An arsenic-driven pump for invisible gold in hydrothermal systems

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doi: 10.7185/geochemlet.2112

Abstract

Pyrite (FeS₂), arsenopyrite (FeAsS) and löllingite (FeAs₂) are exceptional gold concentrators on Earth; yet the exact redox and structural state of this “invisible” gold and the forces driving its intake and release by these minerals remain highly controversial. Here we applied high resolution X-ray absorption spectroscopy to Au-bearing pyrite and iron sulfarsenides from hydrothermal deposits and their synthetic analogues. We show that Au preferentially enters octahedral Fe structural sites [Au(As,S)₆] enriched in As, by forming respectively [AuAs_{1–3}S_{5–3}], [AuAs₃S₃...AuAs₆] and [AuAs₆] atomic units in arsenian pyrite (>0.1–1.0 wt. % As), arsenopyrite and löllingite, implying a formal oxidation state of Au^{II} in the minerals. In contrast, in As-poor pyrite, Au is dominantly chemisorbed as [Au^IS₂] moieties in much lower concentrations. Combined with experimental data on Au mineral-fluid partitioning, our findings imply a universal control exerted by arsenic on gold incorporation in iron sulfides and sulfarsenides *via* coupled Au-As redox reactions. These reactions account for the observed variations in invisible gold contents in the minerals from different hydrothermal deposit types and enable quantitative prediction of iron sulfarsenide ability in controlling gold concentration and distribution in hydrothermal systems.

Received 18 December 2020 | Accepted 17 March 2021 | Published 20 April 2021

Introduction

Pyrite, arsenopyrite and löllingite are the key minerals in hydrothermal systems capable of concentrating gold by up to 10⁶ times its mean crustal and mantle abundance (~1 ng/g). A large part of gold hosted by these minerals is “invisible” or “refractory” (*i.e.* optically undetectable) occurring both as metal nanoparticles (Au⁰) and chemically bound Au, the latter being often the dominant gold state and commonly associated with arsenic on the (sub)micron scale (*e.g.*, Cathelineau *et al.*, 1989; Cook and Chrysosoulis, 1990; Reich *et al.*, 2005). Thus, the redox and structural state of chemically bound Au and its link with As may define a deposit’s economic potential (*e.g.*, Kusebauch *et al.*, 2019), determine the type and cost of Au recovery from ore (*e.g.*, Adams, 2005) and, more generally, affect the gold distribution at the Earth’s crust scale (*e.g.*, Large *et al.*, 2011). Despite significant advances in micro/nanoanalytical techniques over the past 20 years, the fundamental causes of the Au-As relationship and processes that could drive gold, the most chemically inert

metal of the Periodic Table, to such levels of enrichment in a host mineral yet remain enigmatic. Existing interpretations vary from the formation of aqueous Au-As complexes or Au⁰ electrochemical deposition and Au(HS)₂[−] chemisorption on arsenian pyrite and arsenopyrite surfaces or precipitation of gold sulfide phases, to Au entering Fe, S or As crystallographic sites, along with other cation substitutions or structural vacancies, and with the formal oxidation state of chemically bound Au spanning from −1 to +3 and coordination from 2 to 6 (*e.g.*, Arehart *et al.*, 1993; Möller and Kersten, 1994; Simon *et al.*, 1999; Deditius *et al.*, 2014; Pokrovski *et al.*, 2019; Merkulova *et al.*, 2019; Filimonova *et al.*, 2020).

In an attempt to elucidate fundamental factors controlling the nature of invisible Au in arsenian pyrite and Fe sulfarsenides and the role played by As in Au intake, we used high energy resolution fluorescence detection X-ray absorption spectroscopy (HERFD-XAS), which is the most direct method to provide information about a trace element redox state, chemical bonding, and coordination at the atomic scale (*e.g.*, Proux *et al.*, 2017). Both X-ray absorption near-edge (XANES) and extended X-ray

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absorption fine structure (EXAFS) spectra were acquired on a set of thoroughly characterised Au-bearing pyrite and arsenopyrite samples from major metamorphic and sedimentary-hosted gold deposits and their synthetic analogues (including löllingite) prepared in controlled laboratory experiments (Supplementary Information). The obtained spectroscopic and fluid-mineral partitioning data were interpreted using quantum chemistry and thermodynamic approaches to generate a new structural and physico-chemical model that reveals the fundamental role played by arsenic in gold incorporation in pyrite and Fe sulfarsenides.

Atomic State of Gold from Spectroscopic Data

XANES spectra of chemically bound gold in all natural and synthetic arsenopyrite, löllingite and As-rich pyrite (≥ 1 wt. % As) samples examined here significantly differ from those of metallic Au⁰ and other reference compounds in which Au is coordinated by 2 to 4 As/S/Cl atoms or by 6 Sb/Te atoms, implying a different Au local environment in sulfarsenides (Figs. 1, S-6). In contrast, spectra of As-poor pyrites (<0.1 wt. % As) display distinctly lower energy and amplitudes that indicate a lower Au coordination and/or different electronic configuration than in more As-enriched samples. Quantum chemistry simulated XANES spectra of various Au positions in the mineral structure (Supplementary Information) show that Au enters (Au,Fe)(As,S)₆ octahedral sites variably enriched in As (Fig. 2). For löllingite, the measured spectra are perfectly matched by a simulated one for the AuAs₆ site. For arsenopyrite, the spectra are consistent with AuAs₃S₃-AuAs₆ units, rather than simple Au-to-Fe substitution in a stoichiometric FeAs₃S₃ site (Fig. S-8). These interpretations are fully supported by EXAFS analyses that yield 6 ± 1 As atoms at 2.53 ± 0.01 Å bound to Au in löllingite, and 4.5 ± 0.5 As at 2.51 ± 0.02 Å plus 1.5 ± 0.5 S atoms at 2.42 ± 0.05 Å in arsenopyrite (Table S-4). The remarkable similarity of bound Au atomic environment among all natural and synthetic arsenopyrite samples from various geological settings and experimental conditions demonstrates the universality of the Au substitution mechanism. For arsenian pyrites studied here, both XANES and EXAFS data (Figs. 2, S-9) demonstrate Au to be in an As-enriched Fe site, AuAs₃S₃. In contrast, for As-poor pyrite, spectra indicate quasi-linear AuS₂ geometries, which are typical of Au^I aqueous (poly)sulfide species and most thiol and sulfide solids (Pokrovski *et al.*, 2015, 2019). The difference in Au atomic environment between As-poor pyrite on one hand and arsenian pyrite, arsenopyrite and löllingite on the other hand is strong evidence that As directly impacts the mode of Au incorporation.

Structural Model for Chemically Bound Gold in Pyrite and Iron Sulfarsenides

Our spectroscopic results combined with available data are consistent with the structural model shown in Figure 3. The degree of Au enrichment in pyrite generally depends on As content, being the lowest in As-poor pyrite and increasing with As content, as demonstrated by the large body of micro-to-nano scale analyses of Au and As concentrations in the mineral (Reich *et al.*, 2005; Deditis *et al.*, 2014), and also directly evidenced by our and recent experiments (Kusebauch *et al.*, 2019). In As-poor pyrite, Au is dominantly surface-chemisorbed as Au^I (poly)sulfide clusters that may be partly incorporated into structural defects and dislocations depending on crystal growth kinetics (e.g., Wu *et al.*, 2019), and partly expelled as Au⁰ nanoparticles due to the very limited capacity of pyrite to intake Au in the absence of As (Pokrovski *et al.*, 2019). The pronounced change

Figure 1 Gold L₃-edge HERFD XANES spectra (offset vertically) of representative Au-bearing natural (nat) and experimental (exp) pyrite (Py), arsenopyrite (Apy) and löllingite (Lo) samples, and selected reference compounds with indicated Au first shell atomic coordination (see Supplementary Information for details).

in the Au solubility pattern with increasing As content above 0.01–0.1 wt. % As (Fig. 3), as documented in many natural studies, implies a fundamental change in the gold intake mechanism to increased Au partitioning into As-enriched Fe(As,S)₆ sites compared to the pyrite FeS₆ crystallographic site, as evidenced by the direct detection of As in the Au nearest atomic shell (Figs. 2, S-9). The number of As atoms bound to Au (*n*) may display large variability, from below detection limit (*n* < 1) to *n* ≥ 3, as reported in recent XAS studies of some natural and synthetic pyrites with >1 wt. % As (Merkulova *et al.*, 2019; Filimonova *et al.*, 2020). Thus, Au in arsenian pyrite is likely to exhibit a range of Au(As_{*n*}S_{*6-n*}) environments, from S-rich (*n* ≤ 1) to As-rich (*n* ≥ 3). This trend is followed by the continued enhancement of Au binding to As in arsenopyrite and löllingite (*n* > 4; Fig. 3). Formation of Au chemical bonds with As^{-I}, which is the dominant As redox state in the three minerals in most settings, provides a fundamental explanation for the systematically higher invisible Au contents analysed at the micron scale in arsenopyrite and löllingite compared to coexisting pyrite in many hydrothermal deposits (Tables S-3, S-11), as well as for experimentally measured very high Au partition coefficients between iron sulfarsenides and aqueous fluid (>10⁵; Table S-8).

Figure 2 Comparison of Au L₃-edge HERFD XANES spectra of representative samples with quantum chemistry simulated spectra of Au in different structural sites as pictured by the displayed atomic clusters. The spectra of (a) Apy, (b) Lo, and (c) As-rich Py are consistent with Au in an As-enriched [Au(As,S)₆] octahedral site, whereas Au in As-poor Py (c) is in [AuS₂] moieties similar to those in exemplified Au^I-(poly)sulfide complexes.

The available XAS data on natural pyrite and arsenopyrite samples do not reveal atoms other than As or S in the Au nearest shell that might accompany Au incorporation. Thus, direct Au^{II} to Fe^{II} substitution favoured by As^{-I} would be a universal mechanism that does not require specific structural vacancies or charge compensations from other minor elements in different redox

states (Cu^I, Sb^{III}, Fe^{III}, As^{III}). Although the notion of redox state for strongly covalent bonds such as Au-As or Au-S has no strict sense (Cabri *et al.*, 2000), the formal Au^{II} state would be consistent with the three key features of gold coordination chemistry: i) the great majority of formally Au^I and Au^{III} compounds have either 2 (linear) or 4 (square/tetrahedral) Au coordination

Figure 3 Structural model for chemically bound Au in pyrite, arsenopyrite and löllingite (not to scale). The Au coordination is shown by ball-and-stick atomic clusters (Au = pink, S = yellow, As = green, Fe = brown, S₃ = blue, H = grey). Horizontal gray bars indicate the typical range of As contents in each mineral. Empirical Au solubility limit in arsenian pyrite (solid curve; Reich *et al.*, 2005) was extrapolated to Apy and Lo (dashed curve). Note a fundamental transition in the Au incorporation mechanism (vertical dashed line, indicative position), from chemisorption as Au^I-polysulfide complexes at low As content in pyrite to coupled Au-As redox reactions driving Au entry in As-enriched Fe crystallographic sites of the three minerals.

(Cotton and Wilkinson, 1988) poorly compatible with an octahedral site, ii) complexes of Au^{II} coordinated by 4 to 6 ligands (S, P, Se), and often paralleled by [Au...Au] clustering as found in arsenopyrite in this study (Fig. S-8), are well known in chemistry (Laguna and Laguna, 1999), iii) gold in many arsenide and chalcogenide compounds (AuAs₂, AuSb₂, AuTe₂, AuSe) has a formal oxidation state of Au^{II} and a coordination of 6 (ICSD, 2020). Therefore, the favourable coordination geometry coupled with redox-driven Au binding to As are the two key requirements allowing Au enrichment in iron sulfarsenides. These key features distinguish these minerals from other hydrothermal sulfides such as pyrrhotite, chalcopyrite, bornite, or sulfosalts that host very little invisible Au (e.g., George *et al.*, 2017, 2018).

Thermodynamic Model for Gold Solubility in Arsenopyrite and Löllingite

Gold incorporation in iron sulfarsenides may thus be interpreted as a coupled redox reaction between the dominant Au^I/As^{III} redox states in the hydrothermal fluid and Au^{II}/As⁻¹ in the mineral. Because Au in arsenopyrite occurs in a combination of arsenopyrite and löllingite-type sites (Fig. 3), Au solubility and partitioning may be formally approximated by a hypothetical sulfarsenide end member AuAsS-AuAs₂ (equivalent to AuAs_{1.5}S_{0.5}) “dissolved” in arsenopyrite:

where [AuAs_{1.5}S_{0.5}]_{Apy} is the mole fraction of the Au-sulfarsenide end member in the arsenopyrite solid solution, and Au(HS)₂⁻ and As(OH)₃ are the activities of the major Au and As aqueous species in the fluid (Perfetti *et al.*, 2008; Pokrovski *et al.*, 2015). The thermodynamic constants of reactions (Eq. 1) and (Eq. 2), derived from experimental mineral-fluid partition coefficients at 450 °C and 700 bar are log₁₀K₁ = -18.2 ± 0.3 and log₁₀K₂ = -22.4 ± 0.3, respectively (1 s.d.; Table S-9). An analogous model of the AuAs₂-FeAs₂ solid solution is valid for löllingite (Table S-10). The generated constants enable, for the first time, direct predictions of Au mineral-fluid partitioning and solubility in sulfarsenides as a function of the key hydrothermal fluid parameters such as As/S content, redox and pH (Fig. 4). Applying similar quantitative models to pyrite would require more systematic experimental and natural data to account for the large range in the Au(As_nS_{6-n}) site stoichiometry (Fig. 3). The empirical gold solubility limit reported for arsenian pyrite is likely to be defined by reactions analogous to (Eq. 1) and (Eq. 2), thereby reflecting the natural variability limits of the fluid parameters.

Implications

Our new findings help to clarify one of the oldest enigmas of geochemistry about the unique role played by arsenic in Au fate in hydrothermal systems. Our results demonstrate that both arsenopyrite and löllingite are capable of accommodating large concentrations of bound Au (100s to 1000s μg/g) even from Au-poor fluids (<0.1 μg/g Au) in relatively reduced metamorphic and ultramafic rock settings (*f*_{O₂} < NNO; Fig. 4a), whereas in more oxidised orogenic- and porphyry-related systems little Au is incorporated, in full agreement with natural observations (e.g., Deditius *et al.*, 2014). Our quantitative predictions are currently limited at 450 °C, but lower temperatures may further

Figure 4 Gold solubility in arsenopyrite (Apy) and löllingite (Lo) in equilibrium with hydrothermal fluid and native gold, predicted as a function of (a) log *f*_{O₂} (in bars, relative to the nickel-nickel oxide O₂ buffer, NNO) at typical H₂S and As(OH)₃ fluid phase concentrations for the indicated major types of gold deposits, and (b) As and S fluid phase content at *f*_{O₂} of NNO–0.5 within the Apy stability domain (Perfetti *et al.*, 2008) in metamorphic gold deposits (circles; Table S-11 for compilation). Also plotted are equilibrium Au(HS)₂ concentrations in fluid (blue curve), Au Apy/Fluid partition coefficient (*D*(Au)_{Apy/Fluid}, mass units ratio, same y scale, red curve), and Apy-Lo, Apy-pyrrhotite (Po), and Apy-pyrite (Py) equilibrium lines.

favour Au-As redox reactions and Au intake in sulfarsenides, consistent with enhanced equilibrium As partitioning into pyrite (Xing *et al.*, 2019). Surface sorption and mineral growth rate factors may also contribute to Au scavenging (e.g., Wu *et al.*, 2019), but the fundamental arsenic-driven redox control will equally hold. Changes in redox, pH and dissolved As/S contents upon fluid evolution adequately account for the large variability of Au content widely documented in different mineral generations within individual deposits and across mineralised domains in different deposit types (Fig. 4b). Gold intake by and release from sulfarsenides driven by variations in fluid composition appear to be key factors for hydrothermal gold deposit formation. For example, in giant Carlin-type deposits, these factors may have driven focused coupled Au and As-pyrite deposition (Kusebauch *et al.*, 2019). In orogenic-type deposits, first order Au “pumping” from the fluid by pyrite and arsenopyrite, followed by large scale Au liberation from those minerals during further metamorphism, may have provided a gold source and strongly influenced metal endowment, timing of mineralisation, and spatial distribution (Large *et al.*, 2011; Velásquez *et al.*, 2014; Fougereuse *et al.*, 2016). Future advances of *in situ* spectroscopy will offer more systematic quantification of invisible gold along with other valuable trace metals hidden in iron sulfarsenide minerals, thereby enabling a better understanding of trace element geochemical cycles and improving resource assessment, exploration and recovery.

Acknowledgments

This work was funded by the French National Research Agency (RadicalS ANR-16-CE31-0017, SOUMET ANR-2011-Blanc-SIMI-5-6-009), the Institut des Sciences de l’Univers of the Centre National de la Recherche Scientifique, INSU-CNRS (CESSUR-OrPy-AsOrPy), the Institut Carnot ISIFoR (OrPet), and the West African Exploration Initiative (WAXI-P934A). We acknowledge the European Synchrotron Radiation Facility (ESRF) for providing access to beam time and infrastructure,

and AMIRA International for support in field-related aspects. The FAME-UHD project is supported by the French Grand Emprunt EquipEx (EcoX ANR-10-EQPX-27-01), the CEA-CNRS CRG consortium and the INSU-CNRS. DFT calculations were performed using HPC resources from CALMIP (2020-P1037). We thank A.-M. Cousin for invaluable help with figure layout, S. Foulon for tube welding, A. Manceau and B. Tagirov for sharing XAS data and references, and Y. Joly for advice on XANES modeling. Comments by Editor S. Redfern and an anonymous referee greatly improved this article.

Editor: Simon Redfern

Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2112>.

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Cite this letter as: Pokrovski, G.S., Escoda, C., Blanchard, M., Testemale, D., Hazemann, J.-L., Gouy, S., Kokh, M.A., Boiron, M.-C., de Parseval, F., Aigouy, T., Menjot, L., de Parseval, P., Proux, O., Rovezzi, M., Béziat, D., Salvi, S., Kouzmanov, K., Bartsch, T., Pöttgen, R., Doert, T. (2021) An arsenic-driven pump for invisible gold in hydrothermal systems. *Geochem. Persp. Let.* 17, 39–44.

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