilibrium between pyrite and fluid in terms of the Nernst partition coefficient, $D_{py/f} = X_{As(py)} / X_{As(f)}$, where $X_{As(py)}$ and $X_{As(f)}$ are the mass fractions of As in pyrite and fluid, respectively. The hydrothermal fluids responsible for the world's major gold production (e.g., "orogenic gold"; Carlin-type gold; Witwatersrand goldfields) share common features: $T > 200 \,^{\circ}\text{C}$, CO₂-rich (0.05–0.25 mol%), S-bearing, and low salinity (Phillips and Evans, 2004; Mikucki 1998). In these fluids, As exists predominantly in the form of $[As^{3+}(OH)_3]_{(aq)}$ (James-Smith et al. 2010; Kokh et al. 2017), and As solubility controlled by pyrite is described by

$$\begin{aligned} As(OH)_{3(aq)} + \frac{1}{2}FeS_{2(py)} + 2.5H_{2(g)} = \\ \frac{1}{2}FeAs_{2(py)} + HS^{-} + H^{+} + 3H_{2}O, \end{aligned} \tag{1}$$

where (aq) and (g) refer to aqueous and gaseous species, respectively.

Writing the equilibrium constant (logK_{PT}, at fixed pressure [P] and temperature [T]) and rearranging produces:

$$logD_{py/f} = logK_{P,T} + pH + 2.5logf_{H_{2(g)}} - loga_{HS^{-}} + log \underbrace{\frac{\gamma_{FeAs_{2(py)}}}{\gamma_{As(OH)_{3(qq)}} \cdot \gamma_{FeS_{2(py)}}}}_{Effect of composition of fluid and pyrite}, (2)$$

where γ is activity coefficient; *a* is activity; and f is fugacity. Equation 2 indicates a strong dependence of the partitioning upon local fluid

Figure 2. Results of modeling in HCh software (http://www1.geol.msu .ru/deps/geochems/soft /index e.html) of As in pyrite and arsenopyrite in oxidized (left) and reduced (right) fluids as function of temperature (°C, x-axis) and As fraction in the rocks. Simulations apply to rock-buffered systems. where pH is buffered by K-feldspar + muscovite + quartz, fugacities $f_{O_2(q)}$ and fs2(g) (g-gaseous species) are controlled by Fe-mineral assemblage, and As solubility is controlled by Fe-As sulfides. A,B: Solubility of As (in log parts per million) in fluids; thick solid lines represent phase boundaries for Fe-oxide minerals. C,D: Rock mineralogy (colored fields); yellow conditions, including pH, redox $[f_{H_{2(g)}}]$, and sulfur concentration, expressed as activity of the bisulfide ion, $a_{\rm HS}$. The low As contents of pyrite at high temperature are due to low $\log D_{pv/f}$ (Figs. 2C and 2D), which results mainly from the prograde S solubility (Fig. DR2 in the Data Repository) and prograde As solubility in fluids (encapsulated by logK_{PT} in Equation 2). The strong redox dependence of As incorporation into pyrite is due to the fact that As3+ is the main oxidation state of As in aqueous fluids, whereas As1- is predominant in pyrite: the As fraction is higher in pyrite that formed under reduced conditions compared to oxidized conditions (Figs. 2C and 2D). The calculated As partitioning coefficients between pyrite and solution for oxidized conditions (Fig. DR3) correspond well with the experimental and natural data reported by Kusebauch et al. (2018).

The As content of arsenopyrite (FeAsS) has been proposed as a geothermometer in gold systems, based on phase diagrams in the waterfree Fe-As-S system (Kretschmar and Scott, 1976; Sharp et al., 1985). Figure 2 shows that in As-undersaturated systems (i.e., native As absent, corresponding to the vast majority of Au deposits), arsenopyrite coexisting with pyrite has decreasing As content with increasing temperature, although the composition change is small and not suitable for a geothermometer (Figs. 2C and 2D). In As-rich systems where arsenopyrite and löllingite coexist, the concentration of As in arsenopyrite increases with increasing temperature and can be used as a geothermometer. Where arsenopyrite and pyrrhotite coexist, the main control on arsenopyrite composition is the bulk system composition.



isolines represent As fraction in pyrite at equilibrium (XAS(py), in weight percent), red isolines represent As mass fraction in arsenopyrite ($X_{As(asp)}$, in weight percent), and grey dotted isolines are calculated partitioning coefficient of As between pyrite and fluid (D_{ovt}). Asp—arsenopyrite; Hm-hematite; Lö-löllingite; Mt-magnetite; Po-pyrrhotite; Py-pyrite.

¹GSA Data Repository item 2019114, description of the fundamental assumptions for the thermodynamic model of Fe-As-S minerals; details of the fitting procedure and Redlich-Kister formalism used, and the mixing parameters derived in this study; supporting information for the thermodynamic model of fluid-rock interaction, including sulfur concentrations and partitioning coefficients of arsenic between pyrite and solution for simulations in Figure 2; and starting compositions for the model in Figure 3, is available online at http://www.geosociety.org/datarepository /2019/, or on request from editing@geosociety.org.



Figure 3. A: Upgrading of As in pyrite and arsenopyrite. Initial fluids have 100 ppm As and 10 mol% CO_2 . Fluids were equilibrated with sulfur-bearing basalt before reacting with pyrite ores (initial pyrite As:S ratio of 0.01). Solid line represents As concentrations in pyrite, and dashed line, As concentrations in arsenopyrite. Maximum amount of Au for corresponding As concentrations in pyrite are plotted based on empirical solubility limit of Reich et al. (2005). B,C: Backscatter electron (BSE) images of complex growth and recrystallization textures in arsenian pyrite from Au deposits. In these images, lighter shades indicate higher As contents. B: As-rich rims and replacement of As-poor pyrite by As-rich pyrite (Hishikari ore deposit, Japan; image from Morishita et al., 2018; yellow circles and numbers are locations of analyses). C: Recrystallization of arsenian pyrite into porous zone of pyrite (white) with increased As-Au content (Sunrise Dam gold deposit, Western Australia; Au concentrations are shown for three points; image and analyses from Sung et al., 2009).

ARSENIC ENRICHMENT BY MULTI-STAGE HYDROTHERMAL FLUIDS

Several studies have highlighted the importance of multistage hydrothermal events and/or cyclic fluid flows to the formation and refinement of gold deposits (Sibson et al., 1975; Brugger et al., 2000; Bateman and Hagemann, 2004; Sung et al. 2009; Cockerton and Tomkins, 2012; Meffre et al., 2016). This repeated infiltration provides the extremely high fluid:rock ratios apparently required to form high-grade ore zones (Meffre et al., 2016; Mikucki, 1998; Thébaud et al., 2008). Indeed, the concentrations of As and Au in ore-forming fluids are usually relatively low (1-100 ppb Au, 0.10-100 ppm As; Mikucki, 1998; James-Smith et al., 2010; Goldfarb and Groves, 2015). This contrasts with the fact that As-rich zones in arsenian pyrite can contain up to ~2400 ppm Au and 20 wt% As (Reich et al., 2005), which is hard to reconcile with a single mineralization step for each zone.

A key aspect of any multistage As enrichment model is the efficiency of As scavenging from the fluid by reaction with the ores deposited in earlier stages. Hence, we model the infiltration of H₂O-CO₂-As fluids into pyritic rocks using the step-flow-reactor technique with HCh (Shvarov, 1999), in a manner similar to that of the model of Phillips and Evans (2004). The ore fluid is first equilibrated with basalt, which results in an As concentration of ~20 ppm in the fluid. Next, each batch of the fluid is reacted with As-poor pyritic rocks (As:S = 0.01, which is ~0.6 wt% As) at 350 °C, 200 MPa. Details of the modeling and fluid and rock composition are in the Data Repository.

The modeled pyrite and arsenopyrite compositions are plotted as a function of fluid:rock ratio in Figure 3A. Arsenic concentrations in pyrite gradually increase with increasing fluid:rock ratio and reach a maximum value of 5.7 wt% at a fluid:rock ratio of 80. Arsenopyrite forms when the fluid:rock ratio is >80, with As concentrations increasing steeply and reaching a maximum of 48.3 wt% at fluid:rock = 100.

DISCUSSION

The positive correlation between As and Au contents in arsenian pyrite has been well established in many gold systems, including Carlintype (Cline, 2001; Reich et al., 2005), orogenic (Large et al., 2009; Morey et al., 2008), volcanogenic massive sulfide (Wagner et al., 2007), porphyry Cu-Au (Reich et al., 2013), and epithermal deposits (Deditius et al., 2014). Hence, As in pyrite is a good proxy for Au in many deposits. Equilibrium thermodynamic modelling of Au coprecipitation with Fe sulfides is not practical because the scavenging mechanisms remain controversial and mostly involve local conditions: for example, arsenic may enhance Au chemisorption on the surface of Fe sulfides, or local dissolution of Fe-As-S minerals may cause ultra-local reducing conditions, leading to precipitation of Au¹⁺ aqueous complexes at the mineral surface (Pokrovski et al., 2014). Furthermore, Au concentrations in arsenian pyrite range across multiple orders of magnitude up to a solubility limit (Reich et al. 2005); this implies that most arsenian pyrites form from Au-undersaturated fluids. Indeed, in many gold deposits, native gold is a paragenetically late

phase, resulting from recrystallisation of Fe-As sulfides (Fougerouse et al., 2016).

Complex As-Au zoning in pyrites characterized by both oscillatory zoning and secondary dissolution, reprecipitation, and recrystallisation textures is common in, and indeed characteristic of, Au deposits (Large et al., 2009). These variations are usually interpreted in terms of changing fluid sources or temperatures. For example, the As:Au ratio of As-Au-rich hydrothermal rims in pyrite is widely used to indicate fluid source, and further used to distinguish different stages of ore fluids (Thomas et al., 2011; Morishita et al., 2018). Pyrites from the Bendigo gold deposit (Australia) share similar As:Au ratios, suggesting that As-Au may be leached and transported together from the diagenetic and recrystallized metamorphic pyrite in the sediments (Thomas et al., 2011). However, thermodynamic constraints on the partitioning of As between hydrothermal fluid and pyrite indicates that the formation of these As-Au-rich rims via direct precipitation from the parent hydrothermal fluid requires fluids that are extremely enriched in As, which are unlikely to be found in nature. In particular, such fluid cannot be produced by leaching or by pyrite-to-pyrrhotite conversion of diagenetic and recrystallized metamorphic pyrite, which is significantly lower in As and Au (Thomas et al., 2011).

Mikucki (1998) estimated that high fluid:rock ratios (>100-1000) are required to form lodegold deposits, assuming that Au is precipitated from fluids with Au concentration of 1-100 ppb at T < 400 °C. Our modeling shows that fluids with relatively low As concentrations at T<300 °C are able to produce As-rich pyrite via protracted fluid flows. The upgrading model in Figure 3 indicates that As (and Au) enrichment in arsenian pyrite likely results from a refinement process; low-As fluids can effectively enrich As in pyrite through ongoing hydrothermal alteration. This mechanism may also explain the elevated As-Au content in pyrite associated with quartz veins at Bendigo, compared to diagenetic pyrite and metamorphic hydrothermal pyrite (Thomas et al., 2011), due to the higher local fluid:rock ratio required to form quartz veins and reefs. This progressive enrichment of As in pyrite is accompanied by a decrease in pyrite volume (Fig. DR4), which we suggest would serve to generate porosity in individual pyrite crystals and enhance Au sequestration (see Fig. 3).

In conclusion, our results show that the As concentration in pyrite is controlled by temperature, fluid composition, and redox, in addition to the As concentration in the parent fluid. Fluids with low As concentrations are able to form high-As arsenian pyrite and arsenopyrite through extensive hydrothermal alteration, thus forming the As(-Au) enrichment in ores. Externally derived As(-Au)–rich fluids are not necessarily required for forming high-grade pyritic gold ores. Instead, our thermodynamic model shows that dilute fluids can drive remobilization

and reprecipitation of As, forming As enrichment in localized high-grade domains, which would further facilitate Au accumulation. This is consistent with the evidence for high fluid:rock ratio and complex growth and/or dissolution and/or recrystallization textures of pyrite in gold ore zones. The solid-solution model for As in pyrite and arsenopyrite presented here makes it possible to precisely predict As solubility in pyrite and arsenopyrite under temperature- and redox-controlled conditions, which is an important tool for understanding and quantifying Au mobilization and enrichment in hydrothermal gold systems.

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REFERENCES CITED

- Bateman, R., and Hagemann, S., 2004, Gold mineralisation throughout about 45 Ma of Archaean orogenesis: Protracted flux of gold in the Golden Mile, Yilgarn craton, Western Australia: Mineralium Deposita, v. 39, p. 536–559, https://doi.org /10.1007/s00126-004-0431-2.
- Brugger, J., Lahaye, Y., Costa, S., Lambert, D., and Bateman, R., 2000, Inhomogeneous distribution of REE in scheelite and dynamics of Archaean hydrothermal systems (Mt. Charlotte and Drysdale gold deposits, Western Australia): Contributions to Mineralogy and Petrology, v. 139, p. 251–264, https://doi.org/10.1007/s004100000135.
- Cline, J.S., 2001, Timing of gold and arsenic sulfide mineral deposition at the Getchell Carlin-type gold deposit, north-central Nevada: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 96, p. 75–89, https://doi.org/10.2113 /gsecongeo.96.1.75.
- Cockerton, A.B.D., and Tomkins, A.G., 2012, Insights into the liquid bismuth collector model through analysis of the Bi-Au Stormont skarn prospect, northwest Tasmania: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 107, p. 667–682, https://doi.org/10.2113 /econgeo.107.4.667.
- Deditius, A.P., Reich, M., Kesler, S.E., Utsunomiya, S., Chryssoulis, S.L., Walshe, J., and Ewing, R.C., 2014, The coupled geochemistry of Au and As in pyrite from hydrothermal ore deposits: Geochimica et Cosmochimica Acta, v. 140, p. 644– 670, https://doi.org/10.1016/j.gca.2014.05.045.
- Fleet, M.E., and Mumin, A.H., 1997, Gold-bearing arsenian pyrite and marcasite and arsenopyrite from Carlin Trend gold deposits and laboratory synthesis: The American Mineralogist, v. 82, p. 182–193, https://doi.org/10.2138/am-1997-1-220.
- Fougerouse, D., Micklethwaite, S., Tomkins, A.G., Mei, Y., Kilburn, M., Guagliardo, P., Fisher, L.A., Halfpenny, A., Gee, M., Paterson, D., and Howard, D.L., 2016, Gold remobilisation and formation of high grade ore shoots driven by dissolutionreprecipitation replacement and Ni substitution into auriferous arsenopyrite: Geochimica et Cosmochimica Acta, v. 178, p. 143–159, https://doi .org/10.1016/j.gca.2016.01.040.
- Goldfarb, R.J., and Groves, D.I., 2015, Orogenic gold: Common or evolving fluid and metal sources through time: Lithos, v. 233, p. 2–26, https://doi .org/10.1016/j.lithos.2015.07.011.

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- James-Smith, J., Cauzid, J., Testemale, D., Liu, W.H., Hazemann, J.-L., Proux, O., Etschmann, B., Philippot, P., Banks, D., Williams, P., and Brugger, J., 2010, Arsenic speciation in fluid inclusions using micro-beam X-ray absorption spectroscopy: The American Mineralogist, v. 95, p. 921–932, https:// doi.org/10.2138/am.2010.3411.
- Kokh, M.A., Akinfiev, N.N., Pokrovski, G.S., Salvi, S., and Guillaume, D., 2017, The role of carbon dioxide in the transport and fractionation of metals by geological fluids: Geochimica et Cosmochimica Acta, v. 197, p. 433–466, https://doi.org /10.1016/j.gca.2016.11.007.
- Kretschmar, U., and Scott, S.D., 1976, Phase relations involving arsenopyrite in the system Fe-As-S and their application: Canadian Mineralogist, v. 14, p. 364–386.
- Kusebauch, C., Oelze, M., and Gleeson, S.A., 2018, Partitioning of arsenic between hydrothermal fluid and pyrite during experimental siderite replacement: Chemical Geology, v. 500, p. 136–147, https://doi.org/10.1016/j.chemgeo.2018.09.027.
- Large, R.R., Danyushevsky, L., Hollit, C., Maslennikov, V., Meffre, S., Gilbert, S., Bull, S., Scott, R., Emsbo, P., Thomas, H., Singh, B., and Foster, J., 2009, Gold and trace element zonation in pyrite using a laser imaging technique: Implications for the timing of gold in orogenic and Carlin-style sediment-hosted deposits: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 104, p. 635– 668, https://doi.org/10.2113/gsecongeo.104.5.635.
- Meffre, S., Large, R.R., Steadman, J.A., Gregory, D.D., Stepanov, A.S., Kamenetsky, V.S., Ehrig, K., and Scott, R.J., 2016, Multi-stage enrichment processes for large gold-bearing ore deposits: Ore Geology Reviews, v. 76, p. 268–279, https://doi .org/10.1016/j.oregeorev.2015.09.002.
- Mikucki, E.J., 1998, Hydrothermal transport and depositional processes in Archean lode-gold systems: A review: Ore Geology Reviews, v. 13, p. 307–321, https://doi.org/10.1016/S0169-1368(97)00025-5.
- Morey, A.A., Tomkins, A.G., Bierlein, F.P., Weinberg, R.F., and Davidson, G.J., 2008, Bimodal distribution of gold in pyrite and arsenopyrite: Examples from the Archean Boorara and Bardoc shear systems, Yilgarn craton, Western Australia: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 103, p. 599–614, https://doi .org/10.2113/gsecongco.103.3.599.
- Morishita, Y., Shimada, N., and Shimada, K., 2018, Invisible gold in arsenian pyrite from the highgrade Hishikari gold deposit, Japan: Significance of variation and distribution of Au/As ratios in pyrite: Ore Geology Reviews, v. 95, p. 79–93, https://doi.org/10.1016/j.oregeorev.2018.02.029.
- Phillips, G.N., and Evans, K.A., 2004, Role of CO₂ in the formation of gold deposits: Nature, v. 429, p. 860–863, https://doi.org/10.1038/nature02644.
- Pokrovski, G.S., Akinfiev, N.N., Borisova, A.Y., Zotov, A.V., and Kouzmanov, K., 2014, Gold speciation and transport in geological fluids: Insights from experiments and physical-chemical modelling, *in* Garofalo, P.S., and Ridley, J.R., eds., Gold-Transporting Hydrothermal Fluids in the Earth's Crust: Geological Society of London Special Publication 402, p. 9–70, https://doi.org/10.1144/SP402.4.
- Qian, G., Brugger, J., Testemale, D., Skinner, W., and Pring, A., 2013, Formation of As(II)-pyrite during experimental replacement of magnetite under hydrothermal conditions: Geochimica et Cosmochimica Acta, v. 100, p. 1–10, https://doi.org/10 .1016/j.gca.2012.09.034.
- Redlich, O., and Kister, A.T., 1948, Algebraic representation of thermodynamic properties and the classification of solutions: Industrial and Engineering Chemistry, v. 40, p. 345–348, https://doi.org/10 .1021/ie50458a036.

- Reich, M., Kesler, S.E., Utsunomiya, S., Palenik, C.S., Chryssoulis, S.L., and Ewing, R.C., 2005, Solubility of gold in arsenian pyrite: Geochimica et Cosmochimica Acta, v. 69, p. 2781–2796, https:// doi.org/10.1016/j.gca.2005.01.011.
- Reich, M., and Becker, U., 2006, First-principles calculations of the thermodynamic mixing properties of arsenic incorporation into pyrite and marcasite: Chemical Geology, v. 225, p. 278–290, https://doi .org/10.1016/j.chemgeo.2005.08.021.
- Reich, M., Deditius, A., Chryssoulis, S., Li, J.W., Ma, C.Q., Parada, M.A., Barra, F., and Mittermayr, F., 2013, Pyrite as a record of hydrothermal fluid evolution in a porphyry copper system: A SIMS/ EMPA trace element study: Geochimica et Cosmochimica Acta, v. 104, p. 42–62, https://doi.org/10 .1016/j.gca.2012.11.006.
- Seward, T.M., and Barnes, H.L., 1997, Metal transport by hydrothermal ore fluids, *in* Barnes, H.L., ed., Geochemistry of Hydrothermal Ore Deposits (third edition): New York, John Wiley & Sons, p. 435-486.
- Sharp, Z.D., Essene, E.J., and Kelly, W.C., 1985, A re-examination of the arsenopyrite geothermometer: Pressure considerations and applications to natural assemblages: The Canadian Mineralogist, v. 23, p. 517–534.
- Shvarov, Yu.V., 1999, Algorithmization of the numeric equilibrium modeling of dynamic geochemical processes: Geochemistry International, v. 37, p. 571–576.
- Shvarov, Yu.V., 2008, HCh: New potentialities for the thermodynamic simulation of geochemical systems offered by windows: Geochemistry International, v. 46, p. 834–839, https://doi.org/10.1134 /S0016702908080089.
- Sibson, R.H., Moore, J.M., and Rankin, A.H., 1975, Seismic pumping—A hydrothermal fluid transport mechanism: Journal of the Geological Society, v. 131, p. 653–659, https://doi.org/10.1144/gsjgs .131.6.0653.
- Sung, Y.-H., Brugger, J., Ciobanu, C.L., Pring, A., Skinner, W., and Nugus, M., 2009, Invisible gold in arsenian pyrite and arsenopyrite from a multistage Archaean gold deposit: Sunrise Dam, Eastern Goldfields Province, Western Australia: Mineralium Deposita, v. 44, p. 765–791, https://doi.org /10.1007/s00126-009-0244-4.
- Thébaud, N., Philippot, P., Rey, P., Brugger, J., Van Kranendonk, M., and Grassineau, N., 2008, Protracted fluid-rock interaction in the Mesoarchaean and implication for gold mineralization: Example from the Warrawoona syncline (Pilbara, Western Australia): Earth and Planetary Science Letters, v. 272, p. 639–655, https://doi.org/10.1016/j.epsl .2008.05.030.
- Thomas, H.V., Large, R.E., Bull, S.W., Maslennikov, V., Berry, R.F., Fraser, R., Froud, S., and Moye, R., 2011, Pyrite and pyrrhotite textures and composition in sediments, laminated quartz veins, and reefs at Bendigo Gold Mine, Australia: Insights for ore genesis: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 106, p. 1–31, https://doi.org/10.2113/ccongeo.106.1.1.
- Wagner, T., Klemd, R., Wenzel, T., and Mattsson, B., 2007, Gold upgrading in metamorphosed massive sulfide ore deposits: Direct evidence from laserablation–inductively coupled plasma–mass spectrometry analysis of invisible gold: Geology, v. 35, p. 775–778, https://doi.org/10.1130/G23739A.1.
- Zhong, R., Brugger, J., Tomkins, A.G., Chen, Y., and Li, W., 2015, Fate of gold and base metals during metamorphic devolatilization of a pelite: Geochimica et Cosmochimica Acta, v. 171, p. 338– 352, https://doi.org/10.1016/j.gca.2015.09.013.

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