Supplementary materials for: "Barren ground depressions, natural H_2 and orogenic gold deposits: spatial link and geochemical model" - Thermodynamic modelling of gold deposit alteration at low temperature

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We used thermodynamic calculation to estimate the potential for H_2 production during gold deposit alteration in the presence of aqueous fluid at low temperature (50°C < T < 200°C). Orogenic gold deposits are formed during hydrothermal alteration of reduced and/or Fe-bearing rocks by Au-rich H_2O-CO_2 fluids at $\sim$ 550°C (Phillips and Powell, 2010). Carbonates, which formed by the combination of the cations initially present in the host rock and the CO_2 from the fluid (Kerrich and Fyfe, 1981), systematically occur in the deposits described in the above sections. Typical mineralogical assemblage composed of quartz, Fe-carbonates and sulfides is encountered. Fe-carbonate fraction in gold deposits can reach 20 % (Stromberg et al., 2018). Gold deposit mineralogy is thus modelled here with 79 mol.% of quartz, 20 mol.% of siderite ($FeCO_3$), 0.5 mol.% of pyrite (FeS_2) and 0.5 mol.% of pyrrhotite (FeS). The evolution in fluid composition and mineralogy during water/gold deposit interaction is calculated as a function of temperature and fluid/rock ratio with Phreeqc (Parkhurst, 1995) and the Lawrence Livermore National Laboratory database (llnl.dat). For a geothermal gradient of 30°C/km, the pressure is estimated to be above 20 MPa at depths where the temperature exceeds 50°C. In these conditions, bubbling is not predicted and gas species are dissolved in the aqueous fluid. We considered three configurations to model gold deposit alteration during fluid circulation in an aquifer: Model 1 allowing for CH_4 and hydrocarbon production; Model 2 excluding reduced carbon phases (graphite, CH_4 and hydrocarbon) production; Model 3 excluding reduced carbon species and without sulfides (80 mol.% of quartz and 20 mol.% of siderite). Model 2 aims at discussing the influence of CO_2 reduction on H_2 production. Sulfur has several degrees of oxidation and can thus be involved in the oxido-reduction . Model 3 aims at providing a basis for discussing the impact of the presence of sulfides on H_2 generation.

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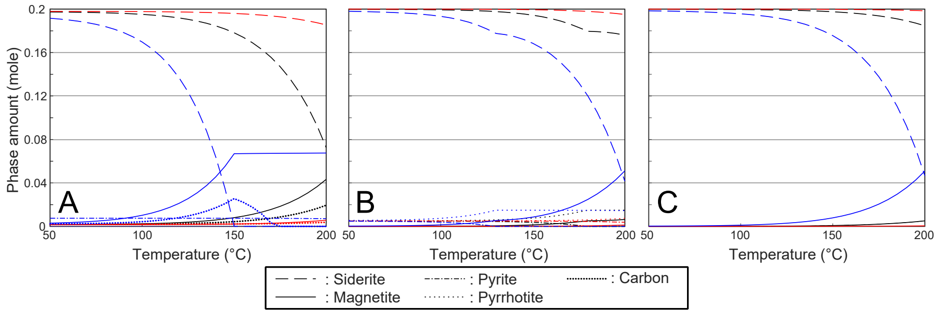

Figure S3: Solid phase amounts as a function of temperature in Model 1 (A; presence of sulfides and formation of reduced carbon phase enabled), Model 2 (B; presence of sulfides and formation of reduced carbon phase excluded) and Model 3 (C; no sulfides and reduced carbon phase formation excluded). Results are displayed for water to rock ratios of 1 (red), 10 (black) and 100 (blue). Quartz amount is out of scale.

H_2 is predicted to form in all simulations due to siderite oxidation coupled with water dissociation according to the following reaction (Figure S3):

$$3FeCO_3 + H_2O = Fe_3O_4 + 3CO_2 + H_2 \tag{S1}$$

However, the amount of produced H_2 varies over several orders of magnitude depending on temperature, water to rock ratio and the used model (Figures S4 and S5). For each model, the amount of produced H_2 increases by approximately two orders of magnitude from 50 to 200°C due to the increase of the equilibrium constant of reaction (S1) with temperature (Figure S4). The dissolved gas concentration in the fluid is fixed by equilibrium with the solid phases. As a result, if the primary solid phases are not exhausted during reaction, the amount of produced H_2 is directly proportional to the water to rock ratio (Figure S4). This is the case for Models 1 and 3. Regarding Model 2, H_2 concentration is not directly proportional to water to rock ratio due to the complete reaction of pyrite at a temperature decreasing as the water to rock ratio increases. H_2 production is 1 to 3 orders of magnitude higher for Model 2 than for Model 1 and approximately 3 orders of magnitude higher for Model 3 than for Model 1 (Figure S4). The maximum H_2 production of 0.9 mol/kg estimated for gold deposits with complete siderite reaction is reached with Models 2 and 3 for a water to rock ratio of 100 at 200°C. A high H_2 production of ~ 0.4 mol/kg can also be reached at temperatures as low as 50°C by increasing the water to rock ratio to 104 for Models 2 and 3, respectively. H_2 molar concentration in the dissolved gas is around 10^{-4}, $10^{-1.5}$ and $10^{-0.5}$ for Models 1, 2 and 3, respectively. These differences are due to H_2 further reaction in Models 1 and 2. In Model 1, H_2 is consumed during CH_4 production according to the following reaction:

$$CO_2 + 4H_2 = CH_4 + 2H_2O \tag{S2}$$

and carbon formation according to the following reaction:

$$CO_2 + 2H_2 = C + 2H_2O \tag{S3}$$

In Model 2, H_2 is partly consumed during pyrite conversion into pyrrhotite (Figure S3B):

$$FeCO_3 + FeS_2 + H_2 = 2FeS + CO_2 + H_2O \tag{S4}$$

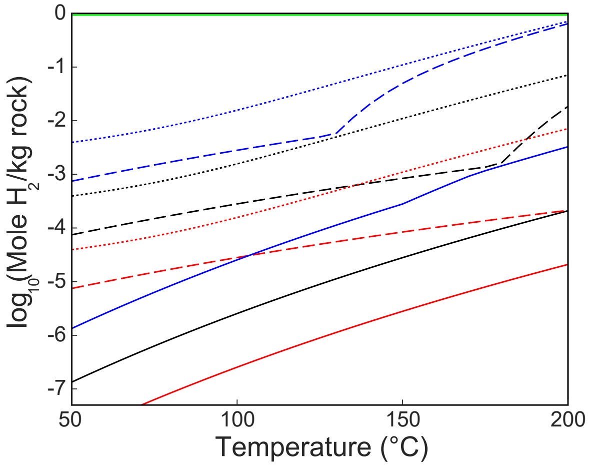

Figure S4: Amount of H_2 produced (in mole) per mass of rock as a function of temperature for Model 1 (plain lines; presence of sulfides and formation of reduced carbon phase enabled), Model 2 (dashed lines; presence of sulfides and formation of reduced carbon phase excluded) and Model 3 (dotted lines; no sulfides and formation of reduced carbon phase excluded). Results are displayed for water to rock ratios of 1 (red), 10 (black) and 100 (blue). The green line corresponds to the maximum H_2 production expected for complete reaction of siderite according to reaction (S1).

In all models, H_2 production occurs in parallel with CO_2 production according to reaction (S1) (Figure S3). The molar fraction of dissolved CO_2 in the fluid depends on pH. At temperatures below 90°C, the pH is neutral for all the models (± 0.5 around neutral pH) and the dominant dissolved carbonic species is HCO_3^-. The pH becomes slightly acidic as temperature increases and reaches values of 1.2, 1 and 0.7 pH units below neutral pH at 200°C for Models 1, 2 and 3, respectively. As a result, the H_2/CO_2 molar ratio in dissolved gases in Model 3 is fixed to 1/3 at temperature above 120°C as expected for reaction (S1) (Figure S5).

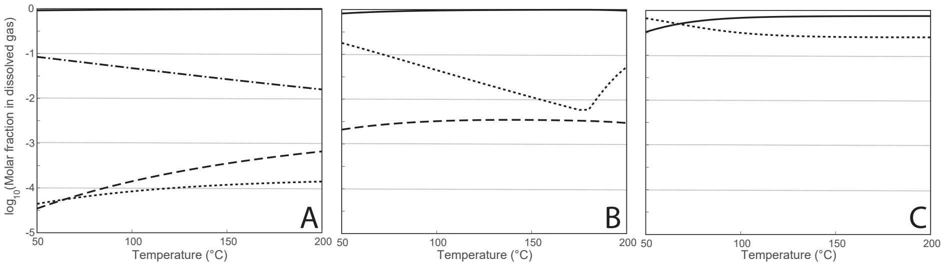

Figure S5: Molar fraction of dissolved gases as a function of temperature for Model 1 (A; presence of sulfides and formation of reduced carbon phase enabled), Model 2 (B; presence of sulfides and formation of reduced carbon phase excluded) and Model 3 (C; no sulfides and formation of reduced carbon phase excluded). H_2, CO_2, CH_4 and H_2S are displayed with dotted, plain, dash-dotted and dashed lines, respectively.

References

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