In situ Raman spectroscopy identification of the \( S_3^- \) ion in S-rich hydrothermal fluids from synthetic fluid inclusions

Nicolas Jacquemet\(^1,\)*, Damien Guillaume\(^1\), Antoine Zwick\(^2\), and Gleb S. Pokrovski\(^1\)

\(^1\)Géosciences Environnement Toulouse (GET, UMR 5563), CNRS, Université de Toulouse, IRD, 14, avenue Edouard Belin, F-31400, Toulouse, France

\(^2\)Centre d'Elaboration de Matériaux et d'Etudes Structurales CEMES-CNRS-Université de Toulouse, 29 rue Jeanne Marvig, F-31055 Toulouse, France

*E-mail: nicolas.jacquemet@get.obs-mip.fr, nicolas_jacquemet@yahoo.fr

Revision 1

Manuscript #4524R

American Mineralogist, November 2013
ABSTRACT

The chemical forms of sulfur in geological fluids control the behavior of this element and associated base and precious metals in magmatic, hydrothermal, and metamorphic environments. However, these forms are insufficiently known at elevated temperature ($T$) and pressure ($P$). In this study, sulfur speciation in model aqueous solutions of thiosulfate and sulfur (~3 wt% of total S) was examined by in situ Raman spectroscopy on synthetic fluid inclusions at $T$-$P$-$\text{pH}$-redox conditions typical of porphyry Cu-Au-Mo deposits. Fluid inclusions were entrapped at 2 kbar and 600 or 700°C in quartz that served as a container for the high $T$-$P$ fluid. Then, the inclusion-bearing quartz samples were re-heated and examined by Raman spectroscopy as a function of $T$ and $P$ (up to 500°C and ~1 kbar). At $T < 200°C$, all fluid inclusions show sulfate ($\text{SO}_4^{2-}$±$\text{HSO}_4^-$) and sulfide ($\text{H}_2\text{S}$±$\text{HS}^-$) in the aqueous liquid phase and elemental sulfur ($S_8$) in the solid/molten phase; these results agree both with thermodynamic predictions of sulfur speciation and the common observation of these three S forms in natural fluid inclusions. At $T \geq 200$-300°C, in addition to these S species, the $S_3^-$ ion was found to appear and grow with increasing temperature to at least 500°C. The formation of $S_3^-$ is rapid and fully reversible; its Raman signal disappears on cooling below 200°C, and re-appears on heating. These new data confirm the recent findings of $S_3^-$ in similar aqueous solutions at $P$ of 5-50 kbar and $T \geq 250°C$; they suggest that $S_3^-$ may account for some part of dissolved sulfur and serve as a ligand for chalcophile metals in fluids from subduction zones and related Cu-Au-Mo deposits. This work demonstrates that in situ approaches are required for determining the true sulfur speciation in crustal fluids; it should encourage future spectroscopic investigations of natural fluid and melt inclusions at high temperatures and pressures close to their formation conditions.

Keywords: Hydrothermal fluid, Raman spectroscopy, sulfur, sulfate, sulfide, trisulfur ion, fluid inclusion
INTRODUCTION

The concentration and chemical forms of sulfur in hydrothermal fluids are controlling factors of metal transport and deposition as sulfide ores in magmatic-hydrothermal environments (e.g., Simon and Ripley 2011; Kouzmanov and Pokrovski 2012; references therein). The widely accepted model of sulfur speciation in crustal fluids at elevated temperatures is that sulfate, sulfide, and sulfur dioxide (the latter mostly in gas phase) are the major S species (Barnes 1979; Hedenquist and Lowenstern 1994; Seward and Barnes 1997). However, this model is largely based on studies of samples brought to the Earth’s surface and analyzed at near-ambient conditions, such as ores, silicate glasses, volcanic sublimates or fluid inclusions in minerals. Little attention has been given in previous work to the fact that sulfur chemistry and solubility in the fluid phase is very sensitive to temperature (T), pressure (P), redox, and acidity (pH) conditions (e.g., Simon and Ripley 2011). Thus, the major weakness in our knowledge of sulfur in deep and hot geological fluids is the lack of in situ approaches for studying such systems. The dominant presence of sulfide and sulfate in hydrothermal fluids has recently been challenged by Pokrovski and Dubrovinsky (2011) who used in situ Raman spectroscopy in a diamond-anvil cell to show that, in addition to those two ‘classical’ S species, the hypersulfide (or trisulfur) ion, S₃⁻, may be stable in S-rich aqueous solution at T from ~300 to at least 450°C and P from 5 to 50 kbar, corresponding to fluids from deep and cold domains of subduction zones. However, it remains uncertain to which extent S₃⁻, and other intermediate-valence S species, may form in less deep fluids responsible for the formation of most metal ore deposits in the crust (P < 1-2 kbar, depth ≤ 5 km).

The only direct witnesses of these fluids are fluid inclusions trapped by minerals during their growth or later deformation. Quantitative analyses of total sulfur concentrations in natural fluid inclusions were performed on inclusion populations by crush-leach methods (e.g., Banks
and Yardley 1992; Bray and Spooner 1992) or on individual inclusions by proton-induced X-ray emission (Ryan et al. 1993), synchrotron X-ray fluorescence (Cauzid et al. 2007), and recently laser ablation-inductively coupled plasma-mass spectrometry (Guillong et al. 2008; Seo et al. 2009; Catchpole et al. 2011, 2012). However, all these methods analyze bulk sulfur contents and cannot assess sulfur redox and speciation which require in situ spectroscopic techniques. Among them, Raman spectroscopy is the best suited, and was used for identifying sulfur species both in natural (e.g., Rosasco and Roedder 1979; Bény et al. 1982; Boiron et al. 1999; Giuliani et al. 2003) and synthetic (e.g., Binder and Keppler 2011) fluid inclusions at ambient temperature. To the best of our knowledge, the only studies at elevated temperatures are those of Jacquemet et al. (2005, 2012) and Pironon et al. (2007) who performed Raman spectroscopy analyzes on H₂S-bearing fluid inclusions up to 200°C. The sulfur species detected in all these studies are sulfate (SO₄²⁻), hydrogen sulfate (HSO₄⁻), sulfur dioxide (SO₂), hydrogen sulfide (H₂S, HS⁻), and elemental sulfur (S⁰).

The present study is aimed at investigating sulfur speciation in model aqueous S-bearing fluids at T-P conditions typical of hydrothermal-magmatic ore formation. For this purpose, synthetic fluid inclusions of such fluids were probed by in situ micro Raman spectroscopy to 500°C and 1 kbar. Results show that sulfur speciation at elevated T-P is different from what may be expected from low-temperature observations; they highlight the importance of in situ approaches for studying geological fluids.

MATERIALS AND METHODS

Experimental strategy and samples

Three model aqueous S-bearing solutions similar to those studied by Pokrovski and Dubrovinsky (2011), prepared from deionized degassed water and analytical-grade chemicals,
were investigated (Table 1): 1) thiosulfate (K$_2$S$_2$O$_3$-Na$_2$S$_2$O$_3$, hereafter named as Thios); 2) thiosulfate + HCl (K$_2$S$_2$O$_3$-Na$_2$S$_2$O$_3$-HCl, Thios-HCl) and 3) elemental sulfur + NaOH (S-NaOH). The total sulfur concentration in these solutions is about 3 wt%, which is comparable to that recently measured in fluid inclusions from porphyry Cu-Au-Mo deposits (Seo et al. 2009, 2012). The three model solutions were entrapped as fluid inclusions in quartz at 2 kbar and 600°C (Thios and Thios-HCl experiments) or 700°C (S-NaOH experiment). These T-P conditions correspond to early stages of the magmatic-hydrothermal evolution of porphyry deposits (e.g., Sillitoe 2010; Kouzmanov and Pokrovski 2012). The quartz crystals hosting inclusions were then examined on a heating stage by Raman micro spectroscopy from ambient temperature to 400 or 500°C (depending on the system, Table 1), covering the typical temperature range of hydrothermal ore deposit formation.

The chemical systems chosen in this study represent a good proxy for natural S-rich fluids in arc-related magmatic-hydrothermal systems, which are characterized by acidic-to-neutral pH and redox conditions close to that of the hematite-magnetite mineral buffer (Einaudi et al. 2003; Kouzmanov and Pokrovski 2012). Redox and acidity buffering in our experiments is achieved through the sulfide-sulfate and sulfate-hydrogensulfate exchange reactions, respectively (see below). These species are produced by breakdown of thiosulfate and dissolution of sulfur at elevated temperatures as shown by many previous experiments in hydrothermal reactors (e.g., Ohmoto and Lasaga 1982; Uyama et al. 1985; Pokrovski et al. 2008; references therein) and thermodynamic calculations below. Because redox reactions between sulfate and sulfide in aqueous solution are rather slow at moderate temperatures (Ohmoto and Lasaga, 1982), complete equilibrium is likely to be not attained in our runs below 200-250°C. Nevertheless, even at such moderate $T$, redox potential is controlled by the sulfate/sulfide ratio, which is almost constant, being imposed by the stoichiometry of decomposed thiosulfate (see below). The sulfate-sulfide
exchange rates rapidly increase with increasing $T$ (Ohmoto and Lasaga, 1982), all our runs at $T > 300^\circ C$ are likely to be close to equilibrium. In addition, as found by Pokrovski and Dubrovinsky (2011) for similar systems at higher pressures, the presence of polysulfide species in our concentrated solutions might further accelerate sulfate-sulfide exchange compared to dilute solutions studied so far (Ohmoto and Lasaga, 1982). Note also that in contrast to redox reactions which require electron transfers, protonation and ion pairing in aqueous solution are usually very fast processes, so that equilibrium among such species (e.g., $SO_4^{2-}, HSO_4^-, NaSO_4^-$) is achieved at any temperature within the run duration.

The calculated equilibrium distribution of dominant sulfur species in the three experimental systems at the $T$-$P$ conditions of the fluid entrapment and Raman spectroscopy analyses is shown in Figure 1. These calculations were performed using the available thermodynamic properties of aqueous and solid sulfur species from reference databases (SUPCRT, JANAF) with minor modifications (see Supplementary Table 1, and Pokrovski et al. 2009 for details), and the HCh computer code (Shvarov 2008). The activity coefficients were approximated using the extended Debye-Hückel equation for charged species and assumed to be unity for neutral species; these models are widely adopted in calculations of hydrothermal fluid-mineral equilibria (Helgeson et al. 1981; Oelkers et al. 2009; references therein). Note that variations of different model parameters (e.g., electrostatic radius, extended Debye-Hückel term) yield insignificant changes in calculated species fractions owing to: a) partial cancellation of activity coefficients in reactions involving similarly charged species as reagents and products (e.g., reaction 1 below), and b) sulfur redox balance imposed by the decomposition of thiosulfate and sulfur.

In the thiosulfate system at near-neutral pH ($5.4 \leq \text{pH} \leq 7.5$, depending on $T$ and $P$), the calculated distribution of sulfur species above 200$^\circ C$ corresponds to an overall sulfide-to-sulfate
ratio of 1 (Fig. 1), as imposed by redox balance according to the thiosulfate disproportionation reaction:

\[ \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} = \text{SO}_4^{2-} + \text{H}_2\text{S} \quad (1) \]

The formation of alkali ion pairs (NaSO_4^-, KSO_4^-), partial dissociation of H_2S to HS^-, and sulfate protonation yielding minor amounts of HSO_4^- (Fig. 1) are added to this reaction. At \( T < 300^\circ\text{C} \), a part of sulfur remains undissolved in the form of solid or molten elemental sulfur due to its low solubility at such temperatures. At more acidic pH (1.2 < pH < 5.5) in the Thios-HCl system below 400°C, a significant fraction of sulfur is in the elemental form; it dissolves with increasing temperature, accompanied by an increase of the amount of H_2S and HSO_4^-, which are the dominant species to 600°C (Fig. 1). Above 400°C, SO_2 is added to these species with fractions increasing with \( T \) and reaching ~ 20% of the total dissolved S at 600°C (Fig. 1). In the S-NaOH system (5.1 < pH < 7.5), the redox balance imposes a sulfide-to-sulfate ratio of ~ 3 in solution at all temperatures (Fig. 1), according to the disproportionation reaction of sulfur in water at near-neutral pH:

\[ 4 \text{S} + 4 \text{H}_2\text{O} = 3 \text{H}_2\text{S} + \text{SO}_4^{2-} + 2 \text{H}^+ \quad (2) \]

Above 300°C molten sulfur dissolves, and above 400°C SO_2 appears in the system with fractions less than 10% of the total dissolved sulfur.

The advantage of using these model systems is that they provide oxygen fugacity (f_{O_2}) and acidity buffering via the reactions:

\[ \text{H}_2\text{S} + 2 \text{O}_2 = \text{SO}_4^{2-} + 2 \text{H}^+ \quad (3) \]

\[ \text{SO}_4^{2-} + \text{H}^+ = \text{HSO}_4^- \quad (4) \]

yielding \( f_{O_2} \) values close to the hematite-magnetite buffer and pH values from 1.2 to 7.5 corresponding to the acidic-to-neutral region (pH of the neutrality point of pure water at our \( T-P \))
conditions is between 5.4 and 7.3). As a result, reactions (1) to (4) impose robust chemical
constraints (redox balance, $f_{O_2}$ and pH) on the experimental systems independently of possible
presence of low-to-moderate amounts of other S species (Pokrovski et al. 2009; Pokrovski and
Dubrovinsky 2011).

Preparation of synthetic fluid inclusions

Fluid inclusion syntheses were conducted following a procedure inspired from Sterner
and Bodnar (1984) and widely adopted in more recent studies (e.g., Lamb et al. 1996; Gibert et
al. 1998; Duc-Tin et al. 2007; Ulrich and Mavrogenes 2008; Zajacz et al. 2010, 2011; Frank et al.
2011; Zhang et al. 2012). Prefractured quartz lamellas were used to trap the fluid inclusions at $T$-
$P$ of the experiments. Quartz lamellas of ~5×2×1.5 mm size were prepared from inclusion-free
natural crystals sampled at Kerguelen Island. The lamellas were heated at 700°C for 15 min,
quenched in water to produce micro-fractures and dried at 700°C to evaporate the capillary water
from the micro-fractures. Gold capsules (40 mm length, 4 mm outside diameter, 0.2 mm wall
thickness) were loaded with 80 - 110 µL of aqueous solution and several quartz lamellas, then
sealed using an electric arc. Sealing was checked by weighing the capsules after they were heated
at 90°C for one hour.

The capsules were put in a cold-seal hydrothermal vessel placed in a horizontal furnace
and connected to a hydraulic pressure line in a configuration similar to that of Gibert et al.
(1998). The vessel was pressurized to 10-20 bar at ambient $T$, then heated to 600 or 700°C during
~1.5 hour. The thermal gradients were ~10°C over the length of the capsule. The final pressure
was adjusted to 2 kbar using the pressure line. After 6-17 days at the experimental $T$-$P$, the
reactor was cooled down in air stream, reaching $T < 100°C$ in less than 10 min. The gold capsules
were weighed to check for eventual leaks, punctured to release H$_2$S (gas), and opened to recover the quartz lamellas, which were double-polished for microscopy analyses. The fluid inclusion homogenization temperatures ($T_h$) were measured by microthermometry at the GET laboratory on a Linkam THMSG-600 heating-freezing stage connected to the microscope and a programmable thermal control unit. The stage was calibrated with pure CO$_2$ fluid inclusions in quartz from Camperio, Central Alps (Mullis et al. 1994; Poty and Stadler 1974) at the CO$_2$ triple (-56.6°C) and critical (+31.1°C) point temperatures and synthetic H$_2$O fluid inclusions in quartz at the H$_2$O triple (+0.2°C) and critical (375.13°C) point temperatures.

**Raman spectra acquisition and analysis**

Spectra were recorded at the CEMES laboratory (Toulouse, France) with a Jobin Yvon Horiba Xplora spectrometer in a back-scattering geometry and using a 532.1 (green) or 637.7 nm (red) solid-state laser as the excitation source (~1-2 μm spot size on the sample). The use of multiple excitation wavelengths allows for more robust identification of certain sulfur species, particularly those exhibiting Raman resonance phenomena, because their Raman peak intensities strongly vary as a function of laser frequency (e.g., Clark and Franks 1975; Clark and Cobbold 1978).

The acquisition was performed using an Olympus BX 5 microscope equipped with a Linkam heating-freezing stage and a dark-field long-working distance (10.5 mm) ×50 objective, in the 35-5042 cm$^{-1}$ spectral window with a grating of 600 lines/mm, an entrance slit of 100 or 200 μm, and a confocal hole of 100 μm; spectral resolution was ~5-10 cm$^{-1}$ and acquisition times varied from 7 to 60 seconds (depending on the signal intensity). The maximal laser power at the sample is ~15 mW. Some spectra were also acquired at lower laser power; they were compared
with the full power spectra to check for eventual laser-induced phenomena (see below). The
spectrometer was calibrated before and after each analytical session using the well-known Raman
stretching vibrations of pure silicon (520.6 cm\(^{-1}\) at 20°C), and oxygen (1555 cm\(^{-1}\)) and nitrogen
(2331 cm\(^{-1}\)) gas from the air. In addition, certain sharp Raman bands of our quartz samples
themselves (e.g., 464 cm\(^{-1}\), see below) provide a complementary check for the energy position
during a Raman session.

The microscope heating-freezing stage allowed the quartz chips to be re-heated and the
different phases in fluid inclusions (solid, liquid, vapor, and supercritical fluid) to be probed at
25, 200, 300, and 400°C (and 500°C for the S-NaOH run). Higher temperatures could not be
reached because of the inclusion’s decrepitation due to the elevated internal pressure. The
pressure inside the fluid inclusions containing vapor and liquid phases at \( T \leq 300°C \) corresponds
to the saturated vapor pressure of the system, which is likely to be slightly higher than the vapor
pressure of pure water or a water-salt solution due to partitioning of H\(_2\)S into the vapor phase (see
Table 1). All inclusions homogenize to liquid at 350-360°C (see below); above that temperature,
the pressure was estimated using linear isochores connecting the homogenization point with the
fluid entrapment point in \( P-T \) space (Fig. 2).

Raman spectra were processed using the Fityk software (Wojdyr 2010). A baseline,
closely matching that of the host quartz spectrum recorded near the fluid inclusion was subtracted
from the fluid inclusion spectrum. To determine their frequency position and area (or integrated
intensity), Raman peaks were fitted with a set of pseudo-Voigt functions, which are a linear
combination of a Lorentzian (L) and a Gaussian (G), with the L/G ratio varied between 0 (pure
Gaussian) and 1 (pure Lorentzian) to account for the wide range of band widths and profiles
depending on the species nature. This type of function was chosen for the sake of consistency
with the previous studies of S species in aqueous solution (e.g., Schmidt 2009; Pokrovski and
Dubrovinsky 2011; Pokrovski and Dubessy 2012); the results being insensitive to the exact function choice within fit uncertainties. Raman peak absolute areas are strongly dependent on the ensemble of acquisition parameters discussed above and the inclusion size and depth, so that normalization is required to be able to compare data for different temperatures and experiments. The only possible ‘internal standard’ in our experimental systems is water whose O-H stretching band between 2800 and 3800 cm\(^{-1}\) is little sensitive to the solute composition in the experimental water-dominated liquid-like solutions. The water band integrated intensity is a direct and smooth function of temperature and fluid density (e.g., Frantz et al. 1993); it was found to change relatively little in our \(T-P\)-density range. In the liquid phase, the O-H peaks area decreases by only a factor of two from ambient temperature to the homogenization point (~350°C, see below), then remains almost constant in the supercritical region at constant density (~0.7 g/cm\(^3\)). Consequently, when determining the peak areas of sulfur species, the spectra of the liquid and supercritical phase were normalized to this band; this allowed a quantitative comparison of their intensities at the same temperature in different experiments. The Raman frequencies and normalized areas of major species bands in the liquid and supercritical phase are reported in Supplementary Table 2. The overall uncertainties of peak areas are between 10 and 30 % of the value depending of the signal intensity.

RESULTS

Phase composition and relationships in the fluid inclusions

Optical microscopy and microthermometry show that all inclusions from the three experiments contain aqueous liquid and vapor at \(T \leq 300°C\) (Fig. 3a-3c). In addition to these phases, solid and molten (above ~115°C) elemental sulfur is detected in the Thios-HCl and S-NaOH experiments (Fig. 3b and 3c; see below for its Raman identification). Sulfur spheres were
also identified on the surface of the recovered quartz lamellas and internal walls of the capsule at ambient conditions after these experiments by optical and scanning electron microscopy (Supplementary Fig. 1). The occurrence of elemental sulfur agrees with thermodynamic predictions of its solubility (Fig. 1).

All inclusions homogenize in a narrow temperature range, with the mean homogenization temperatures ($T_h$) values of 350±2, 352±2, and 360±3°C (± standard deviation) for the Thios, Thios-HCl, and S-NaOH runs as based on 6, 12, and 11 data points, respectively. These $T_h$ values are consistent with the calculated density of the fluids at experimental $T$-$P$ (0.70±0.07 g/cm$^3$ in Thios and Thios-HCl runs, and 0.60±0.06 g/cm$^3$ in S-NaOH runs), assuming that they may be approximated by equivalent NaCl-H$_2$O solutions of same weight concentration and using the SoWat software (Driesner and Heinrich 2007). Such an approximation is more reliable than that by pure water, because the experimental solutions contained Na$^+$ and anions similar to Cl$^-$ (SO$_4^{2-}$, OH$^-$, HSO$_4^-$); its expected uncertainty should not exceed 10 % of the density value in the experimental $T$-$P$ range (e.g., Pokrovski et al. 2009). The density and $T_h$ values strongly suggest that all inclusions in each of the three experiments belong to a single population trapped at the experimental $T$-$P$ (600 or 700°C at 2 kbar).

**Raman spectra of the host quartz**

Raman spectra of the host quartz at ambient conditions (Supplementary Fig. 2) are characterized by three major peaks at 132, 208 and 469 cm$^{-1}$, and a number of minor peaks (~270, 360, 400, 700, 810, 1160 cm$^{-1}$). This pattern is in good agreement with the well-documented Raman spectra of the main peak positions of α-quartz (~130, ~210, and 464-467 cm$^{-1}$ at ambient conditions; RRUFF database at http://rruff.info/). With increasing temperature, most
bands exhibit a small (~3-5 cm\(^{-1}\)) shift towards lower frequencies, and the relative intensities of the low-frequency bands (< 300 cm\(^{-1}\)) increase with increasing \(T\), consistent with the reported temperature dependence of quartz Raman spectra (e.g., Shapiro et al., 1967). The largest changes are observed for the ~210 cm\(^{-1}\) band that exhibits a significant low-energy shift and increasing broadening with temperature, due to changes in the \(\alpha\)-quartz network when approaching the \(\alpha\)−\(\beta\) transition (~573°C, Shapiro et al. 1967).

### Raman spectra of the vapor and solid phases

The detectable gas species in the vapor phase of all inclusions below \(T_h\) are H\(_2\)S and H\(_2\)O (Fig. 4a), unambiguously identified by their well-known symmetric stretching vibration mode frequencies at respectively 2607-2612 cm\(^{-1}\), and 3630-3660 cm\(^{-1}\), depending on temperature and pressure (Frantz et al. 1993; Burke 2001; Frezzotti et al. 2012). In addition, H\(_2\) (gas) was found in the Thios experiment at 300°C (4156 cm\(^{-1}\), Burke 2001). The solid phase in the Thios-HCl and S-NaOH experiments gives three main peaks at ~153, ~221 and ~469 cm\(^{-1}\) (Fig. 4b), which belong to the S\(_8\) solid or molten elemental sulfur (Pasteris 2001; Giuliani et al. 2003; Frezzotti et al. 2012). Note that although the main stretching vibration of S\(_8\) (462-474 cm\(^{-1}\) in different studies) is very close to that of SiO\(_2\) (~464 cm\(^{-1}\)), it cannot come from the host quartz because the other main quartz peaks (~130 and ~210 cm\(^{-1}\), see above) showing no overlap with the S\(_8\) spectrum are very minor in the sulfur spectrum of Figure 4b. The S\(_8\) molecule corresponds to the thermodynamically stable sulfur allotrope at these conditions (Steudel 2003).

### Raman spectra of the liquid and supercritical fluid phases
In the three systems, the Raman spectra of the liquid phase are dominated by the broad asymmetric band of H$_2$O around 3400 cm$^{-1}$ at ambient conditions. As the temperature increases, the intensity of the low-frequency side of the band decreases while the high-frequency side is shifted towards greater frequencies. The band shape and its evolution with temperature are in agreement with those described in detail in previous Raman studies of pure water; they mostly reflect changes in hydrogen bonding (e.g., Frantz et al. 1993; references therein). No detectable differences in the shape and evolution of the H$_2$O band were found among the three experiments, which is consistent with the low solute concentrations relative to that of H$_2$O (e.g., Dubessy et al. 2002).

Among the solute species, SO$_4^{2-}$ is identified in the three systems according to its characteristic S-O$_4$ symmetric stretching vibration between 970 and 980 cm$^{-1}$ (depending on temperature; Dubessy et al. 1992; Schmidt 2009). Note that the spectral resolution does not allow sulfate-alkali ion pairs to be distinguished from the free SO$_4^{2-}$ ion. Thus this band represents the whole sulfate form composed of thermodynamically distinct aqueous species (Supplementary Table 1). Sulfate is visible in the whole temperature range covered by measurements (25-400°C) in the Thios and Thios-HCl systems, and from 25 to 300°C in the S-NaOH system (Fig. 5a-5c). The sulfate peak intensity is highest in the Thios system at near-neutral pH; it decreases with increasing temperature and decreasing pH (cf. Thios versus Thios-HCl). This evolution is in agreement with the thermodynamic calculations predicting the increasing protonation of SO$_4^{2-}$ to form the hydrogensulfate ion (HSO$_4^-$) at acidic pH and elevated $T$ (Fig. 1). The latter species, with a stretching vibration at ~1050 cm$^{-1}$ (Dubessy et al. 1992; Rudolph 1996), is identified in the Thios-HCl experiment at 200°C (Fig. 5b), but at higher $T$ its characteristic Raman peak is hidden within a quartz band and the far more intense second-order overtone of the S$_3^-$ band (see below).
Aqueous hydrogen sulfide (H$_2$S), having an S-H$_2$ stretching vibration at ~2590 cm$^{-1}$ (e.g., Dubessy et al. 1992) is clearly visible in the three systems in the whole $T$ range covered by measurements (Fig. 5a-5c). In addition, its ionic counterpart (HS$^-$) with an S-H stretching vibration at ~2570 cm$^{-1}$ (Meyer et al. 1983) is identified in the Thios system from 25 to 200°C, but disappears in favor of H$_2$S at higher $T$ (Fig. 5a), in agreement with thermodynamic predictions (Fig. 1).

No thiosulfate ions (S$_2$O$_3^{2-}$), which have a narrow SO$_3$ stretching band at ~1000 cm$^{-1}$ easily distinguishable from sulfate (Meyer et al. 1980), and an intense S-S stretching band at ~450 cm$^{-1}$, which should appear at the low-frequency side of the 464 cm$^{-1}$ band of quartz, were detected in the solutions. The absence of thiosulfate is consistent with its irreversible breakdown at temperatures above 200°C (e.g., Pryor 1960; Pokrovski and Dubrovinsky 2011). No sulfur dioxide (SO$_2$, ~1150 cm$^{-1}$, Ni and Keppler 2012; references therein) was observed probably both due to its small amounts at $T < 400$-500°C (Fig. 1) and the overlap of its characteristic peak with those of quartz. No polysulfide ions (S$_n$S$_{2-n}^{2-}$), characterized by multiple S-S stretching vibrations between 350 and 480 cm$^{-1}$ (e.g., Steudel 2003; Tsujimura et al. 2004; references therein) were detected likely owing to their minor amounts ($\leq 10\%$ of total sulfur) as predicted by thermodynamics at $T < 200°C$ (Fig. 1) and overlaps with the intense quartz bands that dominate the Raman low frequencies ($< 500$ cm$^{-1}$).

The most remarkable feature of the Raman spectra in the three experiments above 200°C is the growth of the trisulfur ion (S$_3^{2-}$), which is unambiguously identified by its characteristic resonance spectrum consisting of the enhanced symmetric S-S stretching vibration ($\nu$) at ~530-540 cm$^{-1}$ and its higher-order overtones 2$\nu$, 3$\nu$, 4$\nu$, and 5$\nu$ at ~1070, ~1600, ~2130, and ~2650 cm$^{-1}$, respectively (Fig. 5a-5c). This particular Raman pattern is due to a resonance phenomenon...
favored by the enhanced absorption of the laser light by this blue species at the laser wavelengths used (see Pokrovski and Dubrovinsky 2011 for details and references). The Raman pattern of $\text{S}_3^-$ is unique and cannot be mixed up with that of any other sulfur species (Chivers and Drummond 1972; Chivers and Elder 2013; references therein). The S-S bending vibration ($\delta$) of $\text{S}_3^-$ at $\sim 220$ cm$^{-1}$ and resonance-induced combinatory bending-stretching overtones (e.g., $\nu + \delta$, $\nu - \delta$, $2\nu + \delta$, $2\nu - \delta$, Clark and Franks 1975; Pokrovski and Dubrovinski 2011; Pokrovski and Dubessy 2012) are too weak and/or (partially) hidden by the more intense quartz peaks to be detectable in the inclusions. Similarly, the third Raman active vibrational mode of $\text{S}_3^-$, the S-S asymmetric stretch at $\sim 580$ cm$^{-1}$, was not detected because of its low intensity in the Raman resonance spectrum dominated by the S-S stretch symmetric vibration (Chivers and Elders 2013; references therein).

The S-S stretch vibration of the $\text{S}_3^-$ ion appears at $200^\circ\text{C}$ as a high-frequency shoulder on the large quartz band at $\sim 464$ cm$^{-1}$ and grows, together with its corresponding overtones, with increasing temperature in the three systems (Fig. 5a-5c). The formation of $\text{S}_3^-$ is found to be rapid and fully reversible with temperature changes. On heating, the intensity of the $\text{S}_3^-$ bands stabilizes within a few minutes following the $T$ rise and remains constant during at least several hours at a given $T$. Cooling the inclusion below 300-200$^\circ\text{C}$ results in almost instantaneous disappearance of $\text{S}_3^-$ and quantitative return to the sulfate-sulfide spectrum (Fig. 6). These findings strongly suggest that $\text{S}_3^-$ is not a short-lived transient complex that forms during a certain step in redox reactions between sulfide, sulfate, and sulfur, but it is rather a product of thermodynamic equilibrium among these sulfur species.

The effect of the laser beam power on the $\text{S}_3^-$ formation was checked in the three systems. Spectra on the same inclusions acquired with a laser power reduced by a factor of 2 to 10 were identical to those obtained at full laser power, when normalized to the water band
These results demonstrate that the lasers used in this study neither induce the \(S_3^-\) formation through photochemical reactions, nor locally heat the inclusion which would have increased the \(S_3^-\) abundance. Note that the laser wavelength affects significantly the \(S_3^-\) Raman intensity, which is roughly 50% higher when acquired using the 637.7 nm (red) laser compared to that of the 532.1 nm (green) laser, if \(H_2O\) is used as internal standard (Supplementary Fig. 4). This is in agreement with the maximum absorbance of the \(S_3^-\) blue chromophore ion at 610-620 nm, which favors a resonance phenomenon with the red laser having a wavelength closer to this maximum (Clark and Franks 1975).

**DISCUSSION**

**Comparison with published data**

Our results show that \(S_3^-\) is stable in the aqueous liquid and supercritical fluid phases containing \(~3\) wt% of total dissolved sulfur as sulfate and sulfide, at \(T\) from 200-300 to at least 500\(^\circ\)C and \(P\) to \(~1\) kbar. The systematic growth of the normalized area of the \(S_3^-\) main Raman peak in this temperature range in the three studied systems (Fig. 7) suggests that this species is likely to be also stable at higher temperatures corresponding to the inclusion entrapment (600-700\(^\circ\)C). Accurate quantification of \(S_3^-\) amounts is not possible in the present study due to a) intrinsic limitations of Raman spectroscopy applied to fluid inclusions (e.g., Roedder 1984; Wopenka and Pasteris 1986; Pasteris et al. 1988), b) the presence of numerous intense bands of quartz hiding the less intense peaks of dissolved sulfur species, and c) the absence of adequate standards for the different sulfur species that must be measured in similar fluid inclusions prepared under identical conditions to be comparable with the experimental samples. Nevertheless, a very rough estimation of \(S_3^-\) concentrations may be tempting by comparing the
normalized areas of the $S_3^-$ main peak ($A_{S_3^-}$) from this study (Fig. 7, Supplementary Table 2) with those recently obtained on similar thiosulfate solutions in silica-glass capillary cells by Pokrovski and Dubessy (2012) who used different calibration solutions of sulfate and sulfide to quantify the $S_3^-$ concentration. Comparison of the $A_{S_3^-}$ values of the present work ($A_{S_3^-} \sim 0.5-1.0$ in 0.5 m $K_2S_2O_3$ solutions at 400-500°C, Fig. 7) with those of their study ($A_{S_3^-} \sim 1.5-3.0$ in a 1 m $K_2S_2O_3$ solution at similar $T$-$P$ in which $S_3^-$ attains $\sim 0.3$ m total S, Pokrovski and Dubessy 2012) suggests that $S_3^-$ accounts for at least 0.1 m ($\sim 0.3$ wt%) of dissolved sulfur in the Thios and Thios-HCl experiment.

Although $S_3^-$ has been reported by chemists since 1970s in a variety of different media such as non-aqueous solvents (Chivers and Drummond 1972; Clark and Cobbold 1978; Chivers and Lau 1982), salt melts (Giggenbach 1971), silicate and borate glasses (Winther et al. 1998), pigment minerals (Clark and Cobbold 1978; Reinen and Lindner 1999), and alkali metal-sulfur butters (Chivers and Elder 2013), little information is available about $S_3^-$ in aqueous solution. A blue color was observed $\sim 100$ years ago when sulfur was heated in water with traces of basic salts (see Chivers 1974 and Chivers and Elder 2013 for overviews of old studies), followed much later by UV-visible spectroscopy measurements on aqueous polysulfide solutions to 260°C performed by Giggenbach (1971) who suggested the formation of another hypersulfide ion, $S_2^-$. However, it is now admitted, on the basis of numerous spectroscopic and computational studies of $S_3^-$ in different media since mid-1970 (Chivers 1974; Steudel 2003, Chivers and Alder 2013; references therein), that the blue color is due to $S_3^-$. Batch-reactor studies of sulfur speciation in S-rich high-$T$ aqueous solutions similar to those of this study did not detect $S_3^-$ (Dadze and Sorokin 1993; Pokrovski et al. 2008) likely because of its rapid breakdown to sulfate, sulfide, and sulfur during solution sampling. Recent in situ studies of sulfur by Raman spectroscopy at high
Such conditions are thermodynamically unfavorable for $S_3^-$ formation, which requires presence of both oxidized and reduced sulfur forms. Only three in situ Raman spectroscopy studies at redox conditions potentially favorable for $S_3^-$ formation (sulfate-sulfide coexistence) have been published so far. Bondarenko and Gorbaty (1997) investigated the S-H$_2$O system to 500°C and 1 kbar and reported intense Raman bands at 520-540 and 1060-1090 cm$^{-1}$ that match very well the $S_3^-$ stretching vibration and its second overtone, but tentatively attributed these bands to other species (SO$_3$ and/or S$_2$O$_5^{2-}$). Yuan et al. (2013) examined the S-H$_2$O-CH$_4$-D$_2$O system to ~400°C and 1 kbar in short (< 0.7 h) heating runs, and found at some temperatures, together with H$_2$S, HSO$_4^-$ and SO$_2$, intense bands around 500 and 1400 cm$^{-1}$, which were not identified in their study. The former band might be due to $S_3^-$, but acidic conditions and presumably low S concentrations in their experiments might render its formation unfavorable. Pokrovski and Dubrovinsky (2011) showed that $S_3^-$ is stable above 250°C in solutions similar to those of this study but at much higher pressures (5-50 kbar). The increasing stability of $S_3^-$ at elevated $T$-$P$ was further confirmed by theoretical quantum-chemistry modeling (Tossell 2012).

**Implications**

This study and the recent findings discussed above clearly show that $S_3^-$ forms at high temperatures in S-rich aqueous systems (~few wt% S) containing sulfate, sulfide, and elemental sulfur. The latter three S redox forms are commonly found in natural fluid (Rosasco and Roedder 1979; Bény et al. 1982; Boiron et al. 1999; Giuliani et al. 2003) and melt (Klimm and Botcharnikov 2010) inclusions from different geological contexts. It is thus very likely that the entrapped original fluids (and probably melts) in such systems contained $S_3^-$ at elevated $T$-$P$. However, the majority of Raman studies on such inclusions have been conducted at near-ambient...
conditions, where $S_3^-$ is not stable. The detection of $S_3^-$ in such samples thus requires their heating close to entrapment conditions, which may be technically challenging. Another complication of sulfur speciation analyses in quartz-hosted natural fluid inclusions arises from post-entrapment modifications, such as loss of hydrogen by diffusion (Bodnar 2003; Bakker 2009; references therein) and gain of copper and probably other components (e.g., Lerchbaumer and Audétat 2012). These processes significantly and irreversibly alter the original fluid composition, pH, and redox state. Thus, potential detection of $S_3^-$ and other intermediate redox sulfur forms originally present in high-temperature fluids and melts from natural inclusions is strongly conditioned by the inclusion’s post-entrapment evolution. Nevertheless, the findings of this study should encourage people working on natural fluid and melt inclusions to perform Raman analyses at elevated temperatures to estimate more reliably the sulfur speciation, at least in inclusions that did not ‘suffered’ too much from their post-entrapment history.

The results of the present work in fluid inclusions, together with preliminary data of Pokrovski and Dubessy (2012) in silica-glass capillary cells, extend the pressure range of the $S_3^-$ stability domain to conditions of S-rich magmatic-hydrothermal environments such as porphyry systems hosting large part of economic gold, copper, and molybdenum resources. The chemical similarity of $S_3^-$ to regular polysulfides $S_nS_{2n}^-$, which are known to have strong bonding affinities for soft metals like Au or Cu (Pokrovski et al. 2009), suggests that $S_3^-$ is capable of forming stable complexes with such metals. This was recently qualitatively confirmed by quantum-chemical calculations of Cu-$S_3$ and Au-$S_3$ complexes (Tossell 2012; Mei et al. 2013). The $S_3^-$ ion may thus be a major carrier of chalcophile metals in fluids from porphyry systems, as initially hypothesized by Pokrovski and Dubrovinsky (2011); however, experimental data on the stability constants of $S_3^-$ itself and metal-$S_3^-$ complexes are required to make quantitative predictions of metal transport. The fluids investigated in this study contained dissolved gold supplied by the Au
capsules. Work is currently in progress to determine Au concentrations in synthetic inclusions by LA-ICP-MS and to correlate such analyses with the in situ sulfur speciation reported here in order to quantify the role of $S_3^-$ in Au transport at conditions of magmatic-hydrothermal gold deposits.

Acknowledgments

We are grateful to Editor D. Baker, reviewer B. Mysen, and two anonymous reviewers for their comments. This work was funded by the French National Research Agency (grant SOUMET ANR-2011-Blanc SIMI 5-6 009), and University of Toulouse (grant CO2MET).
REFERENCES CITED


Barnes, H.L. (1979) Solubilities of Ore Minerals. In H.L. Barnes, Ed., Geochemistry of

the CO₂-H₂S-H₂O-S system - Microthermometry and Raman microprobe (MOLE)
analysis - Thermochemical interpretations. Chemical Geology, 37, 113-127.

Planetary Sciences Letters, 301, 190-198.

Course Series, Mineralogical Association of Canada, Vancouver, British Columbia.

Boiron, M.-C., Moissette, A., Cathelineau, M., Banks, D., Monnin, C., and Dubessy, J. (1999)
Detailed determination of palaeofluid chemistry: an integrated study of sulphate-
volatile rich brines and aquo-carbonic fluids in quartz veins from Ouro Fino (Brazil).
Chemical Geology, 154, 179-192.

Bondarenko, G.V. and Gorbaty, Y.E. (1997) In situ Raman spectroscopic study of sulfur-
saturated water at 1000 bar between 200 and 500 °C. Geochimica et Cosmochimica
Acta, 61, 1413-1420.

with photoionization micro-thermal conductivity detectors - application to magmatic
MoS$_2$ and other H$_2$O-CO$_2$ and H$_2$O-CH$_4$ fluids. Geochimica et Cosmochimica Acta, 56, 261-272.


Rulers and Witnesses of Processes within the Earth. Society of Economic Geologists
Special Publication, 10, 285-313.


gold speciation in sulfur-bearing hydrothermal fluids from in situ X-ray absorption 
spectroscopy and quantum-chemical modeling. Geochimica et Cosmochimica Acta, 73, 
2506-2527.

Poty, B. and Stalder, H.A. (1974) Fluid inclusions studies in quartz from fissures of Western and 
Central Alps. Schweizerische Mineralogische und Petrographische Mitteilungen, 54, 
717–752.

Pryor, W.A. (1960) The kinetics of the disproportionation of sodium thiosulfate to sodium sulfide 
and sulfate. Journal of the American Chemical Society, 82, 4794-4797.

Reinen, D. and Lindner, G.-G. (1999) The nature of the chalcogen colour centres in ultramarine-
type solids. Chemical Society Reviews, 28, 75-84.

over a broad temperature range: a Raman study. Zeitschrift für Physikalische Chemie, 
194, 73-95.

Ribbe, Ed., Fluid inclusions, 12, p 79-108. Reviews in Mineralogy, Mineralogical 
Society of America, Washington D.C..

Rosasco, G.J. and Roedder, E. (1979) Application of a new Raman microprobe spectrometer to 
nondestructive analysis of sulfate and other ions in individual phases in fluid inclusions 

and its application to study ore metal segregation between magmatic brine and vapor. 


Table 1. Chemical compositions and temperature and pressure conditions of fluid inclusion synthesis and Raman measurements.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Composition</th>
<th>$T$ (°C), $P$ (bar) of fluid inclusion entrapment</th>
<th>$T$ (°C), $P$ (bar) of Raman measurements</th>
</tr>
</thead>
</table>
| Thios      | 0.45 m K$_2$S$_2$O$_3$ + 0.05 m Na$_2$S$_2$O$_3$ | 600, 2000                                | 25, $P_{sat}$*  
                        |                                         | 200, $P_{sat}$  
                        |                                         | 300, $P_{sat}$  
                        |                                         | 400, 500†     |
| Thios-HCl  | 0.42 m K$_2$S$_2$O$_3$ + 0.04 m Na$_2$S$_2$O$_3$ + 0.51 m HCl | 600, 2000                                | 25, $P_{sat}$  
                        |                                         | 200, $P_{sat}$  
                        |                                         | 300, $P_{sat}$  
                        |                                         | 400, 500†     |
| S-NaOH     | 1.01 m S + 0.37 m NaOH                         | 700, 2000                                | 25, $P_{sat}$  
                        |                                         | 200, $P_{sat}$  
                        |                                         | 300, $P_{sat}$  
                        |                                         | 400, 400†     |
                        |                                         |                                         |                                         |                                         | 500, 900†     |

Notes: m designates molinity (number of moles of solute per one kg of solution).

* $P_{sat}$ = saturated vapor pressure in the two-phase liquid-vapor system, which is approximated by the H$_2$O-NaCl-H$_2$S system, using the PVTX properties of the NaCl-H$_2$O system from Driesner and Heinrich (2007), H$_2$S vapor-liquid partitioning coefficients from Johnson et al. (1992), the sulfur liquid-phase speciation from Figure 1, and approximate mass balance of sulfur between the vapor and liquid phase. These estimations indicate that $P_{sat}$ values in the synthesized fluid inclusions are ~1, 20, and 90 (±10-20%) bar at 25, 200, and 300°C, respectively.

† pressure is determined using the isochores in Fig. 2.
Figure 1. Calculated sulfur species distribution, pH, and oxygen fugacity ($f_{O2}$ in bar) at different T-P conditions in the three systems, using thermodynamic properties of sulfur species available in the literature (see Supplementary Table 1). The fraction of $SO_4^{2-}$ stands for the sum of $SO_4^{2-}$ and its ion pairs NaSO$_4^{-}$ and KSO$_4^{-}$; $HSO_4^{-}$ stands for the sum of HSO$_4^{-}$ and its ion pairs KHSO$_4^{0}$ and NaHSO$_4^{0}$; minor sulfur species (< 1% of total dissolved sulfur) are not shown for clarity.
Figure 2. Pressure-temperature conditions of the fluid inclusion synthesis and Raman spectroscopy analyses.
Figure 3. Fluid inclusion microphotographs obtained during microthermometry measurements in the Thios (a), Thios-HCl (b), and S-NaOH (c) systems. L: liquid, V: vapor, SF: supercritical fluid, S(s): solid elemental sulfur, S(l): molten elemental sulfur.
Figure 4. Raman spectra of aqueous liquid and vapor at 300°C (a) and molten sulfur at 300°C (b) in a representative fluid inclusion from the Thios-HCl experiment. The laser spots on the different phases are shown by crosses. A Raman spectrum of quartz recorded in the proximity of the fluid inclusion is also shown in panel b; the vertical dashed lines indicate the quartz peaks positions. The Raman frequencies of molten sulfur (153, 221, and 469 cm$^{-1}$) correspond to those of the S$_8$ molecular polymorph (Pasteris et al. 2001; Giuliani et al. 2003; Frezzotti et al. 2012).
Resonance bands of $S_3^-$:

(a) Resonance bands of $S_3^-$
- $3\nu_{S-S}$
- $4\nu_{S-S}$
- $5\nu_{S-S}$

(b) Resonance bands of $S_3^-$
- $2\nu_{S-S}$

Raman intensity (a.u.) vs. Wavenumber (cm$^{-1}$)

(a) Raman intensity (a.u.) vs. Wavenumber (cm$^{-1}$)
(b) Raman intensity (a.u.) vs. Wavenumber (cm$^{-1}$)

Resonance bands of $S_3^-$:
- $3\nu_{S-S}$
- $4\nu_{S-S}$
- $5\nu_{S-S}$

SO$_4^{2-}$

$H_2S$($HS^-$)

$HS^-$+$H_2S$

$H_2O$

Resonance bands of $S_3^-$:
- $2\nu_{S-S}$

SO$_4^{2-}$

$HSO_4^-$

$SO_4^{2-}$

$H_2O$

$H_2S$($HS^-$)

$HS^-$+$H_2S$

$H_2O$

Resonance bands of $S_3^-$:
- $3\nu_{S-S}$
- $4\nu_{S-S}$
- $5\nu_{S-S}$
**Figure 5.** Raman spectra of the aqueous liquid and supercritical phase in synthesized fluid inclusions, obtained from the Thios (a), Thios-HCl (b), and S-NaOH (c) systems at the indicated temperatures. The spectra are normalized to 12, 20, and 60 seconds of acquisition in the three systems, respectively, and are offset vertically. The black dots indicate the quartz peaks. At 500°C in the S-NaOH system, the spectra acquisition is affected by quartz surface dis ordering near the α–β quartz transition that may be induced by the laser beam spot, resulting in noisier spectra, peak broadening and intensity increase of the 800 cm\(^{-1}\) peak belonging to β-quartz.
Figure 6. Raman spectra of the aqueous liquid phase at 200°C obtained on heating to and cooling from 400°C in the Thios-HCl experiment. The spectra are normalized to 15 seconds of acquisition time and offset vertically. The black dots indicate the quartz peaks. The quartz peak at ~800 cm\(^{-1}\) obtained at 200°C on cooling is broadened and enhanced due to quartz disordering/phase transition as also observed in the S-NaOH experiment at higher temperature (Fig. 5c).
Figure 7. Normalized integrated intensity of the $S_3^-$ main Raman peak ($A_{530}/A_{2800-3800}$, where $A_{530}$ and $A_{2800-3800}$ stand, respectively, for the areas of the S-S stretching vibration of $S_3^-$ at ~530 cm$^{-1}$ and O-H stretching vibrations of H$_2$O between 2800 and 3800 cm$^{-1}$) acquired with the 532 nm laser in the aqueous liquid and supercritical fluid phase in the three systems as a function of temperature.