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Economic geology: Gold buried by oxygen

Fabrice Gaillard & Yoann Copard

The Witwatersrand Basin in South Africa contains extraordinary amounts of gold. Thermodynamic calculations suggest that the gold may have accumulated there in response to a perfect storm of conditions available only during the Archaean.

The demand for metals continues to grow, but the capital available for prospecting is limited. Scientific innovations and improved understanding of how economically viable mineral deposits form are therefore critical to aid the search for new deposits at moderate cost[1, 2]. The Witwatersrand gold deposit in South Africa is the source of 40% of the gold in circulation. This gold was formed 2.6 billion years ago, during the Archaean, but the precise mechanisms for its formation are unclear. Writing in *Nature Geoscience*, Christoph Heinrich[3] suggests that these extraordinarily rich deposits required abundant volcanism in an oxygen-free atmosphere and life on land, conditions met only during the Archaean.

The amount of gold stored in the continental crust is primarily sourced from magma and cooled magmatic rocks, where it exists in small, diffuse amounts. Most of this gold was endowed in the crust during an intensive magmatic event about 3 billion years ago[4]. Since then, gold has mainly been redistributed within the crust by fluids and accumulated to form large, enriched deposits. On the modern Earth's surface, gold deposition and enrichment only occur by mechanical processes creating placer deposits — sandstones enriched in gold. Such a sedimentary origin is the prevailing hypothesis for the formation of the Witwatersrand deposit[5].

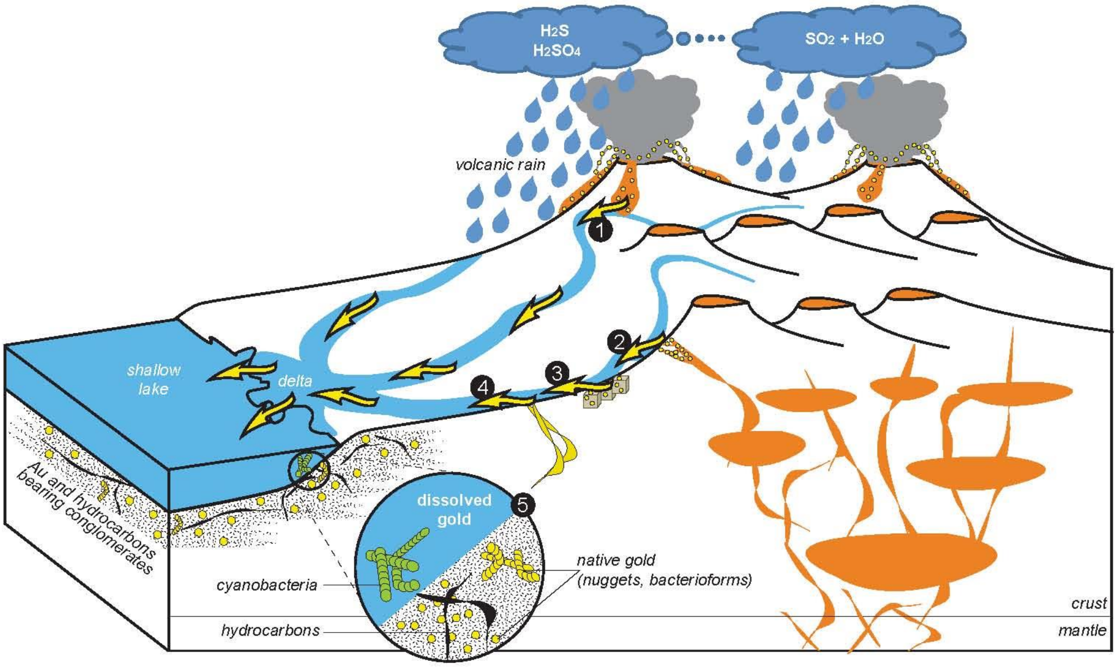
Gold can also accumulate inside Earth's crust, where it is carried by hydrothermal fluids. In contrast to the mechanical deposition of gold at Earth's surface, the dissolution and precipitation of gold inside the crust, where the availability of oxygen is low, is governed by chemical redox reactions[6]. In most cases, the dissolution of gold in hydrothermal fluids requires soluble sulphur in a reduced form. Metamorphic processes at moderate pressure and temperature can provide the chemical environment for the dissolution of gold, as suggested in an alternative model for the Witwatersrand complex[7]. In this model, gold is already in place as sedimentary placer, and remobilization only occurs locally.

Heinrich[3] offers a novel interpretation for the formation of the Witwatersrand deposit. He suggests that although enrichment of the gold may have taken place at the surface in a fluvial environment similar to that which creates placer deposits, the transport and depositional processes operating were chemical, as occurs in hydrothermal fluids circulating in the deeper crust today. It therefore seems possible that anoxic processes that dissolve, transport and accumulate gold deep inside the modern crust were operating at Earth's surface during the Archaean. Heinrich's claim is founded on thermodynamic calculations of chemical reactions that could have occurred in the surface waters that flowed during the Archaean. At that time, abundant volcanism is thought to have generated sulphur-rich volcanic gases[8] creating acidic rains and surface waters. In an oxygen-free atmosphere, such sulphurous volcanic rain could dissolve gold even at ambient temperatures on Earth's surface. Redox reactions between the dissolved gold and Archaean life, such as microbes and carbonaceous material, could have then triggered the deposition of gold in sediments. Although the amount of gold dissolved in the acid rain would have been small, this process could have accumulated enormous quantities of gold over millions of years.

If correct, Heinrich's model implies that similar surface-formed gold deposits may exist in other Archaean terrains, but not in younger rocks. The absence of oxygen in the Archaean atmosphere promoted a chain of reactions that could not occur at Earth's surface today. About 2.4 billion years ago, a rise in atmospheric oxygen triggered the Great Oxidation Event, which completely modified the biogeochemical processes operating at Earth's surfac[9]. Increasing atmospheric oxygen levels would have chased the surface chemical processes involving gold toward deeper regions of the Earth where oxygen is naturally lacking, forming epithermal, porphyry, orogenic, Carlin-type and intrusion-related ore deposits. Thus, the rise of atmospheric oxygen led to the burial of chemical deposits of gold.

Several burning questions about Heinrich's model will surely be debated. For example, the model requires volcanic rain laden with sulphur. Yet, Archaean waters are known to have been depleted in sulphur compared with modern waters[9], probably because the majority of volcanism during the Archaean was submarine, rather than subaerial[8]. The Witwatersrand gold deposit also has high osmium contents[5], implying the gold came originally from the mantle. Heinrich[3] suggests the flood-basalt eruption of the Hlagothi Complex — a large igneous province formed on the Kaapvaal Craton during the Archaean — can satisfy both of these constraints: The long-lived eruption provides a localized, subaerial and sustained source of sulphur-rich volcanic rain and the voluminous erupted basalts provide a mantle source for the gold. But if Heinrich's model delivers a sound mechanism for gold transport in surface waters, it is unclear how osmium, which is abundantly present in the gold deposits, can be carried. Finally, Heinrich's interpretation conflicts with the isotopic signature of the gold deposits, which suggests that the gold particles are older than the sediments hosting the ore[5]. The new mechanism proposed by Heinrich therefore does not bury the two older ones, the placer[5] and the metamorphic fluids[7], but it paves the way for a new vision of the biogeochemistry of gold during the Archaean (Fig. 1).

Figure 1: The Archaean biogeochemistry of gold and the Witwatersrand gold deposit.



The most probable source for the Witwatersrand gold was the basaltic rocks of the Hlagothi Complex (1), shown on the right. Acidic and sulphurous volcanic rains during the Archaean may have weathered gold from basaltic rocks (2), gold-bearing sulphide (3), and gold-bearing veins (4). Gold deposition as nuggets and bacterioforms could have been triggered by redox reactions with hydrocarbons and cyanobacteria, respectively (5). Yellow arrows indicate transport of gold. Christoph Heinrich[3] suggests that this combination of volcanic gases and acid rain, an oxygen-depleted atmosphere and the rise of organic material in the Archaean provided the perfect conditions for formation of the giant Witwatersrand gold deposit. H_2S, hydrogen sulphide; H_2SO_4, sulphuric acid; SO_2, sulphur dioxide; H_2O, water; Au, gold.

The model implies that gold was precipitated *in situ*, by interaction with microbial mats. The involvement of life and organic compounds has long been discussed for the formation of gold deposits[10], and in the Witwatersrand complex an active role for Archaean mats has recently been recognized[11]. Bacteria can aid the dissolution of gold under anaerobic conditions[12]. The precipitation of gold generally occurs by chemical redox reactions that involve carbonaceous material, such as hydrocarbons[13]. Gold deposition can also be triggered directly by living organisms, such as algal and microbial communities[12]. Lastly, it is possible that the oxygen-producing cyanobacteria created locally oxygenated surface waters, rendering gold insoluble and triggering its precipitation.

The redox conditions and the possible involvement of life proposed for the Witwatersrand deposit show similitude with the modern wastewaters and sewage sludges worldwide that are gathering substantial concentrations of gold[14]. In these anthropogenic environments, biological ingredients such as bacteria and carbonaceous matter, can lead to the redox accumulation of gold. Curiously, although some clean methodological approaches have been suggested[15], extraction of gold and other metals from these easily accessible anthropogenic ores has not yet been attempted.

Christoph Heinrich[3] uses thermodynamic calculations to argue that the Witwatersrand Basin was a huge and long-lasting chemical factory, operating and churning out gold thanks to the oxygen-free and volcanic gas-rich nature of the Archaean atmosphere. Organic material and primitive life may also have played a central role. If this model is correct, such deposits may have been common during the Archaean and could be preserved in ancient terrains.

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