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Resolving the role of carbonaceous material in gold precipitation in metasediment-hosted orogenic gold deposits

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ABSTRACT

Carbonaceous material (CM) is commonly associated with gold and sulfides in metasediment-hosted orogenic gold deposits. The role of CM in Au deposition is controversial; CM has been proposed to contribute to gold deposition by reducing Au bisulfide complexes, or by facilitating sulfidation, which destabilizes Au in bisulfide complexes with resultant Au deposition. Integration of petrographic observations, thermodynamic models, and geochemical data from metasediment-hosted orogenic gold deposits in New Zealand, Australia, Canada, and West Africa reveals genetic links between sulfides, CM, and mineralization. The results are consistent with the coexistence of CM and pyrite as a consequence of their codeposition from ore fluids, with a minor proportion of CM originally in situ in the host rocks. Au is deposited when pyrite and CM deposition decreases H_2S concentration in ore fluids, destabilizing $Au(HS)_2^-$

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complexes. Most CM in gold deposits is deposited from CO_2 and CH_4 in ore fluids. These findings are applicable to similar deposits worldwide.

INTRODUCTION

Metasediment-hosted orogenic gold deposits such as the Victorian goldfields of Australia (Bierlein et al., 2001), the Macraes gold deposit of New Zealand (Craw, 2002), and the Paleoproterozoic gold deposits of West Africa (Kříbek et al., 2015) are some of the world's largest. As with most orogenic gold deposits, ore fluids are low salinity, CO_2 rich, often CH_4 bearing, with pH near-neutral, and are proposed to have been generated during the lower greenschist to amphibolite facies transition (Berge, 2011; De Ronde et al., 2000; Goldfarb and Groves, 2015; Tomkins, 2010). Gold in metasediment-hosted orogenic gold deposits is proposed to be sourced from organic, pyrite-rich sediments (Hu et al., 2016; Large et al., 2011; Pitcairn et al., 2006; Thomas et al., 2011). Mineralization commonly occurs in shear zones at pressures of 1–3 kbar and temperatures of 200–400 °C. In auriferous zones, carbonaceous material (CM) is widespread and spatially associated with gold and sulfides (Berge, 2011; Bierlein et al., 2001; Craw et al., 2015; Hu et al., 2015; Kříbek et al., 2015). CM may be in situ, derived from organic matter that was deposited with the sediments and matured during metamorphism (Berge, 2011; Bierlein et al., 2001). Alternatively, CM may be deposited from hydrothermal fluids (Kříbek et al., 2015; Pitcairn et al., 2005). CM has long been thought to contribute to gold deposition, but the role of CM is not well understood. Possible roles for CM were summarized in Hu et al. (2015).

1. In situ CM reduces Au in solution to cause gold precipitation via Reaction 1:

$$4Au(HS)_2^-{}_{(aq)} + C_{(s)} + 4H^+{}_{(aq)} + 2H_2O_{(l)} = 4Au_{(s)} + CO_{2(aq)} + 8H_2S_{(aq)}, \quad (1)$$

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where aq is aqueous (e.g., Cox et al., 1995).

2. Hydrothermal CM deposited prior to mineralization acts as a reductant via Reaction 1.

3. Hydrothermal CM precipitates from fluids with sulfides via Reaction 2; loss of sulfur from solution drives Au deposition via destabilization of aqueous Au-sulfide complexes:

$$2FeO_{(in\ silicates)} + 4H_2S_{(aq)} + CO_{2(aq)} = 2FeS_{2(s)} + C_{(s)} + 4H_2O_{(l)} \quad (2)$$

(modified from Craw et al., 2015).

4. CM plays a physical role in Au precipitation by facilitating the formation of shear zones that focus fluid flow (e.g., Upton and Craw, 2008).

In this study we combine thermodynamic modeling using the HCh software package (Shvarov and Bastrakov, 1999) with new petrographic observations and geochemical analyses of samples from the Macraes gold deposit, New Zealand, and with published geochemical data from similar gold deposits to test these hypotheses. We use Macraes as the primary example because of the availability of an extensive data set and abundant CM in mineralized rocks (Craw, 2002). However, the results are relevant to other similar gold deposits where CM is ubiquitous (e.g., Kříbek et al., 2015).

PETROGRAPHIC OBSERVATIONS

In the Macraes deposit, CM, sulfides, and Au are spatially associated in mineralized rocks. CM is dominantly hydrothermal, introduced during mineralization, exhibiting flat spectra of typical graphite in Fourier transform infrared spectroscopy (FTIR) analysis, although some matured in situ CM showing kerogen FTIR spectra also occurs in the host rocks (Craw, 2002; Henne and Craw, 2012; Hu et al., 2015; Pitcairn et

al., 2005). Gold occurs primarily as microscale inclusions in sulfides (Petrie et al., 2005). Textural analysis suggests that auriferous sulfides are texturally synchronous with, or after the formation of, graphitic microshears that include fine-grained CM and sulfides (Fig. 1; Craw, 2002; Upton and Craw, 2008).

SAMPLES AND METHODS

Mineralized rocks from the Golden Bar pit in the Macraes deposit were analyzed for sulfur (S) and noncarbonate carbon (NCC). Methods were described in Hu et al. (2015, 2016). Additional S and NCC data for mineralized and unmineralized rocks in the Macraes deposit were collected using X-ray fluorescence at the University of Otago, New Zealand (Craw, 2002). Previously unpublished data are listed in Table DR2 in the GSA Data Repository[1]. Extant S and NCC data were obtained from the Victorian goldfield (Australia; Bierlein et al., 2001), the Touquoy Zone deposit (Meguma terrane, Canada; Bierlein and Smith, 2003), several Paleoproterozoic deposits (West Africa; Kříbek et al., 2015), and other Macraes mine pits (Craw, 2002; Petrie et al., 2005). These published data are listed in Table DR3.

The HCh program coupled with the Unitherm database was used for thermodynamic modeling (Shvarov and Bastrakov, 1999). Bulk-rock compositions used in the modeling were derived from Otago Schist and Golden Bar pit samples (Hu et al., 2015). The chemical components of the systems investigated are Al_2O_3-CaO-CuO-K_2O-FeO-MgO-Na_2O-SiO_2-ZnO-Au-As-C-CO_2-S-H_2O. The conceptual model was designed to simulate infiltration of ore fluids generated by underlying metasediments into lower greenschist facies rocks, a process proposed to apply to the Macraes deposit and other similar CM-rich gold deposits (Pitcairn et al., 2006; Large et al., 2011).

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Production of the ore fluid by equilibration of metamorphic fluids with a sedimentary host rock at depth was simulated in an initial model cell in which an H_2O-rich fluid (fluid 1) was equilibrated with a graphite- and Au-bearing rock at 500 °C and 5 kbar. The rock composition was that of a CM-rich sample (FF-13) from the prehnite-pumpellyite facies and is thought to be typical of the source rocks (Hu et al., 2016). Magnetite, pyrrhotite, and pyrite were set in excess in this initial cell to simulate fluid production under $f_{O_2} - f_{S_2}$ (oxygen and sulfur fugacity, respectively) conditions representative of the greenschist-amphibolite transition. Details of fluid 1 and FF-13 rock compositions are provided in Table DR1.

Subsequent model cells were designed to simulate spatial variation in fluid-rock interaction during ore fluid infiltration into lower greenschist metasediments. The composition of these rocks was based on that of a Golden Bar pit sample (GB-01; Table DR1). In the model, the ore fluid infiltrates a notional cell containing GB-01 at 3 kbar and a specified mineralization temperature (T_{min}). After equilibration of the ore fluid with the rock in that cell at T_{min}, the fluid was passed to the next cell at the same pressure and at T_{min}, where it was equilibrated and passed on again. The first cell of this model, where the ore fluids are added to the host rock at T_{min}, simulates the addition of channelized fluid to a host rock with which the fluid is not in thermal or chemical equilibrium. Subsequent cells simulate slower pervasive isothermal and isobaric infiltration of the fluid into the surrounding country rock. Infiltration at 160–400 °C was investigated to assess the effects of fluid infiltration at different levels in the crust (Table DR4).

The integrated fluid:rock ratio for each simulation was 1:1 by mass. Simulations were run to assess the effects of adding this fluid in different numbers of increments,

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from 1 to 20, i.e., with instantaneous fluid:rock ratios between 0.05 and 1. Changes in the instantaneous fluid:rock ratio did not affect the conclusions (Table DR5). Phase separation was neglected because there is no evidence of phase separation reported from Macraes (De Ronde et al., 2000). The dependence of our conclusions on the assumption that the fluid did not reequilibrate between the source and the host rock was also tested by running a model in which the fluid was reequilibrated at T_{min} (e.g., 220 °C) and 3 kbar prior to infiltration into the host rock. The results from this alternative model are consistent with those presented here (Table DR6).

The results for 14 cells are presented here because this number was sufficient to reproduce the mineralogical zoning observed in the field. Note that the bulk composition of GB-01 was set such that fluid was present in the host rock (fluid:rock = 0.025 by mass) prior to ore fluid infiltration. Equilibration between the ore fluid and the country rock thus involves mixing between the country-rock fluid and the infiltrating fluid, as well as reaction between the infiltrating fluid and the host rock. It was therefore necessary to include the host-rock fluid in calculations of species concentration changes during reaction. Changes in species concentrations were calculated for each cell by comparing the concentrations of the species of interest in the unreacted mixture with those in the equilibrated products.

CM abundance is reported as NCC for natural samples and C_{model} for modeled graphite. In reality, CM in natural samples is not pure graphite, but a complex mixture of C-O-H compounds that are difficult to characterize and currently impossible to model. Representation of CM by graphite in the model introduces uncertainty, but primary trends are considered robust because CM will respond

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to external changes in pressure, temperature, and redox in a way similar to graphite. Whole-rock sulfur concentration is referred to as S for natural samples and S_{model} for modeling results.

RESULTS

Geochemical Analyses

In unmineralized rocks, the S and NCC contents are generally <1 wt% (Fig. 2). The data in mineralized rocks show considerable scatter, but the S and NCC contents range to values ~10 times higher than those in unmineralized rocks (Fig. 2).

Thermodynamic Modeling

Calculated mineral assemblages in the mineralized rock are consistent with those observed in the field, comprising graphite, quartz, pyrite, arsenopyrite, calcite, siderite, muscovite, epidote, chlorite, and albite. Infiltration at different temperatures produced assemblages compatible with known phase stability fields (Table DR4). Pyrite and arsenopyrite are predicted to coexist at temperatures <310 °C.

Typical model results for 220 °C, 3 kbar are shown in Figure 3. Deposition of Au, sulfides, and graphite occurs in all cells, but primarily in the first infiltration cell (Fig. 3). Pyrrhotite is stable in the unaltered model host rock, consistent with Pitcairn et al. (2006), but pyrite is the dominant sulfide in infiltrated rocks (Fig. 3A). In unaltered rocks at Macraes, As is present as arsenian pyrite, which cannot be accommodated by the model. Therefore, calculated arsenopyrite is reasonable. Additional arsenopyrite is predicted in the outer margins of the pyrite-rich zone (Fig. 3B). Au precipitation is accompanied by a decrease in the concentration of Au bisulfide complexes (Fig. 3C).

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The H_2 concentration in equilibrated model fluids decreases in cell 1 and increases slightly in the following cells; however, the concentration in each cell is always less than that in unreacted mixtures (Fig. 3D). This means that small amounts of H_2 are consumed during pyrite deposition.

The modeled concentration of graphite (C_{model}) is the sum of graphite in the unreacted rock plus precipitated graphite (Fig. 3E). Precipitated graphite dominates C_{model}, particularly in the first infiltration cell. Infiltrating CO_2 is reduced and precipitates as graphite. Inspection of the mineral modes allows deduction of the amount of CO_2 that is reduced (RE) to form graphite ($CO_{2,RE}$) via

$$CO_{2,RE(aq)} = CO_{2,lost} - CO_{2,carbonates}, \quad (3)$$

where $CO_{2,lost}$ is the CO_2 lost from solution and $CO_{2,carbonates}$ is the CO_2 deposited as carbonate.

Graphite precipitation is also accompanied by a decrease in the CH_4 concentration in the fluid ($CH_{4,RE}$) (Fig. 3E). $CO_{2,RE}$ and $CH_{4,RE}$ account for 51%–53% and 47%–49% of precipitated graphite, respectively. Model results at higher and lower temperatures show the same features (Table DR4).

DISCUSSION AND CONCLUSIONS

Consistency of Rocks with Model Results

Primary trends in mineralized natural rocks are replicated by the model. These include the increase in S and NCC contents (Fig. 2), syndepositional pyrite and graphite (Figs. 1C and 1D), and arsenopyrite peripheral to pyrite (Fig. 1). Features not replicated by the model, such as the late pyrite and arsenopyrite that overprints graphitic microshears (Figs. 1A and 1B), are texturally late and attributed to later fluid flow events,

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and the fact that mineralization is caused by infiltration of multiple fluids with different compositions rather than a monotonous single fluid infiltration event (Large et al., 2012).

Precipitation of Sulfides

The modeled coprecipitation of Au, sulfides, and graphite is most consistent with hypothesis 3 herein. Further information can be gained by an exploration of the electron transfer processes that form pyrite, graphite, and Au from aqueous Au^{+} in Au bisulfide, C^{4+} in $CO_{2,RE}$, C^{4-} in $CH_{4,RE}$, and from S^{2-} in bisulfide and H_2S.

The most obvious change in fluid composition during fluid infiltration is a drop in $CO_{2,RE}$ and $CH_{4,RE}$ concentrations that coincides with graphite deposition. Transfer of electrons between $CO_{2,RE}$ and $CH_{4,RE}$ forms water and graphite via Reaction 4 (e.g., Ohmoto and Kerrick, 1977):

$$CO_{2,RE(aq)} + CH_{4,RE(aq)} = 2C_{(s)} + 2H_2O_{(l)}. \quad (4)$$

Calculated changes in modeled species abundances indicate that this reaction accounts for 94%–98% of precipitated graphite, with >90% of the CO_2 and CH_4 carried into the host rock by the ore fluids. However, the drop in $CO_{2,RE}$ concentration is larger than that of $CH_{4,RE}$, indicating that more $CO_{2,RE}$ than $CH_{4,RE}$ is involved in fluid:rock reaction. Of the graphite that formed by $CO_{2,RE}$ consumption, 2%–6% is not balanced by $CH_{4,RE}$ consumption and requires additional electrons. To investigate the electron transfer processes that formed this additional graphite, the precipitated graphite was split into two components: C_{model1}, graphite that can be accounted for by Reaction 4, and C_{model2}, graphite that cannot be accounted for by Reaction 4.

Formation of pyrite from H_2S in solution requires an electron acceptor because divalent S^{2-} loses electrons to become monovalent S^{-} in pyrite. In light of the $CO_{2,RE}$-

$CH_{4,RE}$ imbalance discussed here, $CO_{2,RE}$ is a possible electron acceptor in the modeled system. The S_{model}:C_{model2} ratio was calculated, because if $CO_{2,RE}$ provides the electron acceptor for H_2S-hosted sulfur, then pyrite and C_{model2} should be correlated. The S_{model}:C_{model2} mass ratio is ~10 in all cells, which corresponds to a molar ratio of 4, as predicted by Reaction 2. Additional S deposition could be driven by transfer of electron to iron, e.g., via

$$Fe_2O_{3(\text{in silicates or oxides})} + 2H_2S_{(aq)} = FeO_{(\text{in silicates})} + FeS_2(s) + 2H_2O_{(l)}. \quad (5)$$

Other electron transfer reactions can be written that involve H_2 and O_2. However, the concentrations of these species in the model fluids are sufficiently low that such reactions could not contribute significantly to the redox budget of the mineralization process.

In natural systems, a combination of reactions such as Reactions 2, 4, and 5 operate during time-integrated fluid flow to produce the observed S and NCC concentrations and petrography. The extent of progress of each reaction would depend on the microenvironment of mineralization in each rock, so the scattered natural data could be produced by a continuum between rocks in which reactions such as Reaction 2 dominated sulfide deposition and those in which reactions such as Reaction 4 dominated graphite deposition (Fig. 2). Fluid infiltration prior to and post-Au mineralization, as well as progress of Reaction 5 and premetamorphic sulfide and CM in the natural rocks, would further alter S and NCC concentrations, so scattered natural data are expected.

Gold Precipitation

The model results suggest that the coexistence of CM and pyrite, often observed in natural samples, may be a consequence of their codeposition from sediment-derived

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fluids, with a minor proportion of CM originally in situ in the host rocks. Deposition of pyrite and CM in the model is accompanied by gold precipitation (Fig. 3C). Au in the model is transported by the gold bisulfide complexes $Au(HS)^0$ and $Au(HS)_2^-$. Decrease of H_2S in the ore fluid drives destabilization of Au bisulfide complexes and causes gold precipitation (e.g., Seward, 1973). This model uses a sediment-derived ore fluid, as suggested by Large et al. (2011), and produces results consistent with observations. However, alternative sources of fluid, such as magmatic fluids, are not excluded by the model.

Implications for Other Gold Deposits

To summarize, most CM is proposed to be hydrothermal, and the primary role of carbon is as CO_2, to accept electrons from aqueous H_2S via Reaction 2. Consequent deposition of CM and pyrite decreases dissolved H_2S concentrations and destabilizes aqueous gold bisulfide complexes. At deposits such as Telfer in Australia, and Carlin in the United States, where host rocks are carbonate rich, decarbonation may provide an additional source of CO_2 (Cline et al., 2005; Goellnicht et al., 1989), so the concepts presented here are only partially applicable to such deposits. However, the results presented here are broadly applicable to sediment-hosted orogenic gold deposits globally, although details, such as the spatial relationships and relative modes of arsenopyrite and the inferred importance of fluid immiscibility, may vary.

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FIGURE CAPTIONS

Figure 1. Photomicrographs of gold-bearing sulfides from the Macraes deposit (New Zealand). A: Transmitted light image of pyrite (circled by dashed lines) surrounded by graphitic shears (dotted lines) that contain fine-grained carbonaceous material (CM) and sulfides, especially arsenopyrite. B: Backscattered electron (BSE) image of pyrite surrounded by graphitic shears. Pyrite is light gray and arsenopyrite is white. C: Transmitted light image of pyrite overprinting graphitic shears. D: BSE image of pyrite overprinting graphitic shears.

Figure 2. Sulfur (S) versus noncarbonate carbon (NCC) by mass from four goldfields compared to model results. A vector from unmineralized rock to cell 1 is used to indicate the modeled trajectory in S versus NCC space. This vector can be considered as the sum of a vector that represents graphite deposition via Reaction 4 (R 4), and a vector toward high S_{model}:C_{model} ratios via sulfide deposition (Reaction 2, R 2).

Figure 3. Results of fluid infiltration at 220 °C, 3 kbar. In cell 0, the concentration of solid components represents the amount in unreacted GB-01 and that of aqueous components represents the total amount in unreacted country-rock fluid or ore fluid. Results of the fluid infiltration are presented in cells 1–14. A: Pyrite and pyrrhotite. B: Arsenopyrite. C: Au and Au bisulfide species. D: H_2 in equilibrated fluids and unreacted mixtures. E: Total graphite (C_{model}), precipitated graphite, $CH_{4,RE}$, and $CO_{2,RE}$ (see text).

[1]GSA Data Repository item 2017xxx, xxxxxxxx, is available online at http://www.geosociety.org/pubs/ft2017.htm or on request from editing@geosociety.org.