# The role of sulfur in molybdenum transport in hydrothermal fluids: Insight from in situ synchrotron XAS experiments and molecular dynamics simulations

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# The role of sulfur in molybdenum transport in hydrothermal fluids: insight from *in situ* synchrotron XAS experiments and molecular dynamics simulations

[1*]*Weihua Liu*, [2]*Barbara Etschmann*, [1]*Yuan Mei*, [2]*Qiushi Guan*, [3]*Denis Testemale, and* [2]*Joël Brugger*

1. CSIRO Mineral Resources, Clayton, Vic, 3168, Australia
2. School of Earth, Atmosphere and Environment, Monash University, Clayton, Vic, 3800, Australia
3. Université Grenoble Alpes, CNRS, Grenoble INP, Institut Néel, 38000 Grenoble, France

**Corresponding author*

## Abstract

Knowledge of the identity and thermodynamic properties of aqueous molybdenum species at elevated temperature is important for understanding the extraction of Mo from source rocks and the formation of hydrothermal deposits. Chlorine and sulfur are two major components in crustal fluids. Several studies have investigated Mo speciation and solubility in chloride-bearing hydrothermal fluids, but little is known about the behaviour of Mo in sulfur-bearing systems at elevated temperature. We used *in-situ* synchrotron X-ray absorption spectroscopy (XAS) measurements and molecular dynamics (MD) simulations to investigate the predominant Mo species in S-bearing (0.04-2 m NaHS) solutions at 30-394 °C (XAS) and 77-300 °C (MD) and 800bar. The XAS data show that, similar to previous room temperature studies, the $S^{2-}$ ion progressively replaces $O^{2-}$ in molybdate ($MoO_4^{2-}$) to form thiomolybdates ($MoO_{4-x}S_x^{2-}$, x =1, 2, 3, 4) with increasing NaHS concentrations at temperature up to 394 °C. The MD simulations confirm the identity and structure of the thiomolybdate species

determined from the XAS experimental data. The speciation calculations based on the formation constants for the thiomolybdate species extrapolated from the room temperature data agree well with the experimental results. This study indicates that thiomolybdate species are likely to be important in transporting Mo in sulfur-bearing, weak-acidic to alkaline, hydrothermal fluids under reduced (sulfide stable) conditions in the Earth crust. Current models of Mo transport in hydrothermal ore fluids need to be re-evaluated to take into account the thiomolybdate species.

# 1. Introduction

Molybdenum (Mo) is mainly mined from magmatic hydrothermal deposits (e.g., porphyry Cu-Mo-Au deposits), where the metals including Mo are transported in high temperature-pressure geological fluids and deposited to form ores under favourable physiochemical conditions (e.g., Seedorff et al., 2005). Molybdenum is also enriched in other hydrothermal systems, including IOCG deposits (e.g., Olympic Dam, South Australia, Ehrig et al. 2012; Uranium roll-front deposits, Bonnetti et al. 2020; Bullock and Parnell 2017). Furthermore, elevated molybdenum concentrations are also found in sedimentary rocks such as shales, and Mo is commonly used as a paleoredox indicator (e.g., Asael et al. 2018; Tessin et al. 2018). Therefore, the identity and thermodynamic properties of the aqueous Mo species prevalent in crustal fluids are important for understanding the formation of hydrothermal Mo deposits and constrain the use of molybdenum as a geological tracer.

A number of experimental and theoretical studies have investigated Mo speciation and solubility in hydrothermal fluids, and the partitioning of Mo between melt, vapour and aqueous phases (e.g., Candela and Holland 1984, Dadze et al. 2017, 2018; Keppler and Wyllie, 1991; Kudrin, 1989, Rempel, et al., 2006, 2008, 2009; Ulrich and Mavrogenes, 2008, Zajacz et al., 2017). These studies suggest that Mo(VI) species predominate under a wide range of redox conditions from oxidised to $MoO_3$(s)/$MoO_2$(s) stable conditions. In pure water, the hydrogen molybdate ($HMoO_4^-$) and molybdate ($MoO_4^{2-}$) ions are thought to be dominant, and their ionization constants were determined up to 300 ˚C by Minubayeva and Seward (2010); molybdic acid, $H_2MoO_4$(aq), predominates only under highly acidic conditions, especially at T>100 ˚C (Borg et al. 2012). Recently, Dadze et al. (2017) obtained the solubility constants for crystalline $MoO_3$(s) in acidic solutions up to 350 ˚C as $H_2MoO_4$(aq) and $HMoO_4^-$, and Saha et al. (2017) used a hydrothermal diamond anvil cell to

measure $MoO_2$(s) solubilities in pure water of 44 ppm and 658 ppm at 600 and 800 ˚C, respectively; however, they were not able to determine the oxidation state and predominant Mo species in the solutions. In pure, low density water vapour, a neutral $MoO_3(H_2O)_n$(aq) with hydration number n up to 3 at 360 ˚C was proposed based on the solubility of $MoO_3$(s) (Rempel et al. , 2006).

The structures of the molybdate and hydrogen molybdate ions show little change with increasing temperature, as evidenced by the synchrotron X-ray absorption study (up to 385 ˚C) of Borg et al. (2012); both species share a tetrahedral coordination, and confirmed by the *first principle* molecular simulations study of Liu et al. (2013). Liu et al. (2013) also predicts the change of the structure of molybdic acid from 6-coordinated $MoO_2(OH)_2(H_2O)_2$(aq) to 4-coordinated, unhydrated $MoO_2OH_2$(aq) with increasing temperatures to 300 ℃. They calculated the acidity constants of molybdic acid up to 300 ˚C with reasonably good agreement with the experimental results by Minubayeva and Seward (2010), in particular for pKa1.

The possibility of Mo(VI) complexation with chloride, the major ligand in many hydrothermal fluids, has also been investigated. Wood et al. (1987) noted that Mo did not complex with chloride in their slightly acidic (pH>3) chloride-bearing experimental solutions (0-5 m NaCl, 25-350 ˚C), and Kurin (1989) proposed that $KHMoO_4$(aq) and $NaHMoO_4$(aq) are responsible for the Mo solubility in 0.05-1 m KCl and NaCl solutions (with 0.1 m HCl to 0.005 m KOH) at 300-394 ˚C. Under much more acidic conditions, Borg et al. (2012) identified oxo-chloro complexes $MoO_mCl_n^{6-2m-n}$ (n up to 5) at the experimental P–T conditions (up to 385˚C at 600 bar), consistent with the solubility study by Dadze et al. (2018), in which they found $MoO_2(OH)_2Cl^-$ predominant in HCl-$HClO_4$-NaCl solutions at 300 ˚C. In HCl-bearing vapour phase, hydrated species $MoO_3(H_2O)_y$(g) predominate in less acidic vapour ($\log f_{HCl(g)} < 0.1$, Hurtig and Williams-Jones, 2014) and $MoO_2Cl_2$(g) is dominant in more acidic conditions (Rempel et al., 2008).

Sulfur is one of the major components in magmatic hydrothermal fluids and volcanic gases, and molybdenite, $MoS_2$, is the main form of Mo in ore deposits. Recent experimental and theoretical studies have shown that sulfur complexes with ore metals, and can be an important transport agent for Au, Cu, Zn and Pd (Pokrovski et al., 2009, Etschmann et al., 2010, 2019, Mei, 2013, 2015 2016; Liu et al., 2014; Brugger et al. 2016). Therefore, it is desirable to investigate the complexation between Mo and S and it's contribute to Mo

transport in hydrothermal fluids. Most previous studies of the hydrothermal transport of Mo focused on Mo speciation in pure water and chloride-bearing systems, with much less work on the behaviour of Mo in hydrothermal sulfur-bearing fluids. Wood et al. (1987) didn't find evidence of Mo-S species in their multi-metal solubility experiments in 0-5 molal NaCl solution with pyrite-pyrrhotite-magnetite buffer for log $fO_2$ and log $fS_2$ at 200-350 ℃ and 0.69-172 bar, whereas Zhang et al. (2012) suggests $NaHMoO_2S_2$ predominant in their experimental solutions at 600-800 ℃ and 2000 bar, but find the solubility of $MoS_2$ increases with decreasing log $fS_2$.

Under the ambient condition, Mo(VI)-S species or thiomolybdates have been suggested to be important in sediment and surface water environments (e.g., Helz et al., 1996, Erickson and Helz, 2000). Thiomolybdate anions ($MoO_{4-x}S_x^{2-}$, x =1, 2, 3, 4) have been studied extensively with different methods (see reviews by Muller et al., 1981; Coucouvanis, 1998; Laurie, 2000; and Smedley and Kinniburgh, 2017). The kinetics and reaction constants of progressive replacement of oxygen by sulfur was established using mainly UV-Vis spectrophotometry (e.g., Harmer and Sykes, 1980; Erickson and Helz, 2000) and theoretical studies (e.g., Bernholc and Stiefel, 1985, El-Issa et al., 1989, Tossell, 2005). These studies generally agree that thiomolybdate species are important in surface waters under reduced environments. In contrast to detailed information available at room temperature, the identity and stability of the thiomolybdates in hydrothermal fluids at elevated temperature and pressure remain unknown. Furthermore, the thiomolybdate anion notably tends to form stable complexes with some transmission metal ions such as Cu(I) (Helz et al., 2011) and Fe(II) (Helz et al., 1996, 2014) at room temperature, indicating the potential for co-transport of Fe and Cu with Mo in reduced, sulfur-rich fluids.

This work aimed to determine the speciation of Mo(VI) in hydrosulfide solutions at elevated temperature and pressure (up to 394 ˚C and 800 bar). We used *in-situ* Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy and X-ray Absorption Near-edge Structure (XANES) data to obtain structural information for the predominant Mo species, combined with *ab initio* molecular dynamics simulations and *ab initio* XANES calculations to provide new insights for Mo transport and deposition in natural and engineered hydrothermal fluids relevant to the hydrothermal (re)mobilisation of Mo and formation of Mo deposits, as well as the hydrometallurgical processing of Mo-bearing ores.

# 2. Methods

## 2.1. XAS experiment

### 2.1.1. Sample solutions

All sample solutions were prepared from deionized water, $Na_2MoO_2.2H_2O$(s) (analytical grade, Sigma Aldrich™) and a stock of 2 m NaHS solution. The NaHS stock solution was prepared by dissolving sodium hydroxide in deoxygenated water, and then bubbling $H_2S$(g) through the solution. This method was used by Helz et al. (1993), Mosselmans et al. (1999), Etschmann et al. (2010) and Mei et al. (2016) for studies on Cu(I) and Zn(II) bisulfide complexes, and it was demonstrated that the oxidation state of the sample solutions (loaded in glassy carbon cells) were within the stability field of the reduced sulfur over a large temperature range (up to 592 ˚C) (Etschmann et al., 2010). The solution compositions are compiled in Table 1.

### 2.1.2. Sample cell and XAS measurement

Molybdenum K-edge (20,000 eV) X-ray Absorption Near Edge Structure (XANES) and Extended X-ray absorption Fine Structure (EXAFS) spectra were measured at beamline 30-BM (FAME) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The setup at the FAME beam line has been described by Proux et al. (2005). A focused beam size of FWHM 300 x 150 ⌙ $m^2$ was used. The incident and transmitted beam intensity $I_0$ and $I_1$ were measured with Si diodes; and fluorescence data were collected concurrently using a 30 element solid state fluorescence detector. The beam energy was calibrated with a Mo foil, such that the maximum of the first derivative of the XANES spectrum was at 20,000 eV.

The high temperature-high pressure cell developed by the “Laboratoire de Cristallographie” (CNRS) was used for XAS measurements of solutions up to supercritical conditions (Testemale et al., 2005). The cell consists of an external water-cooled high-pressure vessel equipped with three 1.5 mm thick beryllium windows enabling collection of fluorescence and transmission signals at a pressure of 800 bar. A sample solution (mass ~0.1 g) was contained inside a glassy carbon tube with an internal diameter of 4 mm. The pressure was applied to the sample by two glassy carbon pistons, using helium as a pressure medium. The glassy carbon tube was placed inside a small cylindrical resistive heater; the heater and tube are installed inside in a water-cooled stainless-steel high-pressure vessel. The temperature of the fluid at the beam location was controlled by a Eurotherm PID controller to

a stability within 0.1 ˚C, and calibrated by correlating the density of a 2 molal NaCl solution at the beam position as a function of temperature, based on measurements of X-ray transmission (e.g., Tooth et al., 2013):

$$\mu_{20\,keV}^{AGS} - \mu_{20\,keV}^{AGS} = \left(\frac{\mu}{\rho}\right)_{20\,keV}^{S} \mu^{s} x \quad (1),$$

where $\mu_{20\,keV}^{AGS}$ is the measured transmission of the autoclave + glassy carbon cell + 800 bar He + solution at 20 keV, $\mu_{20\,keV}^{AGS}$ is the measured baseline transmission without solution, $\left(\frac{\mu}{\rho}\right)_{20\,keV}^{S}$ is the tabulated X-ray mass attenuation coefficient corresponding to the composition of solution *S* at 20 keV (Chantler, 1995), $\rho^{S}$ is the density of the solution (program Sowat, Driesner, 2007; Driesner and Heinrich, 2007), and *x* is the path length of the beam in the solution. The error from the calibration curve is ~ ± 3 ˚C. The details of the autoclave can be found in several previous studies (e.g., Testemale et al., 2005; 2009; Liu et al., 2011; Tooth et al. 2013).

XANES and EXAFS data were analysed with the HORAE package (Ravel and Newville, 2005), using FEFF version 9 (Rehr et al., 2009). The reported errors are at the 1 ᵒ level and taken from the HORAE package.

## 2.2. *Ab initio* molecular dynamics simulations

The simulations of molybdic acid, molybdates and thiomolybdates were performed with solutions containing 1 $H_2MoO_4$, 4 $Na^+$, 4 $HS^-$ and 111 $H_2O$ to represent Na and S concentrations of 2 molal. The nominal Mo concentration is 0.5 molal, but because there is only one Mo atom in the simulation box, there is no Mo-Mo interaction, i.e. Mo behaves as if at infinite dilution in the simulated solutions. Periodic boundary conditions were applied in the *ab initio* MD simulations. We performed simulations at 77 °C, 200 °C and 300 °C at 800 bar to compare with the XAS experiments, and at near-saturation pressure at 200 °C (20 bar) and 300°C (100 bar). The simulations were run in the NVT ensemble with the temperature controlled by the Nosé thermostat for both the ions and electrons (Nosé, 1984, Hoover, 1985). For these constant volumes calculations, the densities were taken from the equations ofstate of a 2 molal NaCl solution (Driesner, 2007; Driesner and Heinrich, 2007),

an approximation that has been widely used in hydrothermal aqueous geochemical systems. Details of the physical conditions for each simulation are listed in Table 2. To test the stability of molybdic acid and thiomolybdates, simulations with six different initial species, i.e., $H_2MoO_4$, $MoO_4^{2-}$, $MoO_3S^{2-}$, $MoO_2S_2^{2-}$, $MoOS_3^{2-}$ $MoS_4^{2-}$, were conducted at each T-P condition, for a total of 25 simulations

*Ab initio* molecular dynamics simulations were performed using the CP2K/QUICKSTEP package, which implements density functional theory (DFT) using a mixed Gaussian basis sets and plane-waves approach (Hutter et al., 2014). Goedecker-Teter-Hutter (GTH) pseudopotentials (Goedecker et al., 1996; Hartwigsen et al., 1998) were used for the core electrons with a cutoff of 280 Ry (3809.6 eV) for the electron density, and the double-zeta valence polarized (DZVP) basis sets were utilised for Mo, Na, S, O and H (VandeVondele and Hutter 2007) together with BLYP exchange-correlation functional (Lee et al., 1988; Becke, 1988). The BLYP functional generally provides a good description of the structural properties of water including O–O interactions, H-bond statistics, angular distributions, coordination numbers, and radial distribution functions when compared with experiments (Gillan et al., 2016; Lin et al., 2012). However, as discussed in our previous studies using the BLYP exchange correlation functional (Mei et al., 2018; Guan et al., 2020), we note that there is a well-known tendency for most functionals, including BLYP, to over-structure liquid water (Lee and Tuckerman, 2006; Lin et al., 2012). For example, Bankura et al. (2014) showed that BLYP, like most other functionals, best reproduces the hydrogen-bonded network of water at ambient conditions when using an elevated temperature (80 °C in their case), and it could be argued that there is a temperature offset of approximately 50-55 °C between the computed data as compared to the experimental structure of the solvent at room temperature. Therefore, here we performed simulations at 77 °C (350K) to reproduce the solution at room temperature. A simulation timestep of 0.5 femtosecond (fs, $10^{-15}$ second) was chosen for all simulations. To achieve good statistics, all the simulations were calculated for 9-15 ps including a 2 ps equilibration. The radial distribution functions (RDF) and the coordination number (integrals of RDF) were calculated using VMD (Humphrey *et al.*, 1996) to extract the averaged structural information and to compare with the XAS data. As discussed previously (e.g., Mei et al., 2020), *ab initio* MD simulations are computationally intensive. *Ab initio* MD studies published by researchers from various groups (Jahn and Schmidt, 2010; Sulpizi et al., 2013; Liu et al., 2013a, b; Wagner et al., 2017; Stefanski and

Jahn 2020) indicate that it is viable to represent the geometrical and thermodynamic properties of solute and solvent molecules within manageable simulation times of tens of picoseconds.

## 2.3. *Ab initio* XANES calculations

*Ab initio* XANES spectra were calculated with the FDMNES program (Joly, 2001). The final states were calculated by the Finite Difference Method (FDM) to solve the Schrodinger equation in the cluster. The FDM can provide accurate calculation especially for structure of low-symmetry aqueous complexes (Joly, 2001; Brugger et al., 2007), as in this study. To compare with the experimental spectra, the calculated spectra were convoluted with a Lorentzian function of energy-dependent width to account for the core-hole lifetime broadening (4.52 eV; Krause and Oliver, 1979) and the inelastic plasmon interactions with the photoelectron. The energy resolution of the monochromator was taken into account by convoluting the calculated XANES spectra with a Gaussian function (width of 1.024 eV). We also calculated the XANES spectra of the five Mo-O-S complexes simulated with molecular dynamics ($MoO_{4-x}S_x^{2-}$, x = 0-4) at 77 and 300 ℃. 40 frames were chosen at every 0.2 ps from each MD simulation box and the final spectra were obtained by taking the average of FDMNES simulations of the 40 frames. The radius cutoff of all calculations was 5 Å.

# 3. Results

Molybdenum K-edge XANES and EXAFS spectra for the sample solutions with variable NaHS concentrations between 0.07 to 2 molal (Table 1) were collected between 30-394 ˚C at 800 bar, as well as the spectra of molybdenum reference compounds, including the molybdate solution for comparison. In general, the data collected from the solution are of good quality for EXAFS analysis at temperature up to 286-330 ˚C, and then only XANES data are used at higher temperatures up to the maximal temperature values for each solution listed in Table 1. At higher temperatures than the maximal temperatures, the intensity of the spectra dropped dramatically, and the signal become noisier due to a reduced metal solubility and precipitates on the wall of the cell, as a result of the decrease in solution density (e.g., Pokrovski et al. 2005; Liu et al. 2008; Mei et al. 2014). Most spectra of precipitates are too noisy to identify, but the spectrum of the highest NaHS concentrations (Sol6) has similarity with the spectrum of molybdenite ($MoS_2$) (see insert in Fig. 1b); therefore, the precipitates are likely to be molybdenite. For all the samples, only the good quality XANES and EXAFS of the solution phase are used in the data analysis.

In the following sections we describe the qualitative analysis of the XANES spectra, followed by the quantitative refinement of the EXAFS data for the determination of the coordination structure (bond distance, ligand types and coordination numbers) and predominating species. The results of the molecular dynamics simulations and XANES calculations of the major Mo-O and Mo-S species are then described and compared with the experimental results.

## 3.1. XANES

*Effect of NaHS concentration:* The XANES spectra of sample solutions as a function of NaHS concentration at 30 and 286 ˚C are plotted in Fig. 1a and 1b respectively, together with the spectra of two end-member references, $Na_2MoO_4$ solid (containing the $[MoO_4]^{2-}$ moiety – we use [ ] to refer to the moiety of a species throughout the text) and $(NH_4)_2MoS_4$ (s) (containing the $[MoS_4]^{2-}$ moiety). The spectra of the sample solutions plot between the spectra of these two references, with the dominant absorbing species in the sample solutions evolving from $[MoO_4]^{2-}$-like to $[MoS_4]^{2-}$-like structures with increasing bisulfide concentration. The $[MoO_4]^{2-}$ structure has a distinctive pre-edge peak at ~20,005 eV (Feature A), which is associated with the 1s – 4d transition, and related to (i) the number of Mo=O bonds per Mo atom and (ii) the symmetry of the structure, the more symmetrical structures having a smaller

pre-edge (Borg et al., 2012 and references therein). The pre-edge peak of the spectrum of the $[MoS_4]^{2-}$ moiety at 20,003 eV is smaller than that of the $[MoO_4]^{2-}$ moiety at 20,005 eV (Fig. 1a). At both temperatures (30 and 286 °C), the pre-edge feature decreases with increasing NaHS concentration, indicating an increased contribution of the $[MoS_4]^{2-}$-like species. The features B, C, and D also show systematic changes as a function of NaHS concentration, consistent with the features of the two end-member spectra.

*Effect of increasing temperature*. Temperature has a smaller effect on the XANES spectra than $HS^-$ concentration (Fig. 2). The spectral changes with increasing temperatures are mainly reflected in the growing pre-edge peak (feature of the $[MoO_4]^{2-}$ moiety) with increasing temperature for most solutions (except for low NaHS solutions such as Sol14 and Sol12), indicating increased contribution from $[MoO_4]^{2-}$ with increasing temperature.

## 3.2. EXAFS

The changes of the EXAFS spectra as a function of NaHS concentration (Fig. 3) are similar to the trend of the XANES spectra. In particular, the (phase uncorrected) Fourier transform of the EXAFS shows a decreasing intensity of the first peak at ~1.3 Å and increasing intensity of the second peak at ~1.8 Å (Fig. 3) with increasing NaHS concentration. Quantitative EXAFS refinements (Table 3) reveal that the first peak is due to Mo-O interaction and the second peak is due to Mo-S.

EXAFS refinement of a molybdate standard ($Na_2MoO_{4(s)}$)containing the $[MoO_4]^{2-}$ moiety) indicates 4 oxygen around Mo atom at average distance of 1.775(4) Å, similar to the Mo-O distance in molybdate solution (1.771-1.777 Å, Borg et al. 2012). The EXAFS refinement of the $(NH_4)_2MoS_4$(s) reference compound ($[MoS_4]^{2-}$ moiety) yields an average Mo-S bond distance of 2.192(5) Å. This value is similar to the published individual Mo(VI)-S bond distances in $[MoS_4]^{2-}$ moiety determined by EXAFS refinements (2.20 Å in $(NH_4)_2MoS_4$(s), Bostick et al., 2003; 2.18 Å in $MoS_4^{2-}$ solution, Dahl et al, 2013) and by single crystal diffraction (2.1773(5) -2.2013(8) Å in $(NH_4)_2MoS_4$(s); average = 2.1844(6) Å; Hill et al., 2010). The fitted bond distance of the Mo-S bonds for solutions S5 and S6 with the highest NaHS concentrations, where the Mo-S peaks are most significant (Fig. 4), are also around 2.20 -2.21 Å at 30°C (Table 3); however, the refined Mo-S bond distances of solutions with a low concentration of NaHS and higher temperatures have longer distances of ~2.25-2.29 Å (Table 3). This is due in part to the larger uncertainties in Mo-S distance because of the lower number of coordinated S, but also reflects the effect of the dominating

Mo-O bond. This is confirmed by the molecular dynamics simulations that indicate slightly longer (0.02-0.03 Å) Mo-S distances at elevated temperatures for mixed Mo-S and Mo-O species (See section 3.3).

The fitted number of S ligands increases with increasing NaHS concentrations at all temperatures, at the expense of the number of O atoms, reflecting an increased contribution from thio species (Table 3; the examples at 30 and 286 ˚C are plotted in Fig. 5). At the highest NaHS concentration (Sol6), the fitted number of S ligands is 3.1(2) at 30 ℃; with increasing temperature to 200 ℃, the S ligand number increases to 3.4 , but at 286 ℃ and higher temperature, the S peak decreases notably and the O peak increases (Fig. 3b); this reflects an increase in O ligand numbers at those temperatures relative to lower temperatures (Table 3). The temperature dependence of the EXAFS spectra is consistent with, but more apparent than the change of the pre-edge feature in the XANES (Fig. 2). It is notable that while EXAFS analysis provides the average numbers of S and O ligands, it cannot distinguish explicitly the identity of the species present, i.e., for an equal ratio of S:O ligands obtained from the EXAFS refinement, it is not possible to tell whether it is 1:1 mixture of $MoO_4^{2-}$ and $MoS_4^{2-}$, or predominantly a mixed ligand complex such as $MoS_2O_2^{2-}$.

## 3.3. *Ab initio* MD

The results of simulations of Mo(VI) speciation in solutions containing 2 m $NaHS^{=}$ at experimental pressures (800 bar) and at near saturation pressure (200 ℃, 20 bar and 300 ℃, 100 bar) are listed in Table 4. Overall, the simulations show that fourfold tetrahedral complexes are stable in all simulations. Apart from some deprotonation for simulations that started with $H_2MoO_4$(aq), no ion exchange was observed during the simulation (up to 25 ps). Our previous studies show that in the MD simulations on the scale of picoseconds, it is difficult to observe simple ligand exchange between ions with charge of -1 such as $Cl^-$, $HS^-$ and $OH^-$ due to the slow exchange kinetics even at elevated temperatures (Mei et al. 2015, 2016, 2020).

### 3.3.1. Molybdate and hydrogen molybdate ions

As shown in Table 4, jobs 1A, 2A, 3A, 4A, 5A that started with $H_2MoO_4$(aq) established that the hydrogen molybdate ion, $HMoO_4^-$, was the predominant species over the entire temperature range, with a minor amount of $H_2MoO_4$(aq) at 77 ℃ (representing room T), 800 bar and a minor amount of molybdate ion, $MoO_4^{2-}$, at 300 ℃, 100 bar. The molybdate

ion is stable in most of the simulations that started with $Na_2MoO_4$ (simulation 6-11, Table 4), except one solution (simulation 11) at 300 °C in which the stable species is $HMoO_4^-$. Snapshots of the structures for the observed molybdate and hydrogen molybdate ions are shown in Fig. 6. The Mo-O distance in $MoO_4^{2-}$ is ~1.80(3) Å at 77 °C, which is consistent with Liu (2013)'s values of 1.79 Å for Mo-O distance in $MoO_4^{2-}$ . For $HMoO_4^-$, our MD results show that the Mo-OH bond distances (~1.92-1.94 Å) are notably longer than the Mo-O distances (~1.77 Å) (Table 4), also similar to the previous MD results ($d_{Mo-O}$ = 1.76 Å and $d_{Mo-OH}$ = 1.79 Å, Liu et al., 2013a; $d_{Mo-O}$ = 1.72 Å and $d_{Mo-OH}$ = 1.8 Å, Zhang et al., 2018). Fig. 7 shows the radial distribution functions (RDF) and the coordination numbers (CN; integral of RDF) of Mo-O/S at 300 ºC, 800 bar. For simulation 5A, where $HMoO_4^-$ is the predominant species, the RDF peak ranges from 1.7 – 2.0 Å (blue solid line) reflecting the Mo-O bond, which was split into one large peak at 1.77 Å and one small peak at 1.92 Å. The CN (dashed blue) curve shows the first peak results in a CN of 3 (corresponding to three Mo-O bonds) and the second peak adds one more ligand (corresponding to one Mo-OH bond), with a total CN of four. The simulated Mo-O bond distances for molybdate are also consistent with the experimental EXAFS results for molybdate ($d_{Mo-O}$ = 1.771-1.777 Å, Borg et al., 2012; 1.775(4) Å, this study).

### 3.3.2. Thiomolybdates

All simulations of thiomolybdates show that fourfold tetrahedral complexes are stable. The geometrical properties of all MD runs are listed in Table 4. Fig. 8 shows the snapshots of thiomolybdates ($MoO_{4-x}S_x^{2-}$, x =1, 2, 3, 4) calculated at 300 ºC, 800 bar from MD simulations. As shown in Table 4, the Mo-O and Mo-S bonds are easily distinguishable by their lengths (~0.45 Å difference), with Mo-O distances of 1.78-1.79 Å and Mo-S distances of 2.23-2.28 Å. This is reflected in the RDF plot (Fig. 7), consistent with the systematic change of Mo-O and Mo-S peaks in the Fourier transforms of the EXAFS data (Figs. 3, 4), and the bond distances from the MD simulations agree well with the fitted EXAFS results of Mo-S distances of 2.20-2.3 Å (Table 3). In particular, both the EXAFS refinements and the MD results predict slightly longer (0.02-0.05 Å) Mo-S distances at elevated temperatures for mixed thiomolybdates ($MoO_{4-x}S_x^{2-}$, x =1, 2, 3). This may indicate that temperature favours the loosening of the Mo-S bond in the mixed species.

Similar to the simulations for molybdates, no ligand exchange or proton exchange was observed during these simulations. As mentioned before, ligand exchange is unlikely to be observed in such short simulation times, and in this case, it is even more difficult to see the exchange between $O^{2-}$ and $S^{2-}$ given their strong affinity with $Mo^{6+}$ due to their differences in electronegativity. The MD results shown here provide geometrical properties of thiomolybdates for *ab initio* XANES calculations and provide an independent check and comparison with EXAFS data.

### 3.4. *Ab initio* XANES calculations

The XANES spectra calculated using FDMNES and selected experimental spectra are plotted in Fig. 9. Although the peaks in the experimental spectra are broader than the calculated spectra, the major spectral features observed in the experimental data are confirmed by *ab initio* XANES simulations. As shown in Fig. 9, the pre-edge peak (Feature A) has a slight shift to higher energy (blue shift) when the structure changes from $[MoS_4]^{2-}$ to $[MoO_4]^{2-}$, with increased intensity for the $[MoO_4]^{2-}$ structure. The peak (Feature B) that is prominent in the spectrum of the $[MoS_4]^{2-}$ moiety decreases with decreasing the number of S ligand and is absent in the spectrum of the $[MoO_4]^{2-}$ structure. These features are consistent with the experimental XANES spectra of the two end member references and the sample solutions (Fig. 9), though the after-edge features C and D in the experimental spectra are not reproduced in the XANES simulations. The spectral changes from 77 °C to 300 ˚C are minimal, confirming the rigid structure of the thiomolybdate structures.

## 4. Discussions and conclusions

### 4.1. Comparison to previous studies at room temperature

It has long been documented that thiomolybdate species are important in surface environments (Muller et al., 1981; Coucouvanis, 1998; Laurie, 2000). Our results from EXAFS analysis, *ab initio* MD simulations and XANES calculations confirmed the formation of thiomolybdates in reduced sulfur-bearing solutions. Several UV-Vis spectroscopic studies (e.g., Harmer and Sykes, 1980; Erickson and Helz, 2000) suggest that thiomolybdate anions prevail in reduced sulfur-bearing fluids, and have established the kinetics of stepwise replacement of $O^{2-}$ ions by $S^{2-}$. In particular, Erickson and Helz's (2000) UV-Vis study provided the formation constants of the thiomolybdates, and proposed that a sharp transition

occurred between $MoO_4^{2-}$ to $MoS_4^{2-}$, where a 3-fold change in $H_2S$ concentration results in a 100-fold change in the $MoO_4^{2-}/MoS_4^{2-}$ ratio, and $MoS_4^{2-}$ becomes predominant in the solution. In our experiment we identified a mixture of $MoO_4^{2-}$ and $MoS_4^{2-}$ in the most solutions, with the $MoS_4^{2-}$ predominant in the high NaHS concentration solutions. The fitted maximum S ligand number is 3.4 in the 2 m NaHS solution at 200 °C (Table 3). We did not observe 100% $MoS_4^{2-}$ in any solutions, as we were not able to prepare a sufficiently concentrated solution, due to the precipitation of $MoS_2$, for XAS measurement at the lower pH (6-8) where $MoS_4^{2-}$ would be more predominant as shown in the previous studies at room temperatures (e.g., Erickson and Helz, 2000),

Using the formation constants for the $MoO_{4-x}S_x^{2-}$(x =1, 2, 3, 4) species determined by Erickson and Helz (2000) and the thermodynamic properties of molybdate species (Minubayeva and Seward, 2010) and molybdenite by Robie and Hemingway (1995), we calculated the stability fields of predominant Mo species in a solution of 0.01 m Mo and 0.1 m total sulfur at 25 ºC (Fig. 10a). Under reduced conditions, molybdenite predominates in solutions with a wide range of pH, and molybdate species under more oxidised conditions; which is contradictory to the thiomolybdate species observed in our experiments and previous UV-Vis studies (e.g., Harmer and Sykes, 1980; Erickson and Helz, 2000). For the sake of showing the only predominating aqueous species, we removed the molybdenite from the calculations, and the results show that $MoS_4^{2-}$ predominates when pH<11, and mixed $MoS_4^{2-}/MoO_4^{2-}$ species in pH 11-12 (Fig. 10b), which is qualitatively consistent with previous studies and our experimental results, where no precipitation of molybdenite is observed in the experimental solutions. There are two possible explanations for the absence of molybdenite in the experimental solution: either slow precipitation of molybdenite precipitation is too slow to be observed, and/or uncertainties in the thermodynamic properties of molybdenite causing overestimation of its stability.

## 4.2. Stability of thiomolybdate at high P-T

Our experimental results show that the thiomolybdate species with various ratios of sulfur and oxygen ligands are stable in our experimental solutions up to 330 °C. In the absence of experimental determination of thermodynamic properties for thiomolybdate species at elevated P-T conditions, it is useful to extrapolate the available data at ambient temperatures to elevated temperatures. The validity of these extrapolations can be evaluated

by comparison with the experimental EXAFS results, and the models can be used to assess the role of the thiomolybdates in transporting molybdenum in ore fluids.

Erickson and Helz (2000) determined the stability constants for ($MoO_{4-x}S_x^{2-}$) in $H_2S$-bearing solutions at 25 °C. Based on their data, we used the isocoulombic approach (Gu et al., 1994) to extrapolate the formation constants of the $MoO_{4-x}S_x^{2-}$ species up to 300 °C and water saturated pressure (Table 5).

The basic assumption of the iso-coulombic extrapolation is that when a reaction has equal numbers of like-charged species on both sides of the reaction (iso-coulombic reaction), both heat capacity and entropy changes are small and tend to cancel one another, and the change of free energy is constant and independent of temperature (Gu et al., 1994, Liu et al, 2012):

$$DG_T^0 = DG_{T_r}^0 = -R \cdot T \cdot \ln K_T \quad (2)$$

where $DG_{T_r}^0$ and $DG_T^0$ refer to the standard Gibbs free energy ($J \cdot mol^{-1}$) of reaction at reference temperature $T_r$ (298.15 K) and the experimental temperature $T$ (in Kelvin), $R$ is the ideal gas constant ($J \cdot K^{-1} \cdot mol^{-1}$) and $K_T$ is the equilibrium constant for the iso-coulombic reaction. Therefore, the log $K$ for an iso-coulombic reaction at experimental temperature can be estimated from the log $K$ values at the reference temperature where the thermodynamic properties are available (e.g., Liu et al., 2012):

$$\log K_T = \frac{T_r}{T} \log K_{T_r} \quad (3)$$

In the case of the thiomolybdate species, it is convenient that all the reactions of the replacement of $O^{2-}$ by $S^{2-}$ meet the requirement of iso-coulombic reactions, i.e., species on both sides of the reactions are equally charged:

$$MoO_4^{2-} + H_2S(aq) = MoO_3S^{2-} + H_2O(l) \quad (4)$$

$$MoO_3S^{2-} + H_2S(aq) = MoO_2S_2^{2-} + H_2O(l) \quad (5)$$

$$MoO_2S_2^{2-} + H_2S(aq) = MoOS_3^{2-} + H_2O(l) \quad (6)$$

$$MoOS_3^{2-} + H_2S(aq) = MoS_4^{2-} + H_2O(l) \quad (7)$$

Therefore, the stepwise formation constants for these species at elevated temperatures can be estimated with the room temperature data of Erickson and Helz (2000) using Eq. (3), and the results are compiled in Table 5.

Based on the extrapolated data, the stability of the thiomolybdate and molybdate species were estimated as a function of pH and Eh at 300 °C in a solution with 0.1 m total sulfur (Fig. 10c). The thiomolybdate species, in particular $MoS_4^{2-}$, is predicted to be stable in the solution with slightly acidic to neutral pH (pH 6-8) under reduced conditions (sulfide stable), and molybdate species ($HMoO_4^-$ and $MoO_4^{2-}$) under more oxidised (sulfate stable), and acidic conditions (sulfide stable) (pH<6 at 300 °C),. Similar to the room temperature situation, our experimental results are qualitatively consistent with the extrapolation based on the room temperature data, i.e., mixed ligand species ($MoO_3S^{2-}$ to $MoOS_3^{2-}$) are present in the solution with pH values of 8.5-9, and $MoS_4^{2-}$ would predominate in wide pH ranges (pH 5 - 8.5 at 300 °C). Such pH range covers the major pH buffers in geological fluids, such as K-feldspar-Muscovite-Quartz (KMQ), $H_2S/HS^-$ and $CO_{2(aq)}/HCO_3^-$, as shown in Fig. 10.

Therefore, both our experimental data and the extrapolations from room temperature thermodynamic properties indicate that the thiomolybdate species may contribute to Mo transport in hydrothermal sulfur-rich fluids with neutral to alkaline pH range under reduced conditions, and current models of Mo transport in hydrothermal ore fluids need to be re-evaluated to take into account the thiomolybdate species. It is notable that in very acidic solutions the molybdenite would precipitate in sulfide-stable solutions (Fig. 10c). Previous solubility study of Zhang et al. (2012) suggested $NaHMo_2S_2$ as predominant Mo – S species but they found negative trend of molybdenite solubility with increasing *log* $fS_2$ at 600-800 °C and 2000 bar. Apart from the difference in the experimental temperatures and pressures between the two studies, their experimental solutions have pH range of 1-2 (measurement of quenched solutions, Zhang et al., 2012), which is too acidic to see the impact of thiomolybdate on the solubility of molybdenite, as indicate in Fig 10c. To this end, further experimental studies are needed to improve the thermodynamic properties for the thiomolybdate species at wide range of P-T conditions in order to accurately assess the role of thiomolybdate in transporting Mo (and possibility of transporting other metal ions such as Cu and Fe) in hydrothermal fluids. Finally, Our experiments show that Mo(VI) species predominate at high P-T in solutions with reduced sulfur, consistent with the previous studies in chloride solutions and vapours cited; therefore, Mo(VI) is likely to be the main oxidation state of molybdenum in typical hydrothermal ore fluids. Under extremely reduced conditions Mo(V) and/or Mo(IV) species may occur, but they are not considered due to a lack of experimental evidence and thermodynamic data for these species.

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764 Table 1 Sample compositions. pH values are calculated from the compositions of NaHS,
765 $Na_2MO_4$ and NaCl using HCh modelling package and the default database (Shvarov, 2008).

| Solution | Composition (m: mole/kg) | T (°C) | pH (30 °C, 800 bar) | pH (286°C, 800 bar) |
|---|---|---|---|---|
| Sol 5 | 0.004 m $Na_2MoO_4$, 1.13 m NaHS | 30, 103, 194, 286 | 11.5 | 8.5 |
| Sol 6 | 0.006 m $Na_2MoO_4$, 2.00 m NaHS | 30, 103, 194, 286 | 11.4 | 8.5 |
| Sol 8 | 0.008 m $Na_2MoO_4$, 0.28 m NaHS | 30, 103, 194, 286, 370, 394 | 11.9 | 8.8 |
| Sol 10 | 0.009 m $Na_2MoO_4$, 0.28 m NaHS, 1.0 m NaCl | 30, 103, 194, 286, 330 | 11.8 | 8.7 |
| Sol 12 | 0.009 m $Na_2MoO_4$, 0.070 m NaHS | 30, 103, 194, 286, 330, 370 | 11.8 | 8.6 |
| Sol 14 | 0.009 m $Na_2MoO_4$, 0.04 m NaHS | 30, 103, 194, 286, 330, 370 | 12.0 | 8.8 |
| Sol 15 | 0.007 m $Na_2MoO_4$, 0.43 m NaHS | 30, 103, 194, 286, 330, 370, 394 | 11.8 | 8.7 |

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767 Table 2. Details of ab initio MD simulation using CP2K.

| solution composition | Job ID | T (°C) | P (bar) | Density of box (g/cm$^3$) | Box size (Å) |
|---|---|---|---|---|---|
| 1 $H_2MoO_4$, 4 $Na^+$, 4 $HS^-$, 111 $H_2O$ | 1 | 77 | 800 | 1.11146 | 15.277 |
| | 2 | 200 | 20 | 0.9911 | 15.872 |
| | 3 | 200 | 800 | 1.02915 | 15.674 |
| | 4 | 300 | 100 | 0.8844 | 16.486 |
| | 5 | 300 | 800 | 0.94216 | 16.142 |
| 1 $MoO_4^{2-}$, 2 $Na^+$, 111 $H_2O$ | 6 | 77 | 800 | 1.0740 | 15.053 |
| | 7 | 200 | 800 | 0.9859 | 15.489 |
| | 8 | 300 | 800 | 0.8887 | 16.034 |
| 1 $MoO_4^{2-}$, 4$Na^+$, 2$HS^-$, 111 $H_2O$ | 9 | 77 | 800 | 1.1039 | 15.165 |
| | 10 | 200 | 800 | 1.0183 | 15.578 |
| | 11 | 300 | 800 | 0.9260 | 16.079 |

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Table 3 EXAFS refinement (nO and nS; number of oxygen and sulfur ligands; rO and rS: Mo-O and Mo-S bond distances, $n_{tot}$: number of total ligands; $\sigma^2$: Debye-waller factor; E0: shift of energy; $\chi^2$_red: reduced $\chi^2$, R-factor: goodness of fit. Fitting range in R space: 1-3 (Å)).

| .T | nO | rO (Å) | nS | rS (Å) | $\sigma^2$ | E0 | $\chi^2$_red | R-factor | k-range |
|---|---|---|---|---|---|---|---|---|---|
| **Sol 14** | **0.04 m HS-** | | | | | | | | |
| 30 | 3.8(1) | 1.766(5) | 0.2(1) | 2.276 (fix) | 0.002(1) | 6.6(6) | 128 | 0.016 | 3-11 |
| 103 | 3.8(1) | 1.769(5) | 0.2(1) | 2.276 (fix) | 0.002(1) | | | | 3-11 |
| 194 | 3.3(2) | 1.760(6) | 0.7(2) | 2.29(2) | 0.002(1) | | | | 3-11 |
| 286 | 3.4(1) | 1.758(5) | 0.6(1) | 2.28(2) | 0.002(1) | | | | 3-11 |
| 330 | 3.8(1) | 1.764(5) | 0.2(1) | 2.31(8) | 0.002(1) | | | | |
| 330 | 4.0(2) | 1.763 (fix) | 0.0(2) | | 0.0029(8) | 2.2(9) | | | 3-11 |
| **Sol 12** | **0.07 m HS-** | | | | | | | | |
| 30 | 3.3(2) | 1.763(9) | 0.7(2) | 2.276 (fix) | 0.002(1) | 6.0(7) | 221 | 0.031 | 3-11 |
| 103 | 3.4(2) | 1.765(6) | 0.6(2) | 2.266 (fix) | 0.002(1) | | | | 3-11 |
| 194 | 3.2(1) | 1.763(6) | 0.8(1) | 2.286 (fix) | 0.004(1) | | | | 3-11 |
| 286 | 3.3(2) | 1.768(6) | 0.7(2) | 2.286 (fix) | 0.003(1) | | | | 3-11 |
| 330 | 3.5(2) | 1.767(8) | 0.5(2) | 2.286 (6) | 0.003(1) | | | | 3-11 |
| **Sol 8** | **0.28 m HS-** | | | | | | | | |
| 30 | 3.0(1) | 1.76(2) | 1.0(1) | 2.24(3) | 0.002(1) | 1(2) | 431 | 0.038 | 3-8.5 |
| 103 | 2.7(3) | 1.75(1) | 1.3(3) | 2.24(2) | 0.002(1) | 5(2) | | | 3-12 |
| 194 | 2.8(3) | 1.75(1) | 1.2(3) | 2.25(2) | 0.002(1) | 5(2) | | | 3-12 |
| 286 | 3.1(2) | 1.75(1) | 0.9(2) | 2.27(3) | 0.003(1) | 5(2) | | | 3-12 |
| **Sol 10** | **0.28 m HS- + 1 m NaCl** | | | | | | | | |
| 30 | 2.6(2) | 1.760(9) | 1.4(2) | 2.26(1) | 0.0023(8) | 4(1) | 281 | 0.042 | 3-11 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 103 | 2.5(2) | 1.760(9) | 1.5(2) | 2.27(1) | 0.0026(8) | | | | 3-11 |
| 194 | 2.4(3) | 1.75(2) | 1.6(3) | 2.27(2) | 0.003(2) | | | | 3-10 |
| 286 | 2.8(2) | 1.750(9) | 1.2(2) | 2.28(2) | 0.0025(9) | | | | 3-11 |
| 330 | 3.0(2) | 1.75(1) | 1.0(2) | 2.28(3) | 0.003(1) | 6(2) | | | 3-11 |
| | | | | | | | | | |
| **Sol 15** | **0.43 m HS-** | | | | | | | | |
| 30 | 2.4(2) | 1.75(1) | 1.6(2) | 2.25(1) | 0.002(1) | 5.2(7) | 153 | 0.024 | 3-11 |
| 103 | 2.3(1) | 1.746(6) | 1.7(1) | 2.239(7) | 0.0014(5) | | | | 3-11 |
| 194 | 2.6(2) | 1.741(8) | 1.4(2) | 2.25(1) | 0.002(1) | | | | 3-11 |
| 286 | 2.9(2) | 1.747(7) | 1.1(2) | 2.26(1) | 0.002(2) | | | | 3-11 |
| 330 | 3.1(2) | 1.750(7) | 0.9(2) | 2.26(2) | 0.002(1) | | | | 3-10 |
| | | | | | | | | | |
| **Sol 5** | **1.1 m HS-** | | | | | | | | |
| 30 | 1.0(1) | 1.688 (fix) | 3.0(1) | 2.211(5) | 0.0025(5) | 6.4(5) | 171 | 0.018 | 3-10 |
| 103 | 0.4(1) | 1.668 (fix) | 3.6(1) | 2.206(4) | 0.0017(4) | | | | 3-11 |
| 194 | 1.0(2) | 1.738 (fix) | 3.0(2) | 2.212(7) | 0.0025(9) | | | | 3-11 |
| 286 | 2.4(2) | 1.748(9) | 1.6(2) | 2.26(1) | 0.0035(9) | | | | 3-11 |
| | | | | | | | | | |
| **Sol 6** | **2 m HS-** | | | | | | | | |
| 30 | 0.9(1) | 1.708 (fix) | 3.1(1) | 2.210(5) | 0.0015(6) | 6.1(4) | 157 | 0.016 | 3-12 |
| 103 | 0.7(2) | 1.718 (fix) | 3.3(2) | 2.210(5) | 0.0018(6) | | | | 3-12 |
| 194 | 0.6(1) | 1.738 (fix) | 3.4(1) | 2.212(4) | 0.0021(5) | | | | 3-12 |
| 286 | 1.7(1) | 1.738 (fix) | 2.3(1) | 2.229(6) | 0.0032(6) | | | | 3-11 |

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776 Table 4. Simulation results of molybdate and thiomolybdate species.

| Initial configuration of Mo | Job ID | T (ºC) | P bar | MD time (ps) | species | Species time (ps) | Mo-S | | | Mo-O | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | CN | R (Å) | $\sigma_S^2$ (Å$^2$) | CN | R (Å) | $\sigma_O^2$ (Å$^2$) |
| $H_2MoO_4$ | 1A | 77 | 800 | 13.64 | $H_2MoO_4$& $HMoO_4^-$ | 12.64 | 0 | - | - | 4 | 1.81(4) | 0.0057 |
| | 2A | 200 | 20 | 15.55 | $HMoO_4^-$ | 14.05 | 0 | - | - | 3(O)<br>1(OH) | 1.77(4)<br>1.93(4) | 0.0014<br>0.0019 |
| | 3A | 200 | 800 | 10.30 | $HMoO_4^-$ | 9.30 | 0 | - | - | 3(O)<br>1(OH) | 1.77(4)<br>1.92(5) | 0.0013<br>0.0021 |
| | 4A | 300 | 100 | 13.49 | $HMoO_4^-$ & $MoO_4^{2-}$ | 11.99 | 0 | - | - | 4 | 1.81(5) | 0.0058 |
| | 5A | 300 | 800 | 10.17 | $HMoO_4^-$ | 9.17 | 0 | - | - | 3(O)<br>1(OH) | 1.77(3)<br>1.92(5) | 0.0012<br>0.0027 |
| $MoO_3S^{2-}$ | 1B | 77 | 800 | 10.16 | $MoO_3S^{2-}$ | 9.16 | 1 | 2.25(5) | 0.0026 | 3 | 1.79(3) | 0.0011 |
| | 2B | 200 | 20 | 11.13 | $MoO_3S^{2-}$ | 10.13 | 1 | 2.27(6) | 0.0031 | 3 | 1.79(4) | 0.0013 |
| | 3B | 200 | 800 | 10.39 | $MoO_3S^{2-}$ | 9.39 | 1 | 2.27(5) | 0.0025 | 3 | 1.79(4) | 0.0017 |
| | 4B | 300 | 100 | 10.02 | $MoO_3S^{2-}$ | 9.02 | 1 | 2.27(6) | 0.0031 | 3 | 1.79(4) | 0.0020 |
| | 5B | 300 | 800 | 10.45 | $MoO_3S^{2-}$ | 9.45 | 1 | 2.28(6) | 0.0036 | 3 | 1.79(4) | 0.0018 |
| $MoO_2S_2^{2-}$ | 1C | 77 | 800 | 10.07 | $MoO_2S_2^{2-}$ | 9.07 | 2 | 2.24(4) | 0.0017 | 2 | 1.79(3) | 0.0011 |
| | 2C | 200 | 20 | 9.51 | $MoO_2S_2^{2-}$ | 8.51 | 2 | 2.27(5) | 0.0030 | 2 | 1.78(3) | 0.0012 |
| | 3C | 200 | 800 | 10.20 | $MoO_2S_2^{2-}$ | 9.20 | 2 | 2.25(6) | 0.0030 | 2 | 1.79(4) | 0.0014 |
| | 4C | 300 | 100 | 10.02 | $MoO_2S_2^{2-}$ | 9.02 | 2 | 2.26(6) | 0.0036 | 2 | 1.79(4) | 0.0020 |
| | 5C | 300 | 800 | 10.38 | $MoO_2S_2^{2-}$ | 9.38 | 2 | 2.26(6) | 0.0038 | 2 | 1.78(4) | 0.0017 |
| $MoOS_3^{2-}$ | 1D | 77 | 800 | 10.55 | $MoOS_3^{2-}$ | 9.55 | 3 | 2.23(4) | 0.0016 | 1 | 1.78(3) | 0.0009 |
| | 2D | 200 | 20 | 9.23 | $MoOS_3^{2-}$ | 8.23 | 3 | 2.24(6) | 0.0033 | 1 | 1.78(4) | 0.0014 |
| | 3D | 200 | 800 | 10.02 | $MoOS_3^{2-}$ | 9.02 | 3 | 2.24(5) | 0.0023 | 1 | 1.78(4) | 0.0013 |
| | 4D | 300 | 100 | 9.89 | $MoOS_3^{2-}$ | 11.02 | 3 | 2.25(6) | 0.0034 | 1 | 1.77(4) | 0.0017 |
| | 5D | 300 | 800 | 10.54 | $MoOS_3^{2-}$ | 9.54 | 3 | 2.25(6) | 0.0037 | 1 | 1.78(4) | 0.0014 |
| $MoS_4^{2-}$ | 1E | 77 | 800 | 10.51 | $MoS_4^{2-}$ | 9.51 | 4 | 2.23(5) | 0.0024 | 0 | - | - |
| | 2E | 200 | 20 | 10.21 | $MoS_4^{2-}$ | 9.21 | 4 | 2.23(5) | 0.0024 | 0 | - | - |
| | 3E | 200 | 800 | 10.26 | $MoS_4^{2-}$ | 9.26 | 4 | 2.23(5) | 0.0027 | 0 | - | - |
| | 4E | 300 | 100 | 9.90 | $MoS_4^{2-}$ | 8.90 | 4 | 2.23(6) | 0.0031 | 0 | - | - |
| | 5E | 300 | 800 | 10.63 | $MoS_4^{2-}$ | 9.63 | 4 | 2.23(6) | 0.0033 | 0 | - | - |
| $MoO_4^{2-}$ | 6 | 77 | 800 | 17.73 | $MoO_4^{2-}$ | 16.73 | - | - | - | 4 | 1.80(3) | 0.0011 |
| | 7 | 200 | 800 | 24.89 | $MoO_4^{2-}$ | 23.89 | - | - | - | 4 | 1.80(4) | 0.0016 |
| | 8 | 300 | 800 | 15.48 | $MoO_4^{2-}$ | 14.48 | - | - | - | 4 | 1.81(4) | 0.0018 |
| $MoO_4^{2-}$ | 9 | 77 | 800 | 14.78 | $MoO_4^{2-}$ | 13.78 | - | - | - | 4 | 1.80(3) | 0.0011 |
| | 10 | 200 | 800 | 13.04 | $MoO_4^{2-}$ | 12.04 | - | - | - | 4 | 1.80(4) | 0.0017 |
| | 11 | 300 | 800 | 10.37 | $HMoO_4^-$ | 9.37 | - | - | - | 3(O)<br>1(OH) | 1.77(3)<br>1.94(5) | 0.0012<br>0.0025 |

777

778 Table 5 The stepwise formation constants for thiomolybdate species extrapolated from
779 Erickson and Helz (2000).

| Temperature (℃) | 0 | 25 | 60 | 100 | 150 | 200 | 250 | 300 |
|---|---|---|---|---|---|---|---|---|
| $MoO_4^{2-}$ + $H_2S(aq)$ = $MoO_3S^{2-}$ + $H_2O(l)$ | 5.67 | 5.19 | 4.64 | 4.15 | 3.66 | 3.27 | 2.96 | 2.70 |
| $MoO_3S^{2-}$ + $H_2S(aq)$ = $MoO_2S_2^{2-}$ + $H_2O(l)$ | 5.24 | 4.80 | 4.30 | 3.84 | 3.38 | 3.02 | 2.74 | 2.50 |
| $MoO_2S_2^{2-}$ + $H_2S(aq)$ = $MoOS_3^{2-}$ + $H_2O(l)$ | 5.46 | 5.00 | 4.47 | 4.00 | 3.52 | 3.15 | 2.85 | 2.60 |
| $MoOS_3^{2-}$ + $H_2S(aq)$ = $MoS_4^{2-}$ + $H_2O(l)$ | 5.33 | 4.88 | 4.37 | 3.90 | 3.44 | 3.08 | 2.78 | 2.54 |

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# Figure captions

Fig. 1. Molybdenum K-edge XANES spectra as a function of NaHS concentration at 30 ℃ (a) and 286 ℃ (b). Dotted lines in (a) represent standard structures: Also shown in (a) are the measured spectra of $[MoO_4]^{2-}$ moiety in $Na_2MoO_{4(solid)}$, and $[MoS_4]^{2-}$ in $(NH_4)_2MoS_{4(solid)}$.

Fig. 2. Evolution of the XANES spectra for all sample solutions as a function of temperature, from 30 ºC (blue line) to the maximum experimental temperature as labelled (red line). The temperature increments for each sample are listed in Table 1.

Fig. 3. Fourier transforms of the EXAFS spectra at 30 ℃ (a) and 286 ℃ (b). The solid lines are measured data and dashed lines are the fits using the parameters listed in the Table 3. Also shown in (a) are the spectra of $[MoO_4]^{2-}$ moiety in $Na_2MoO_{4(solid)}$, and $[MoS_4]^{2-}$ in $(NH_4)_2MoS_{4\ (solid)}$.

Fig. 4. Molybdenum K-edge EXAFS spectra in K-space (a) and Fourier transforms of EXAFS (b) collected at 30 ˚C to the maximum temperature as labelled for all sample solutions. The solid lines are measured data, and dashed lines are the fits using the parameters listed in Table 3. The composition and temperature increment for each sample are listed in Table 1.

Fig. 5. The change of ligand number derived from the EXAFS refinement as a function of NaHS concentration at 30 ˚C (a) and 286 ˚C (b) and 800 bar.

Fig. 6. Snapshots of hydrogen molybdate ions and molybdate species, determined from the MD simulations.

Fig. 7. Radial distribution function (RDF; solid lines) and coordination number (CN; dashed lines) for simulation 5A, 5B, 5C, 5D, 5E and 8.

Fig. 8. Snapshots of thiomolybdates determined from the MD simulations (bond distances see Table 3).

Fig. 9. The calculated XANES spectra using FDMNES and select experimental spectra. The XANES calculations are based on the molecular dynamic simulations of the structures for the species (see legend) at 77 and 300 ℃. The Molybdenum K-edge (20,000 eV) was subtracted from the experimental energy for the x-axis of experimental spectra. The $[MoO_4]^{2-}$ standard is $Na_2MoO_4$ and $[MoS_4]^{2-}$ is $(NH_4)_2MoS_4$ solids.

Fig. 10. Predominant Mo species in sulfur-bearing solutions (total Mo = 1 ppm, total sulfur = 0.1 m) as a function of pH and oxygen fugacity at 25 (a, b) and 300 ℃ (c, d). The calculations are done using The Geochemist's Workbench (Bethke, 2007) and the default thermodynamic database. The presence of molybdenite is suppressed in (b) and (d) to show only the fields of aqueous Mo(VI) species, The solubility contour of molybdenite of 10 and 100 ppb are also shown in (c). Blue dashed lines show the boundaries between stability fields of sulfur species, and the greyed areas show the estimated pH ranges of the experimental solutions (Table 1). Also shown in Fig c and d are the positions of the pH buffers of $CO_2$(aq)/$HCO_3^-$ and K-feldspar-Quartz-Muscovite (KMQ, $aK^+ = 0.1$).