

Organic Matter in Forming Gold-Deposits

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Carbonaceous organic matter occurs under various phases and forms, where its fine characterization is mostly restricted to petroleum and coal geology. As a consequence, few studies have integrated the complete link between various forms of organic matter and metals to decipher hydrothermal ore concentrating processes. The study of Dill et al., integrating the concentration of sulfides and oxides with the interaction of silicates and organic matters, is an example of the next step to reach for defining the complex role of organic matter for the formation of orogenic gold deposits.

orogenic gold deposits

carbonaceous organic matter

hydrocarbons

graphite

CO-rich fluids

colloidal gold

1. Introduction

For at least 6000 years, the use of gold marked a change for humanity: the use of metals. Gold was the first metal used because it occurs in a native form. Gold is insoluble under surface conditions and non-oxidable, so its physical properties are conserved. Presenting a shining yellowish color like that of the sun and exhibiting extreme malleability, gold was first used for ornamental purposes and later as a medium of exchange and coinage. The first exploitations were from rivers or dried riverbeds, where gold was physically concentrated as nuggets. Later, gold was extracted from quartz vein outcroppings at surfaces. Both types of gold extraction are still in use today.

Humans have always had a fascination and irrational relationship with gold. Gold was and is still a physical means for conserving values (e.g., ^[1]). Consequently, wars, invasions, colonizations, and territorial conquests (gold rushes) were established and driven. Gold, as has any other substance, positively and negatively impacted human development. Artisanal gold extractions are still providing revenue for 15–20 million persons worldwide ^[2], whereas hundreds of mines are producing gold commercially in more than 42 countries (www.gold.org (accessed on 21 March 2021)).

In the inorganic world of metals, minerals, and rocks, consideration of the roles of organic matter in accumulating, solubilizing, and precipitating gold in lodes was not a natural way of thinking for geologists. At first, it may appear paradoxical that the ultimate noble metal requires organic matter for concentration. In this contribution, I address recent advances regarding the role of carbon-rich organic matter in forming rich and large gold deposits in three stages: (1) the source stage, when gold in seawater accumulates in organic-rich sediments; (2) the mobilization stage, when gold is solubilized by hydrocarbon-metal complexes and colloidal nanoparticles for hydrothermal

transport along faults; and (3) the precipitation stage. It is demonstrated that unusual CO₂-rich, H₂O-poor fluids, documented for some of the largest and richest orogenic gold deposits, are the result of chemical reactions involving hydrocarbon degradation, hence demonstrating the fundamental role of carbonaceous organic matter.

2. Fluid Composition and Generation

The fluid composition of orogenic gold deposits was estimated from the study of fluid inclusions for more than 70 years (e.g., [3][4]). Hundreds of studies have detailed the mineralizing fluids from worldwide examples covering all ages (e.g., [5]). The fluids are aqueous with low salinity (<5 wt% NaCl equiv.), ubiquitous CO₂, and variable contents of N₂, CH₄, and, in some cases, H₂, C₂H₆, H₂S, He, and Ar. Thermodynamic calculations have demonstrated that metamorphic dehydration of seafloor rocks is a viable mechanism for producing abundant aqueous-carbonic and low-salinity fluids. Elmer et al. [6] and Phillip and Powell [7] demonstrated that seafloor rocks, hydrated initially by hydrothermal seawater convection cells at oceanic ridges [8], release fluids at the metamorphic transition of greenschist to amphibolite, mostly when chlorite is converted to amphibole. Metamorphic fluids have a more diverse volatile composition than other fluids, such as seawater, magmatic fluids, or meteoric fluids, because they are generated by devolatilization of lithologies, where organic compounds in sedimentary rocks contribute to C-O-H-S-N contents [9].

Of particular interest, CO₂-rich and H₂O-poor fluid inclusions have been documented from some world-class gold districts and deposits, such as those at the Red Lake [10], Ashanti [11] and Tarkwa goldfields [12], and the Detour Gold and Wona deposits [9]. Fluids for these deposits also contain CH₄, N₂, and C₂H₆. The origins of these fluids are still debated (e.g., [3][9]).

For the Paleozoic Ashanti gold belt, Western Africa, Goldfarb et al. [13] suggested that devolatilization of abundant carbonaceous schists and cherts could lead to a variety of carbon-bearing molecular components within metamorphic C-O-H-S fluids bearing gold. Such a sedimentary source is confirmed by the compositions of stable carbon isotopic mixture in quartz-hosted, CO₂-rich fluid inclusions [14]. These unusual fluids are thus likely derived from the metamorphism of carbonaceous-rich sedimentary rocks. Nonetheless, these fluids are associated with either very high-grade or very large gold deposits, suggesting that CO₂-rich and H₂O-poor fluids have unrecognized potential for forming exceptional orogenic gold deposits.

3. Sources of Gold

The sources of gold for orogenic deposits have been reviewed by numerous authors (e.g., [15][16][17]). Gold can be sourced from intrusion degassing (e.g., [18]) and oceanic basalt devolatilization (e.g., [19][20][21]). However, carbonaceous- and pyrite-rich sedimentary rocks, commonly referred to as black shales, are considered one of the most important sources (e.g., [15][22][23][24][25][26][27][28]).

Gold and other trace metals occurring in sedimentary pyrite can be liberated by recrystallization and hydrothermal replacement processes occurring under metamorphic conditions, corresponding to the pyrite–pyrrhotite transition

[23][24][29][30][31]. Gold concentrations in nodular pyrite average 0.09 ppm [32] but can reach 10 ppm Au in orogenic gold districts (e.g., [33][34][35]). Considering that nodular pyrite can constitute up to 20% of black shales and that black shales are very extensive marine sediments, these rocks may constitute a significant volume for providing gold. In addition, because pyrrhotite (Fe_{1-x}S) has a lower S content (37.67% vs. 53.45%) than pyrite (FeS_2), the conversion can also provide S in solution for solubilizing gold [36]. Gaboury [15] stated that, in addition to gold, fluids and ligands (HS^-) can all be sourced from the metamorphism of black shales and associated rocks under amphibolite conditions.

Using a solid-probe mass spectrometer system [37], Gaboury [9] documented that ethane (C_2H_6) is present in fluid inclusions from orogenic gold deposits, ranging in age from ~2800 Ma to ~100 Ma. Ethane is sourced from thermally degraded organic matter because the values of $\text{CH}_4/(\text{C}_2\text{H}_6 + \text{C}_3\text{H}_8)$, expressed as C1/C2+ in hydrothermal fluids, are lower than 100 [38]. Consequently, ethane provides a reliable tracer for the involvement of carbonaceous and pyritic shales at depth in the formation of gold deposits [9].

The ultimate support for a sedimentary gold source model is provided by the link between gold dissolved in oceans and the temporal distribution of orogenic gold deposits. This was first proposed by Tomkins [39] and later documented by Large et al. [32] by using gold concentrations in primary pyrites from black shales. Oxidizing seawater conditions are favorable for gathering gold in nodular sedimentary pyrite in black shales [32]. The lack of major orogenic gold deposits from the middle to late Proterozoic (~1800 to 800 Ma—the boring period) is interpreted as being related to low levels of Au in the oceans [32]. During this period, the deep oceans were anoxic and sulfidic [40], hence limiting the bacterial reduction of sulfate and the incorporation of gold in primary pyrite [15]. The occurrence of orogenic gold deposits in Neoproterozoic time, such as those in Sudan, which also contain ethane [25], coincides with the reappearance of oxygenic conditions in the oceans [32][41].

4. The Fundamental Involvement of Organic Matter

Therefore, the roles of carbonaceous matter appear fundamental for (1) concentrating gold in organic-rich sediments by bacterial reactions, (2) solubilizing gold as hydrocarbon-phase metal and colloidal gold nanoparticles during the hydrothermal remobilization of gold in lodes and veins, and (3) precipitating gold (**Figure 1**). Carbonaceous- and pyritic-rich shales would provide gold, HS^- ligands, and fluids, in addition to various organic C-H-N-S compounds, having the potential to enhance the gold carrying capacity of mineralizing fluids. Furthermore, hydrocarbons in the fluids may enhance gold precipitation with graphite.

For gold sourced from organic-rich pyrite-bearing shales, all three of the reviewed processes could operate sequentially to form orogenic gold deposits.

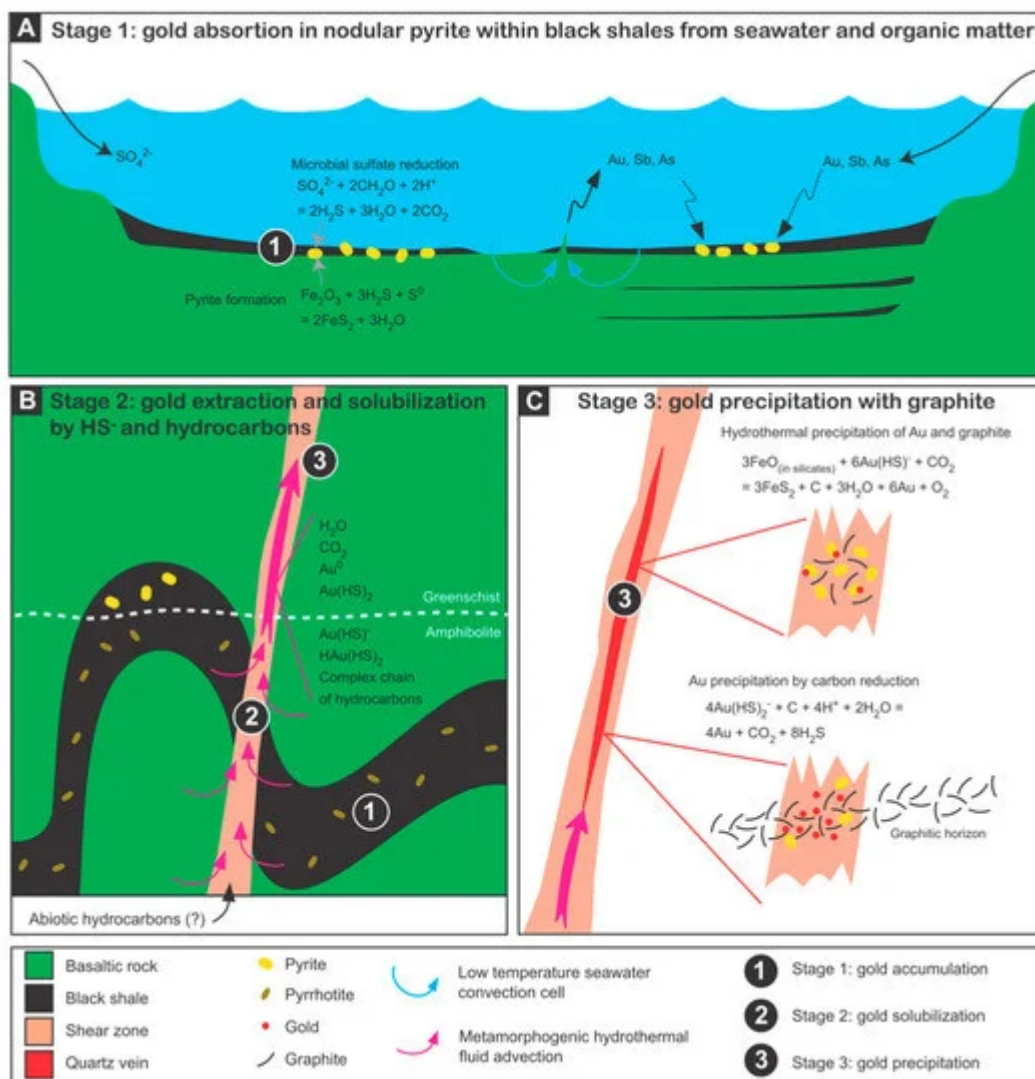


Figure 1. Schematic representation of the role of carbonaceous organic matter in the formation of orogenic gold deposits in three stages. **(A)** Source stage when gold in seawater accumulates in primary pyrites from the bacterial reduction of sulfate in organic material-rich sediments. **(B)** Mobilization stage when gold is solubilized by hydrocarbon-metal complexes and as colloidal gold nanoparticles for hydrothermal transport along faults following basin inversion and related tectonic shortening and metamorphism. Hydrocarbons are generated by thermal maturation of black shales or from abiotic deep contributions. **(C)** Precipitation stage when gold is co-precipitated with graphite from hydrocarbon-rich fluids or when gold is precipitated by carbon-rich reducing horizons.

However, in the prograde metamorphic context, it seems unlikely that black shales would provide hydrocarbon gases, as the organic matter would have been transformed in graphite and semi-graphite before reaching the greenschist/amphibolite facies boundary [43]. One possible explanation for generating hydrocarbon-bearing fluids lies in the late metamorphic thermal rebound model [45]. In this model, fluids are generated late during the exhumation after the rapid burial of rocks induced by the regional tectonic shortening. Buried cooler, hydrated, and organic matter-bearing rocks are later overprinted by thermal isograd rebound and re-equilibration of the newly formed crust. This model is coherent with the late origin of orogenic gold deposits [44].

The recent study of the Witwatersrand basin [45] also provides support to the possibility of having hydrocarbons at temperatures higher than the oil window (60–150 °C) reached during diagenesis and catagenesis (e.g., [46]). Hydrocarbon gases and minor oils were involved during hydrothermal gold precipitation at a temperature of 350 ± 50 °C [45], whereas oil, gas, and bitumen are interpreted to be sourced mostly from underlying black shale units [47].

Conversely, abiotic hydrocarbons (e.g., [48][49]; **Figure 1B**) may enhance gold solubility by forming organic-gold complexes or facilitating colloidal transport, regardless of the gold source, as proposed for the High Grade Zone (HGZ) of the Perron gold deposit in the Archean Abitibi Belt, Canada [50]. Nevertheless, the importance of organic matter for forming orogenic gold deposits is a relatively new concept, and this is especially true for gold transport by hydrocarbon-rich fluids. Re-assessments of numerous gold deposits, especially those with unusual CO₂-rich and H₂O-poor fluid inclusions, are thus necessary.

Hydrothermal reactions involving the consumption of water and C₂H₆, the ultimate proxy for the involvement of gold-bearing carbonaceous matter at depth [9], account for CO₂-rich, H₂O-poor fluids, as follows:



Ethane and methane are also common constituents of CO₂-rich fluids. In addition, the presence of H₂ in the mineralizing fluids in the Otago Schist [26] confirms that the chemical reactions (Equations (1) and (2)) are viable for the ultimate production of CO₂-rich, H₂O-poor fluids. Consequently, if these unusual fluids result from hydrocarbon consumption, then hydrocarbons may be indicative of (1) a favorable sedimentary source for gold, (2) enhanced gold solubility involving hydrocarbon-metal complexes and colloidal gold, and (3) efficient gold precipitation with graphite.

Although the genetic roles of organic matter were previously underestimated, the geological settings are supportive. The Witwatersrand goldfield, the largest in the world, is hosted along the margins of a very large Archean sedimentary basin (300 km × 100 km), with >4.5 km thick shales and argillites at its base [51]. The Giant Muruntau mine, the largest single orogenic gold deposit, with >5300 T Au (>170 Moz Au), is hosted in iron-rich and carbonaceous Ordovician to Early Silurian marine clastic rocks [52][54]. The Palaeoproterozoic Birimian belts of Western Africa comprise abundant graphitic shales rich in nodular gold-bearing pyrite [33]. These belts showed the highest rates of discovery of significant (>1 Moz Au/31 tonnes) deposits in the last decade [13]. The largest Palaeozoic goldfields are primarily hosted in sedimentary sequences, including the Victorian (Australia) and Mother Lode (CA, USA) districts.

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