Lifting the cloak of invisibility: Gold in pyrite from the Olympic Dam Cu-U-Au-Ag deposit, South Australia

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ABSTRACT

“Invisible gold” refers to gold (Au) occurring either within the lattice of a host sulfide or as discrete nanoparticles (NPs, <100 nm diameter) within a host that are only observable when imaged at very high magnifications. Previous research has regarded the physical form of invisible gold to be partially controlled by the concentration of arsenic (As) in the host sulfide, with stability fields for lattice-bound vs. Au-NPs defined by an empirical Au-As solubility curve. We undertook micrometer- and nanoscale analysis of a representative sample of As-Co-Ni-(Au)-bearing pyrite from Cu-mineralized breccias in the deeper part of the Olympic Dam Cu-U-Au-Ag deposit (South Australia) to define the location and physical form of Au and accompanying elements. Trace element geochemistry and statistical analysis show that >50% of pyrites contain measurable Au and As, and plot below the Au-As solubility curve. Au and As are geochemically associated with Te, Bi, Pb, Ag, and Sn. Primary oscillatory zoning patterns in pyrite defined by As-Co-Ni are reshaped by processes of dissolution-reprecipitation, including new nanoscale growth and rhythmic misorientation structures. Low-angle slip dislocations, twist-wall boundaries and deformation-dipole nanostructures are associated with Te-Bi-Pb-enrichment and host Au-Ag-telluride nanoparticles (NPs). Electrum NPs occur associated with pores coated by Bi-Ag-tellurides or within chalcopyrite particles. Bi-Pb-sulfotellurides, petzite, and sylvanite were identified by atomic-scale scanning transmission electron microscopy. The data support trace element (re)mobilization during pyrite deformation at the brittle to ductile transition (0.5–1 kbar, 300–400 °C) during brecciation. Au-NP formation is decoupled from initial As incorporation in pyrite and instead fingerprints formation of strain-induced, chalcogen-enriched nanoscale structures. Pore-attached NPs suggest scavenging of Au by Bi-bearing melts with higher rates of fluid percolation. Similar scenarios are predictable for pyrite-hosted “invisible Au” in pyrite from other deposits that experienced multiple overprints. Unveiling the cloak of invisibility using contemporary micro- to nano-analytical techniques reveals new layers of complexity with respect to the trace/minor element incorporation in mineral matrices and their subsequent release during overprinting.

Keywords: Pyrite, invisible gold, Au-Ag-tellurides, Bi-Pb-(sulfo)tellurides, Olympic Dam, HAADF STEM

INTRODUCTION

“Invisible gold” (Cook and Chryssoulis 1990) refers to gold that is either present within solid solution (hosted directly in the crystal lattice) or as discrete inclusions of gold, electrum, or other Au-bearing minerals, <1 μm in size, within a host mineral, that is commonly pyrite or arsenopyrite. Such gold is undetectable by conventional optical or scanning electron microscopy (SEM). Since the first visualization of a gold nanoparticle in pyrite (Palenik et al. 2004), rapid advances of in situ microanalytical techniques and case studies of invisible gold in different ore types have enabled the physical and chemical state of Au in pyrite to be characterized in ever greater detail and at ever better spatial resolutions. This empirical data has been accompanied by various experimental studies as well as thermodynamic modeling that has advanced the understanding of the mechanisms involved and the geochemical controls on incorporation of invisible gold within common sulfides (e.g., Reich et al. 2005; Deditius et al. 2008; Cook et al. 2013; Fougerouse et al. 2016a, 2016b, 2021; Pokrovskii et al. 2019, 2021; Xing et al. 2019).

Incorporation of Au into pyrite is considered to be mediated by arsenic (Reich et al. 2005; Deditius et al. 2014), with many examples of Au-bearing arsenian pyrite documented from a wide range of deposit types (e.g., Morey et al. 2008; Large et al. 2009; Gregory et al. 2015; Li et al. 2019; Morishita et al. 2019). Reich et al. (2005) proposed an empirical model for gold in pyrite and defined a maximum solubility limit of Au in pyrite that can be related to As content. The relationship was defined as $C_{Au} = 0.02 \times C_{As} + 4 \times 10^{-5}$, where $C$ represents concentration (mol%).

Recently, geochemical modeling coupled with high-resolution X-ray absorption spectroscopy data allowing identification...