Gold speciation in hydrothermal fluids revealed by in situ high energy resolution X-ray absorption spectroscopy

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Abstract

Gold mobilization, transfer, and concentration in the Earth’s crust are controlled by hydrothermal sulfur- and chloride-bearing fluids. Yet the exact chemical identity, structure, and stability of Au-bearing species and, in particular, the respective contributions of the sulfide (HS⁻) and trisulfur ion (S₃•⁻) ligands to Au transport lack direct in situ evidence. Here we employed high energy resolution fluorescence detection X-ray absorption spectroscopy (HERFD-XAS) on aqueous sulfate/sulfide/S₃•⁻-bearing solutions at typical hydrothermal temperatures and pressures (T = 350 °C, P = 600 bar) to reveal differences in dissolved Au spectral signatures indicative of contrasting fluid-phase Au speciation as a function of acidity and redox conditions. Combined with in situ Au solubility measurements and quantum-chemical and thermodynamic modeling, our spectroscopic data provide direct evidence for the Au(HS)S₃•⁻ complexes predominant at acidic-to-neutral and alkaline conditions, respectively. Our findings thus directly confirm a recent speciation scheme for Au in aqueous S-bearing fluids established using less direct methods, and highlight an important role of the trisulfur ion in gold mobilization and concentration in hydrothermal-magmatic deposits associated with subduction zones. More generally, our results show that HERFD-XAS enables the identification of structural and coordination features in metal complexes virtually unresolvable using classical XAS techniques. By avoiding limitations of less direct techniques, our integrated high-resolution spectroscopic approach opens perspectives for studies of the speciation and solubility of gold and other metals in high T-P fluids, and potentially silicate melts, inaccessible to direct observation in nature.

Keywords: Gold, sulfur, trisulfur radical ion, hydrothermal fluid, ore deposit, high energy resolution fluorescence detection X-ray absorption spectroscopy (HERFD-XAS), X-ray absorption near edge structure (XANES), solubility, density functional theory (DFT), first-principles molecular dynamics (FPMD)

Introduction

Gold deposits on Earth result from an exceptional concentration phenomenon yielding metal contents in ore a thousand to a million times higher than those in most crustal and mantle rocks whose Au average concentration is ~1 ppb (Frimmel 2008; Saunders et al. 2018). This spectacular enrichment process is ensured by aqueous fluids transporting gold mostly as sulfide and chloride types of complexes (e.g., Helgeson and Garrels 1968; Boyle 1969; Seward 1989; Garofalo et al. 2014). However, the exact chemical identity and stability of such complexes and their capacity to carry the noblest metal of the Periodic Table yet remain controversial. Most available studies, conducted using traditional solubility methods applied to hydrothermal-magmatic fluids (e.g., see Pokrovski et al. 2014 for an overview), generally agree that the most likely Au-bearing species are the aurous (AuI) dichloride AuCl₂; common in acidic, saline, oxidized conditions, and the dihydrogen sulfide Au(HS)₂; dominant in neutral to basic, S-bearing, reduced fluid compositions. In contrast, the role of other potentially important AuI-bearing ligands, such as the polysulfide radical ions S₅⁻ and S₆⁻, has not been yet definitely recognized, despite the growing body of studies demonstrating that these sulfur forms are stable across a wide temperature (T) and pressure (P) range of acidic-to-neutral sulfate/sulfide-bearing hydrothermal-magmatic fluids associated with subduction zones (Pokrovski and Dubrovinsky 2011; Jacquemet et al. 2014; Pokrovski and Dubessy 2015; Barré et al. 2017; Schmidt and Seward 2017; Colin et al. 2020). The lack of direct data on gold-sulfur radical ion interactions is mostly because the gold solubility...
pattern is a complex function of various fluid parameters such as acidity, chlorinity, redox, and S speciation. This complexity makes it difficult a straightforward and unambiguous analysis of bulk solubility data in terms of aqueous species identity, in particular in the absence of more direct in situ molecular-level information (e.g., Pokrovski et al. 2014, 2019).

Synchrotron-based X-ray absorption spectroscopy (XAS) is the most direct in situ method for providing such information about the first-shell coordination environment and the identity and number of ligands around the metal in an aqueous complex. In the last 20 years, this method has emerged as a key complement to the traditional solubility approach in hydrothermal fluids for several metals and metalloids (e.g., Pokrovski et al. 2002, 2005; Bazarkina et al. 2014; Brugger et al. 2016; Testemale et al. 2004, 2011; references therein), including gold (e.g., Pokrovski et al. 2009a, 2009b, 2015; Trigub et al. 2017a; Tagirov et al. 2019).

However, the traditional XAS method is weakly sensitive to light elements (e.g., H in HS- type ligands) and beyond-the-nearest-shell atoms [e.g., polysulfide ligands Au-S-(Sn) or alkali ion pairs Au-Cl-Na/K], as well as to ligands with similar atomic numbers (e.g., S-16 vs. Cl-17). As a result, questions yet remain open about the identity and abundance of Au aqueous complexes with polysulfide ions in S-bearing hydrothermal fluids (e.g., Pokrovski et al. 2009a, 2015; Mei et al. 2013; Trigub et al. 2017a), as well as about the significance of alkali-ion pairs of the anionic chloride and sulfide Au species in magmatic fluids [e.g., NaAuCl2], KAu(HS)2, Zajacz et al. 2010; Mei et al. 2014; Tagirov et al. 2019]. These limitations of traditional XAS are particularly severe in the case of aurous species, which all have quasi-linear first-shell geometries L-AuI-L and very similar AuI-L interatomic distances (where L is the Cl or S ligand; Pokrovski et al. 2009a, 2009b).

Recent developments in high energy resolution fluorescence detection X-ray absorption spectroscopy (HERFD-XAS) devices at synchrotron beamlines potentially enable to overcome these fundamental limitations of traditional XAS, making it possible to: (1) reveal spectral features poorly resolved using standard XAS detection techniques employing solid-state detectors and (2) significantly increase signal-to-noise ratio especially for dilute systems such as metals in fluids or trace elements in complex mineral matrices (e.g., Proux et al. 2017). Whereas HERFD-XAS methods are increasingly applied to study redox and structural state of trace elements such as gold in major sulfide minerals and catalytic materials (e.g., van Bokhoven et al. 2006; Trigub et al. 2017b; Merkulova et al. 2019; Pokrovski et al. 2019, 2021), their application to high T-P fluids yet remains challenging. In an attempt to provide a more resolved picture of gold-sulfur complexes and to further develop in situ approaches for metals in hydrothermal fluids, here we used HERFD-XAS to directly measure the molecular speciation and solubility of gold at 350 °C and 600 bar in two model aqueous S-bearing fluids representative of those that have formed hydrothermal gold deposits. Combined with atomistic simulations of Au complexes and thermodynamic calculations of sulfur and gold speciation, our results provide direct evidence for gold-trisulfur ion complexes in hydrothermal fluids and open further perspectives for studying, using HERFD-XAS approaches, the metal speciation and transport by fluids and melts in the lithosphere.

**Methods**

**Experimental strategy and conditions**

Gold solubility and Au L3-edge HERFD-XAS spectra in the aqueous phase have been measured at 350 °C and 600 bar for two fluid compositions of contrasting pH and redox parameters (Table 1; Figs. 1a and 1b) at which two different Au-S complexes were predicted to be dominant according to the available thermodynamic data (Pokrovski et al. 2014, 2015), Au(HS)2 (experiment 1) and Au(HS)3 (experiment 2), formed according to the formal dissolution reactions:

\[
\text{Au(s)} + \text{H}_2 \text{S} + \text{S}_n^2- + \frac{1}{2} \text{O}_2 = \text{Au(HS)}_n^2+ + \frac{1}{2} \text{H}_2 \text{O} \\
\text{Au(s)} + \text{H}_2 \text{S} + \text{HS}^- + \frac{1}{2} \text{O}_2 = \text{Au(HS)}_2^+ + \frac{1}{2} \text{H}_2 \text{O} \tag{1}
\]

Our choice of fluid compositions is based on extensive literature data of Au solubility and traditional XAS measurements in thiosulfate solutions. Thiosulfate is non-toxic and stable at ambient temperature, making it easy to handle and accurately load into the optical cell; it breaks down to sulfate, sulfide, and S2− on heating, providing the source of sulfur ligands (e.g., Jacquemet et al. 2014; Pokrovski et al. 2015; Kokh et al. 2020):

\[
\begin{align*}
\text{S}_2\text{O}_3^2- + \text{H}_2\text{O} & = \text{SO}_4^{2-} + \text{H}_2\text{S} \\
19 \text{H}_2\text{S} + 5 \text{SO}_4^{2-} & = 2 \text{H}^+ - 8 \text{S}_2^- + 20 \text{H}_2\text{O} 
\end{align*} \tag{2}
\]

The addition of acid (HCl) or base (KOH or NaOH) to the initial thiosulfate solution enables controlled pH value choice and buffering:

\[
\begin{align*}
\text{SO}_4^{2-} + \text{H}^+ & = \text{H}_2\text{SO}_4 \\
\text{H}_2\text{S} - \text{HS}^- & = \text{H}^+ + \text{H}_2\text{O} 
\end{align*} \tag{3}
\]

Equilibrium between the dominant sulfate and sulfide species at elevated temperatures (>250 °C) imposes oxygen fugacity (fO2) ranging from –HM + 1 at acidic pH to –HM–1.5 at neutral-to-basic pH (where HM denotes the log fO2 value of the conventional hematite-magnetite mineral buffer):

\[
\text{H}_2\text{S} + 2 \text{O}_2 = \text{SO}_4^{2-} + 2 \text{H}^+ \tag{4}
\]

In addition, ion pairs of the sulfate and sulfide anions with alkalis (K+ or Na+) along with minor amounts of SO4−2, molecular sulfur (Sm, both aqueous and molten), and polysulfide diions S2n− contribute to aqueous sulfur speciation, depending on pH, as predicted using the available thermodynamic data and shown in Figure 1a [see Kokh et al. (2020) for details and data selection]. It can be seen that the two experimental compositions chosen here significantly differ in terms of pH, redox, and HS− and S2− ligand concentration, leading to an Au speciation contrast according to reactions 1 and 2. Not only our chosen compositions and T-P conditions provide robust constraints on the experimental system, but they do also offer a good analog for natural S-rich (to several wt% S) fluids in arc-related magmatic-hydrothermal porphyry Cu-Au-Mo and associated epithermal deposits at T of 200–500 °C, P of 100–1000 bar, a wide pH (3–8) and redox (HM±2 range), where sulfate and sulfide coexist (Einaudi et al. 2003; Kouzmannov and Pokrovski 2012).

**In situ high-resolution XAS measurements**

High energy resolution fluorescence detection X-ray absorption spectroscopy (HERFD-XAS, hereafter HR-XAS for simplicity) analyses at the Au L3-edge (11.919 keV) of the two experimental fluids were performed at FAME-UHD (BM16) beamline (Proux et al. 2017) of the European Synchrotron Radiation Facility, Grenoble, France, using a recently developed crystal analyzer spectrometer operating in HERFD mode (Lorens et al. 2012). Compared to conventional synchrotron-based XAS- and X-ray absorption near-edge structure (XANES) measurements, HERFD-XAS provides miniaturized XAS spectrometers providing high time-resolution data acquisition, using a combination of solid-state and high-resolution detectors. As a result, HERFD-XAS improves the dynamic range of XAS measurements, making it possible to study fast and slow chemical reactions. High energy resolution HERFD-XAS experiments were conducted in two model aqueous S-bearing fluids representative of those that have formed hydrothermal gold deposits. Combined with atomistic simulations of Au complexes and thermodynamic calculations of sulfur and gold speciation, our results provide direct evidence for gold-trisulfur ion complexes in hydrothermal fluids and open further perspectives for studying, using HERFD-XAS approaches, the metal speciation and transport by fluids and melts in the lithosphere.

**Table 1. Summary of the HR-XAS experiments at 350 °C and 600 bar conducted in this study**

<table>
<thead>
<tr>
<th>Run number, starting solution composition (m, mol/kg fluid)</th>
<th>pH(H2O)</th>
<th>log fO2 (vs. HM)</th>
<th>log fS2O32−/fSO42−</th>
<th>Dominant Au species</th>
<th>Estimated standard error (±2 s.d.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp 1: 0.46m K3S2O3 + 0.20m HCl</td>
<td>4.3</td>
<td>+1.1</td>
<td>-0.2</td>
<td>Au(HS)2</td>
<td>±0.2</td>
</tr>
<tr>
<td>Exp 2: 0.51m K3S2O3 + 0.29m KOH</td>
<td>7.1</td>
<td>-1.5</td>
<td>-0.3</td>
<td>Au(HS)3</td>
<td>±0.30</td>
</tr>
</tbody>
</table>

* Measured total dissolved Au concentration in solution saturated with metallic gold, derived from the absorption edge height of XAS spectra in transmission and fluorescence modes (see Online Material); b Predicted using thermodynamic modeling (see Fig. 1 for detailed S and Au speciation in the fluid).
Sulfur species concentration (mol/kg fluid) vs Fluid pH (350°C, 600 bar)

Gold species concentration (mol/kg fluid) vs Fluid pH (350°C, 600 bar)

**Figure 1.** Sulfur (a) and gold (b) speciation in a 0.5m K$_2$S$_2$O$_3$ aqueous solution of this study predicted as a function of fluid pH (controlled by addition of KOH or HCl) at 350°C and 600 bar, using the recent thermodynamic data sources (Pokrovski et al. 2015; Kokh et al. 2020; references therein). Vertical dashed line (marked as pH 0) indicates the pH of the neutrality point of water at the given T and P; vertical dotted lines show the compositions of the two experiments of this study (Table I). The oxygen fugacity is indicated relative to the hematite-magnetite buffer (HM, in log$_{10}$Fe$^{3+}$/Fe$^{2+}$ units). ΣSO$_4$ and ΣHS denote the sum of concentrations of sulfate-type (SO$_4^{2-}$, KSO$_4$, HSO$_4^-$, KHSO$_4^-$) and sulfide-type (HS$^-$ and KHS$^-$) species, respectively. The break in the species curve pattern at pH ~4.4 reflects the onset of molten sulfur (S$_m$) formation at more acidic pH. Red circles in b show the average Au solubility measured in the experiments of this study (error bars = standard deviation estimated at 95% probability level; see the Results section).

XAS spectroscopy, HR-XAS has two major advantages: (1) a significant gain in spectral resolution compared to nominal resolution defined by the core hole width of the absorption edge; this gain allows accurate detection of different features in the X-ray absorption near-edge structure (XANES) spectral region, which is indicative of Au coordination environment but is generally poorly expressed in nominal-resolution spectra (e.g., Pokrovski et al. 2015, 2021), and (2) the ability to efficiently filter out all unwanted contributions from elastic scattering and fluorescence from other elements in the fluid matrix, and thus significantly improve both the limit of detection for Au and signal-to-noise spectral ratio. The beamline X-ray optics incorporated a Si(220) double-crystal monochromator with sagittal focusing (beam spot full-width at half maximum at the sample ~100 × 200 μm$^2$), Rh-coated mirrors for harmonic rejection, and a crystal analyzer spectrometer with 3 Si(660) crystals held in Helgas atmosphere in a Rowland circle geometry (1 m diameter). The experimental spectral resolution was measured to be 0.9 ± 0.1 eV at the La$_3$ Au fluorescence line, which corresponds to a significant gain in resolution compared to classical mode (core-hole lifetime broadening is 5.54 eV at Au L$_2$-edge; Campbell and Papp (2001)). High-resolution fluorescence XANES, together with EXAFS (extended X-ray absorption fine structure), spectra were recorded using a Vertex EX-90 mono-element detector. The use of such an energy-resolved detector (band width ~200 eV) allowed counting the photons diffracted by the spectrometer crystals in Bragg conditions for Au L$_3$ (Bragg’s angle = 85.71°) and removal of all other contributions due to energy-resolved detection, thereby greatly improving the resulting signal-to-noise ratio. Transmission (nominal-resolution) spectra were simultaneously recorded using silicon diodes collecting scattered radiation from a Kapton foil placed in the incident and transmitted X-ray beam. Energy calibration of each scan was checked using a gold metal foil whose L$_2$-edge energy was set to 11919.0 eV as the maximum of the spectrum first derivative. The accuracy of this calibration over the whole experimental duration is about ±0.5 eV.

Experiments were carried out using a hydrothermal autoclave developed at the Néel Institute (Testemde et al. 2005) and described in detail elsewhere (Pokrovski et al. 2006). The runs were conducted at 350 ± 2°C and 600 ± 1 bar by allowing a piece of gold foil to react with an aqueous thiosulfate solution in the glassy-carbon inner cell and following the established procedures (Pokrovski et al. 2009a, 2009b). To enable the HR-XAS measurements, the autoclave was tilted from its vertical position to match the required Bragg angle of the crystal analyzers (Fig. 2). Multiple XAS scans were recorded as a function of time both to monitor the eventual spectra evolution and to improve spectral statistics. No changes in the spectra, which might arise from X-ray beam-induced photochemical phenomena or reactions with the cell walls, were detected (apart from minor evolution of total Au dissolved concentrations, see Online Materials). The absence of such phenomena is in agreement with both the stability of Au-S species in well-buffered systems as those of this and previous (e.g., Pokrovski et al. 2009a) studies and the known chemical inertness of the glassy-carbon cell material (Pokrovski et al. 2006). Dissolved Au concentrations in the fluid were estimated using two independent methods: (1) from the amplitude of the absorption edge height of the Au L$_3$-edge transmission spectra from the classical X-ray absorption relation and using the known fluid density and absorption path length through the cell (e.g., Pokrovski et al. 2005, 2009a), and (2) from the amplitude of the fluorescence spectrum corrected for X-ray absorption by the fluid and calibrated using a HAuCl$_4$ standard solution of known Au concentration (see Online Materials).

In this study, we focus on the HR-XANES spectral region because the extended X-ray absorption fine structure (EXAFS) region is not significantly affected by the energy-resolution improvement and has been the subject of extensive detailed work (Pokrovski et al. 2009a, 2015) that could not reveal any significant differences in the EXAFS signal for different Au$^+$-polythiosulfide type of complexes in the fluid.

**Quantum-chemistry ab initio modeling of XANES spectra using FDMNES**

Direct and unambiguous interpretation of XANES spectra, particularly in high-resolution mode, would ideally require reference compounds with Au molecular environments being as close as possible to those of the samples. Because of the lack...
their geometries. For illustrations in this study, we have therefore chosen those generated using B3LYP, for consistency with the FPMD simulations that used the BLYP-type functionals.

FPMD-generated complex conformations, also used in XANES calculations, were taken from extensive simulations analogous to our previous study of Au complexes in hydrothermal solutions (Pokrovski et al. 2015). However, calculating a XANES spectrum from each FPMD snapshot using the FD method would be computationally too demanding in light of the too large number of FPMD snapshots (at least 100) needed to fully represent the FPMD trajectories. Therefore, a limited number of representative conformations from the FPMD simulations for a given Au complex has been extracted using a clustering method (six configurations per species; see Online Materials for details). For each of the four selected Au species, the six extracted configurations (Online Materials Fig. OM2) were used to calculate 6 XANES spectra by the FD method. The resulting spectra, weighted by the cluster size (i.e., number of configurations in each cluster), were then summed up to obtain the average XANES spectrum expected to be representative of the whole set of FPMD snapshots for a given species. Water molecules beyond the first Au atomic shell were also considered in the calculation of the XANES spectra but were found to have a negligible effect, in agreement with the generally low sensitivity of the XAS signal to distant and distorted shells. The average FPMD-derived Au-S and Au-O distances for the S-bearing Au species are generally ~0.05 Å longer than their DFT-derived counterparts (Online Materials Table OM2), but this difference has a minor effect on the calculated XANES spectra. The observed differences in calculated distances using the same BLYP functional and the same basis set are attributed to the use of a pseudopotential for Au in FPMD that approximates the effect of core electrons. This approximation is required in FPMD simulations of liquids to significantly reduce the computer time, whereas the far less computationally demanding static DFT methods treat both core and valence electrons explicitly. Similar minor discrepancies in the calculated distances between static DFT and FPMD have also been found for other metals (e.g., Spezia et al. 2008, 2012). The FPMD-derived spectra for the four Au-S species were compared with their static DFT-derived spectra and with the experiment (Online Materials Figs. OM3 and OM4).

**Results**

**Gold solubility**

The obtained Au concentrations averaged over all data points from transmission and fluorescence scans are 0.004 ± 0.002m and 0.007 ± 0.004m (~± standard deviations, 2 s.d.) in experiments 1 and 2, respectively (see Online Materials for details). These values are in excellent agreement with equilibrium Au solubility predictions using the thermodynamic properties of sulfur species and Au complexes established in recent studies (Pokrovski et al. 2015; Kokh et al. 2020 and references therein). It can be seen in Figure 1b that Au(HS)S is predicted to be far the dominant Au species in the acidic run (experiment 1), whereas the concentrations of the traditional sulfide species such as Au(HS)2 and Au(HS)(H2O)2 are 50 to 100 times smaller. Likewise, in the basic pH run (experiment 2), Au(HS)2 is ~10 times more abundant than Au(HS)S2. Thus, our measurements provide robust independent support of the recently suggested Au speciation scheme involving the Au-trisulfur ion complex, which plays an important role in acidic-to-neutral S-rich fluids (Pokrovski et al. 2015, 2019), whereas the traditional hydrogen sulfide complex Au(HS)2 quantitatively accounts for Au speciation and solubility in neutral to moderately alkaline fluids (e.g., Seward 1973; Pokrovski et al. 2009a, 2014). Our new data, together with recent extensive, in situ and ex situ experiments within the hydrothermal T-P range (200–500 °C, <1 kbar), do not provide evidence for additional or alternative Au-S-type complexes invoked in some older studies conducted before the discovery of the trisulfur ion; e.g., Au(HS)2(OH)2, Au(HS)(SO3)2, Au(HS)(H2S)2, Au2(S2)3 (Seward 1973; Hayashi and Ohmoto...
Gold HR-XANES spectra

It can be seen in Figure 3 that the use of HERFD mode provides a spectacular improvement in the spectral resolution, with each spectral feature neatly emphasized and background absorption removed, compared to “traditional” fluorescence or transmission acquisition modes. For example, the HR-XANES spectrum of the AuCl₄⁻ complex from a standard HAuCl₄ solution used for calibration (Fig. 3a) is characterized by a very intense pre-edge feature due to 2p-5d electron transition typical for square-planar coordinated Au³⁺ compounds (e.g., Pokrovski et al. 2009b) and at least three distinct post-edge resonances, whereas all these features are significantly damped in the nominal-resolution spectra. Likewise, the HR-XANES spectra of Au⁺ sulfur complexes from both hydrothermal experiments show a neatly expressed narrow white line at ~11920 eV and an intense post-edge resonance at ~11930 eV, whereas their transmission spectra exhibit high noise and barely distinguishable features (Fig. 3b). Note that even though nominal-resolution fluorescence spectra on similar solutions, using longer acquisition times and higher Au concentrations recorded in recent studies, were characterized by higher signal-to-noise ratios (Pokrovski et al. 2009a, 2015), they still had poorly resolved spectral shapes (Fig. 3b).

By contrast, there are small but systematic differences in HR-XANES spectra of the two experiments here, with a higher magnitude of the white line and a larger width of the post-edge resonance with its tail shifted to higher energies for experiment 1, as apparent in Figure 4. Because the exact electronic-level interpretation of the origin of different XANES spectra resonances for aqueous species of the same metal redox state and coordination is difficult at present, here we have chosen a more empirical, but far more practical, approach by direct comparisons with FDMNES-simulated XANES spectra of different Au-S species. Their structures were either generated by static DFT calculations or extracted from FPMD configurations as six representative geometric clusters averaged according to their respective weights (Online Materials1 Fig. OM3). It can be seen in Figure 4 that these theoretical XANES spectra of Au(HS)₂⁻ and Au(HS)S⁻ exhibit essentially the same differences as the experimental spectra, with higher white-line amplitude and a first post-edge main resonance shift toward higher energies for the Au(HS)S⁻ cluster. Note that minor variations in the geometry and Au-ligand interatomic distances of structures generated by both static DFT with different exchange-correlation functionals, and averaged FPMD clusters extracted from a large number of snapshots, were found to produce similar FDMNES-calculated XANES spectra for a given species, but distinct energy positions and resonance features among the different species (Online Materials1 Fig. OM3). It is thus concluded that, at least in the case of Au-S complexes formed at our conditions, the observed differences in the HR-XANES spectra are mostly due to the presence of additional S atoms in the next-nearest shell of Au, arising from the S⁻ ligand. Note that neither EXAFS nor lower-resolution XANES spectra (Pokrovski et al. 2009a, 2015; Trigub et al. 2017a) were able to provide such evidence that can only be gained from HR-XANES data such as those of the present study.

Furthermore, XANES spectra for two other, more stoichiometrically and structurally contrasting, Au⁺-S complexes, Au(HS)(H₂O)⁰ and Au(S⁻)₂, were also modeled using the FDMNES code (Fig. 5; Online Materials1 Fig. OM4). As ex-
Figure 4. Comparison between measured and calculated Au L₃-edge HR-XANES spectra of aqueous Au species. Measured spectra (solid curves) are from the two experiments of this study at 350 °C and 600 bar in acidic (exp 1) and slightly alkaline (exp 2) sulfidic solutions, in which Au(HS)S³⁻ and Au(HS)₂⁺ are predicted to be the major species, respectively (see Fig. 1b). Simulated XANES spectra are obtained by FDMNES calculations using the species structures from DFT geometry optimizations (dotted curves) and shown in ball-and-stick style (Au = pink; S = yellow; S³⁻ = blue; H = gray), and using the FPMD extracted representative clusters of configurations averaged according to their respective weights (see Online Materials). Gray arrows indicate differences in the experimental spectra, showing a slightly higher white-line amplitude and higher-energy broadening of the first post-edge resonance in the acidic solution. The same differences are apparent between the calculated spectra, supporting the change in Au speciation from Au(HS)S⁻ in acidic to Au(HS)⁺ in alkaline solution, which can only be directly revealed by the high-resolution spectroscopic approach.

expected, the calculated spectra of each species strongly contrast in shape and show significant energy shifts and amplitude differences compared with the experimental spectra. These differences further attest to the much smaller (if any) contributions of those species to the Au fluid-phase speciation and the resulting gold solubility measured in this study, as also confirmed by thermodynamic predictions (e.g., Fig. 1). In conclusion, our data provide direct spectroscopic evidence, which could only be gained using high-resolution XAS methods, for the existence of the Au(HS)S⁻ complex in hydrothermal fluids. Its existence is also consistent with available less direct spectroscopic, solubility, and molecular simulations acquired so far and interpreted by taking account of the S³⁻ ion in the aqueous sulfur speciation scheme (Mei et al. 2013; Pokrovski et al. 2015, 2019).

Implications

Our results highlight the potential of the high-resolution XAS methods for in situ studies of metal speciation in aqueous fluids at elevated temperatures and pressures and, in particular, for resolving minor atomic-level differences in aqueous species structures and coordination environment, otherwise inaccessible by classical spectroscopy methods (Fig. 4). Behind these small structural differences are “hidden,” however, large differences in complex stoichiometry and ligand identity that greatly impact the overall metal solubility and mobility in geological fluids (Fig. 1). As a result, to be fully successful in resolving chemical speciation, high-resolution spectroscopy should be combined with direct metal solubility measurements and thermodynamic and molecular modeling.

Through this combination, our study offers new insight into the long-standing debate about how gold could be massively carried by hydrothermal fluids and form large economic deposits on Earth. In particular, our study provides direct spectroscopic confirmation of the importance of sulfur radical species, such as the trisulfur ion S³⁻, for transporting gold in geological fluids. Gold-trisulfur complexes operate within the acidic-to-neutral pH range of sulfide/sulfate-bearing hydrothermal fluids at temperatures above 300 °C, by significantly increasing Au solubility and mobility compared to common Au complexes with Cl⁻ and

Figure 5. Comparison of the Au L₃-edge XANES spectrum measured in the hydrothermal fluid of experiment 1 with FDMNES-simulated spectra of different Au-complexes whose structures are generated by DFT geometry optimizations using the B3LYP functional. The best match of the experimental spectrum is achieved with the Au(HS)S⁻ complex, in agreement with thermodynamic calculations of Au speciation and solubility for this experiment (Fig. 1b).
HS⁻ ligands traditionally considered in economic geology and geochemistry research. As such, S²⁻ may significantly contribute to gold transfer and concentration in the convergent margin geodynamic settings hosting porphyry Cu-Au-Mo and related deposits that are characterized by large S fluxes and redox conditions of the sulfide-sulfate-sulfur dioxide (coexistence of sulfur, hydrogen, and oxygen) that can alter the chemical potential of these species. This has important implications for the understanding of gold mobility and speciation in hydrothermal systems.

In this work, we focus on the in situ spectroscopic characterization of gold in hydrothermal fluids, particularly focusing on the role of sulfur and its incorporation into gold minerals. The authors use synchrotron X-ray absorption spectroscopy (XAS) to study the gold-sulfur interface at the nanoscale, providing insights into the speciation and transport of gold in these systems.

Acknowledgments
I. Kieffer, F. Lahera, O. Proux, and R. M. Rovezi are acknowledged for their help with the synchrotron experiments. Special thanks go to Y. Joly for advice on the ANR Investissement d’Avenir (ANR-11-IDEX-0004-02), the CEA-CNRS CRG consortium, and the INSU-CNRS. The authors also acknowledge the Centre National de la Recherche Scientifique (IDRIS) for access to high-performance computing facilities. The authors thank A. Garofalo, P.-S. Fricker, T. D. Rhett, and N. L. Garrels for discussions. The authors acknowledge the ANR-10-EQPX-27-01, the CEA-CNRS CRG consortium, and the INSU-CNRS for access to high-performance computing facilities. The authors thank A. Garofalo, P.-S. Fricker, T. D. Rhett, and N. L. Garrels for discussions.

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American Mineralogist, vol. 107, 2022

Endnote:

1Deposit item AM-22-38008, Online Materials. Deposit items are free to all readers and found on the MSA website, via the specific issue’s Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2022/3Mar2022_data/ Mar2022_data.html).