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## Abstract

Rare Earth elements (REE) are gaining importance due to their increasing industrial applications and usefulness as petrogenetic indicators. REE-sulfate complexes are some of the most stable REE aqueous species in hydrothermal fluids, and may be responsible for REE transport and deposition in a wide variety of geological environments, ranging from sedimentary basins to magmatic hydrothermal settings. However, the thermodynamic properties of most REE-sulfate complexes are derived from extrapolation of ambient temperature data, since direct information on REE-sulfate complexing under hydrothermal conditions is only available for Nd, Sm and Er to 250 ˚C (Migdisov and William-Jones, 2008, 2016).

We employed *ab initio* molecular dynamics (MD) simulations to calculate the speciation and thermodynamic properties of yttrium(III) in sulfate and sulfate-chloride solutions at temperatures and pressures up to 500 ºC and 800 bar. The MD results were complemented by *in situ* X-ray absorption spectroscopy (XAS) measurements. Both MD and XAS show that

yttrium(III) sulfate complexes form and become increasingly stable with temperature (≥200 ˚C). The MD results also suggest that mixed yttrium-sulfate-chloride complexes (that cannot be distinguished from mixtures of chloride and sulfate complexes in XAS experiments) form at ≥350 ˚C. Two structures with two different Y(III)-S distances (monodentate and bidentate) are observed for Y(III)-sulfate bonding. The formation constants, derived via thermodynamic integration, for the Y(III) mono- and di-sulfate complexes parallel the trends for those of Nd, Sm and Er determined experimentally to 250 ˚C.

The derived formation constants were used to fit revised Helgeson-Kirkham-Flowers equation-of-state parameters that enabled calculation of formation constants for $Y(SO_4)^+$ and $Y(SO_4)_2^-$ over a wide range of temperatures and pressures. The presence of sulfate increases the solubility of Y(III) under specific conditions. Since the stability of sulfate is redox sensitive, Y(III) solubility becomes highly redox-sensitive, with rapid precipitation of Y minerals upon destabilisation of aqueous sulfate.

Keywords: yttrium, rare earth elements, sulfate, *ab initio* molecular dynamics, thermodynamics, *in situ* XAS.

# 1 Introduction

Rare earth elements (REE) are the 15 metals from lanthanum to lutetium; yttrium and scandium are often added, due to similar geochemical behaviour. These metals are in increasing demand due to their unique applications (Naumov, 2008; McLemore, 2011; Massari and Ruberti, 2013); their supply is highly concentrated in a few countries, resulting in their classification as critical minerals (Ram et al., 2019; Jowitt et al. 2020). Hydrothermal processes play an important role in the enrichment of REE (Migdisov et al., 2016), either in conjunction with magmatic processes (e.g. the world's largest REE deposit at Bayan Obo, China; Smith et

al., 2000) or in purely hydrothermal settings over a wide range in conditions (e.g., the Iron Oxide Copper Gold (IOCG) deposit at Olympic Dam, South Australia; Bastrakov et al., 2007; Xing et al. 2019; or the low temperature (<125 ˚C), basinal-brine related deposits of the Browns Ranges, Northern Australia; Richter et al., 2018; Nazari-Dehkordi et al., 2020). The near universal occurrence of the REE at low, but detectable levels, together with slight, systematic differences in their responses to changing physico-chemical conditions, make them powerful petrologic indicators for a wide variety of geological environments (Brugger et al., 2008; Williams-Jones et al., 2012; Migdisov et al. 2016).

In order to develop more effective exploration methods for REE deposits and to optimise the applications of REE as petrogenetic tools, it is beneficial to understand the mechanism of REE transport in hydrothermal fluids. REE transport is a function of solution composition (transporting and precipitating ligands, including $Cl^-$, $F^-$, $SO_4^{2-}$, $PO_4^{3-}$, $CO_3^{2-}$, etc…), other chemical parameters such as pH, temperature (T) and pressure (P), and the stability of REE-bearing minerals. As a ligand, sulfate is known to play a critical role in many geological environments, including seafloor vent fluids (Bach et al., 2003; Wang et al., 2020); volcano-hydrothermal systems (Inguaggiato et al., 2015); subduction fluids (Debret and Sverjensky, 2017; Rielli et al., 2017); and many magmatic hydrothermal systems (Panina, 2005). REE form strong sulfate complexes under ambient conditions (Gimeno Serrano et al., 2000; Lozano et al. 2020) and a direct link between sulfate-rich fluids and REE mineralization has been reported in a variety of deposits. Sulfate is for instance abundant in fluid inclusions associated with REE mineralisation in the granite-related Capitan Pluton, New Mexico (Banks et al., 1994; up to 24,210 ppm $SO_4^{2-}$) and in the quartz syenite-hosted bastnaesite deposits of the Gallinas Mountains, New Mexico (Williams-Jones et al., 2000; McLemore, 2011). Though most REE deposits are associated with magmatic carbonatites (González-Álvarez et al., 2021), late-magmatic mobilisation by hydrothermal fluids played an important role in upgrading the ores,

and sulfate-rich fluids are associated with many of these deposits, including the Mianning-Dechang REE belt, western Sichuan province, China (Xie et al., 2015), and the Huanglongpu carbonatites, China (Cangelosi et al., 2020).

Based on these observations, Cui et al. (2020) and Cangelosi et al. (2020) recently suggested that REE-sulfate complexes, rather than REE chloride complexes, may account for REE transport in these environments, despite the higher availability of chloride in crustal fluids (Migdisov and Williams-Jones, 2014). However, data on the speciation and thermodynamic properties of most REE-sulfate complexes are limited to extrapolations from room temperature (Wood, 1990; Haas et al., 1995; Migdisov et al., 2016) and a few experimental studies to 250˚C (Migdisov et al., 2006; Migdisov and William-Jones 2008). Room-temperature thermodynamic data for aqueous REE complexes, including $Y(SO_4)^+$ and $Y(SO_4)_2^-$, were selected by Spahiu and Kastriot (1995) based on an extensive literature review. Schijf and Byrne (2004) determined the formation constants of $REE(SO_4)^+$ at ambient conditions (ionic strength = 0.66 m and T = 25 ˚C) by solubility experiments, showing a relatively higher stability for LREE compared to HREE. Migdisov and Williams-Jones (2008) (including a re-interpretation of the Nd data published by Migdisov et al., 2006) measured the temperature dependence of the formation constants of Nd(III)-, Sm(III)- and Er(III) mono- and di-sulfate complexes by spectrophotometry, finding that the di-sulfate complex increases in stability relative to the mono-sulfate complex as temperature increases from 25˚C to 250˚C, the maximum experimental temperature. In addition to these experimental studies, theoretical quantum-chemical studies have characterised the stoichiometry and geometry of Y(III)-aqua, -chloride and -fluoride complexes under ambient, hydrothermal and subduction conditions. Ikeda et al. (2005a,b) characterised the hydration structure of $Y^{3+}$ at room temperature, and Liu et al. (2012) calculated the $pK_a$ of the hydrolysis reactions of $Y^{3+}$ at room temperature. Guan et al. (2020) combined *ab initio* molecular dynamic method and *in situ* X-ray absorption

spectroscopy to determine the Y(III)-Cl complexes present at temperature up to 500 ˚C and their formation constants, and Stefanski and Jahn (2020) used *ab initio* molecular dynamics to characterise the geometry and thermodynamics of Y(III)-Cl and Y(III)-F complexes under subduction zone conditions (800 ˚C, 13 and 45 kbar). To date, no quantum chemical study of Y(III)-sulfate (or any other REE-sulfate) complexes are reported, and experiments are limited to temperatures of 250 ˚C. Recently, Zhang and Yan (2022) used classical MD simulations to show that heavy REE (Lu) form more stable aqueous complexes than light REE (La) with a number of ligands, including sulfate; however, the classical MD method used in their study provides relatively large discrepancy between MD-derived and experimental stability constants (3-4 log units for sulfate).

Here, we aim to improve our understanding of the role of sulfate complexes in the mobility of yttrium using a combination of *ab initio* molecular dynamics (MD) simulations and *in situ* X-Ray Absorption Spectroscopy (XAS) to decipher the nature and geometry of yttrium(III)-sulfate complexes to magmatic-hydrothermal conditions. Thermodynamic properties for key species are then estimated using thermodynamic integration. This combined approach can provide accurate information about the geometry and stability of metal complexes in hydrothermal fluids (Mei et al., 2013, 2014, 2015a, 2015b, 2016; Brugger et al., 2016; Etschmann et al., 2019). Based on the new results, we discuss the mobility of Y(III) in both sulfate-rich and sulfate-chloride solutions under hydrothermal conditions, and provide a better understanding of REE transport and mineral precipitation in hydrothermal systems.

# 2 Method

## 2.1 *Ab initio* molecular dynamics

The *ab initio* molecular dynamics simulations were conducted with the CP2K/QUICKSTEP (Kühne et al., 2020) and Car-Parrinello Molecular Dynamics (CPMD, version 3.1.17, Car and Parrinello, 1985) packages. Both CP2K and CPMD were used for unconstrained simulations to study the geometry of Y-sulfate complexes, while CPMD was used for the thermodynamic integration simulations aimed at retrieving formation constants for the most important complexes. Due to differences in methods (Car-Parrinello vs. Born-Oppenheimer), *ab initio* MD simulations by CPMD are more CPU intensive than with CP2K. For example, one picosecond (ps) of data required ~1,400 CPU hours using CPMD for a simulation box containing 55 water molecules with a density of 1.03 g/cm$^3$ (300 ºC, box 3, Table 1), but one order of magnitude more resources ( ~14,400 CPU hour per ps) are required for a simulation box containing twice the amounts of water molecules (box 1, Table 1). In contrast, 460 CPU hours were required to collect 1 ps of real time data using CP2K for a simulation box with 111 water and a density of 1.11 g/cm$^3$ (200 ˚C, box 2, Table 1). In this study, we first compared the unconstrained MD results (e.g., bond distance) between CP2K and CPMD, finding no significant difference in the predictions from both codes (details in the Results section below); we employ the more efficient CP2K for longer (>40 ps) MD simulations, but we use the framework we developed in previous studies with CPMD for the derivation of stability constants for ligand exchange reactions using thermodynamic integration.

CP2K and CPMD employ the Kohn-Sham (Kohn and Sham, 1965) density functional theory with mixed Gaussian and Slater plane wave basis sets, respectively. The temperature was controlled by a Nosé-Hoover chain thermostat; periodic boundary conditions were applied to eliminate surface effects; and all simulations were conducted in the NVT canonical ensemble. In CP2K, the core electrons were modelled by Goedecker-Teter-Hutter (GTH)

pseudopotentials (Goedecker et al., 1996; Hartwigsen et al., 1998; Krack, 2005) and double-zeta valence polarized (DZVP) basis sets (VandeVondele and Hutter 2007) together with the BLYP exchange correlation functional (Becke, 1988; Lee et al., 1988). In CPMD, the BLYP exchange correlation functional was also used but in combination with the most-commonly used Troullier-Martins norm-conserving pseudopotentials (Troullier and Martins, 1991). Previous studies (e.g., Lin et al., 2012; Mei et al., 2015a) have shown that the BLYP functional can accurately describe aqueous metal-ligand interactions, especially at high temperature. In CP2K, a timestep 0.5 femtosecond (fs) was chosen, but a shorter simulation timestep of 0.073 fs was required in CPMD. The shorter time step required by the Car-Parrinello MD in CPMD is responsible for most of the increase in processing resources relative to CP2K.

Simulations were conducted at 200-500 ºC, 800 bar to compare with XAS experiments. Sulfate and chloride concentrations of 1-2 molal (*m*) were chosen to represent the hydrothermal fluids with manageable computing time, at ionic strengths that are common in geological fluids and manageable using commonly used activity coefficient models (Brugger et al. 2016; Helgeson et al., 1981). The densities of the solutions were set according to the equation of state of NaCl(aq) at targeted P-T conditions (Driesner, 2007; Driesner and Heinrich, 2007). Radial distribution functions (RDF) and coordination numbers (integrals of RDF) were calculated using VMD (Humphrey et al., 1996). Details of the simulation boxes and software used are listed in Table 1.

## 2.2 *Ab initio* thermodynamic integrations

*Ab initio* MD provides information on the geometric and stoichiometric properties of Y-sulfate complexes; however, in most cases the ligand exchange rates are longer than the time scale of the *ab initio* MD simulations achievable with current high performance computing infrastructure (typically <<100 picoseconds (ps); Mei et al., 2015a, Guan et al., 2020). Even

175 though ligand residence times decrease with increasing temperature to a point where individual
176 ligand exchange reactions can be easily observed via *ab initio* MD, the exchange rates are
177 generally not sufficient to allow measurements of the relative stabilities of the various
178 complexes by examining the distribution of species in the simulations. In the case of REE at
179 room temperature, the water and sulfate residence times vary in the range 100-1000 ps (Fay et
180 al., 1969; Richens 2005). Different methods have been developed to provide accurate statistical
181 sampling with achievable computing resources. Here we use the thermodynamic integration
182 method (Sprik, 1998; Sprik & Ciccotti, 1996) to determine the equilibrium constants of ligand
183 exchange reactions. As previous studies introduced and benchmarked this method for metals
184 complexed to small inorganic ligands in hydrothermal conditions (e.g., Mei et al., 2013), only
185 a brief summary is provided here. A predefined reaction path was set by defining the distance
186 ($r$) between the metal (Y) and the ligand ($SO_4^{2-}$) from the equilibrium distance ($r_I$) to a distance
187 ($r_{II}$) where there are no interactions between Y(III) and $SO_4^{2-}$. This is achieved by constraining
188 the Y-S distance. The average force ($f(r)$) required to constrain the Y(III)-S($SO_4^{2-}$) distance at
189 each step can be calculated from simulations conducted for at least 7 ps, which is sufficient
190 time to sample a significant representation of Y(III) configurations. The free energy surface of
191 the ligand exchange reaction was obtained by integrating $f(r)$ over the constrained distance $r$:

192 $$\Delta A_{I\to II} = -\int_{r_I}^{r_{II}} f(r)dr \quad (1)$$

193 The free energy difference of the reaction is independent from the reaction path (Guan et
194 al., 2020). The Gibbs free energy of the reaction, $\Delta_r G$, is approximated as $\Delta A_{I\to II}$ by assuming
195 that the pressure is constant during the reaction (Mei et al., 2013). The constrained MD
196 simulations were run under all the conditions of box 3 (Table 1) with CPMD. To further test
197 the effect of the box size on the results of the thermodynamic integrations, one set of
198 thermodynamic integration calculations was conducted within simulation box containing 111
199 water molecules at 300 ˚C (box 1). Because of the high demand for CPU resources of the

simulation in such a big box, we reduced the minimum simulation time to ~5 ps (instead of 7 ps) at each distance in this calculation.

The standard state Gibbs free energy of reaction ($\Delta_r G^\Theta$) can be derived from the measured Gibbs free energy of reaction ($\Delta_r G$) using:

$$\Delta_r G^\Theta = \Delta_r G + RT \ln \frac{C_A \gamma_A \cdot C_B \gamma_B}{C_c \gamma_c \cdot C_D \gamma_D} \qquad (2)$$

where $c_i$ is the concentration of the $i^{th}$ compound in the reaction A + B → C+ D, and $\gamma_i$ is the activity coefficient of each species; $\Delta_r G^{\Theta,c}$ is calculated assuming $\gamma_i = 1$, and $\Delta_r G^\Theta$ using activity coefficients described in the following paragraph. The concentrations $c_i$ were defined using the initial (at distance $r_I$; reactants) and final ($r_{II}$; products) configurations in the *ab initio* thermodynamic integration. For example, for the reaction $Y^{3+} + SO_4^{2-} = Y(SO_4)^+$, the initial equilibrated simulation box contains 1 m $Y^{3+}$ + 2 m $SO_4^{2-}$; the final contains 1 m $Y(SO_4)^+$ + 1 $SO_4^{2-}$. For the reaction $Y(SO_4)^+$ (b) + $SO_4^{2-}$ = $Y(SO_4)_2^-$, the concentrations of all species are equal to 1; hence, in this case, no correction is required if activity coefficients are neglected (equation (2)).

A more accurate estimate of the standard Gibbs free energy for the complex-forming reactions was obtained using the B-dot extension of the Debye-Hückel theory (Helgeson et al., 1981) to estimate the activity coefficients of the ions in the reaction:

$$\log \gamma_i = -\frac{z_i^2 A_\gamma I^{1/2}}{1 + a_i B_\gamma I^{1/2}} + \dot{B}_\gamma I \qquad (3)$$

where; $z_i$ is the charge of ion $i$; $I$ is the ionic strength in molality; $a_i$ is the ion size parameter (Å); $A_\gamma$ and $B_\gamma$ are defined in Tables 1 and 2 in Helgeson and Kirkham (1974), $\dot{B}_\gamma$ is an empirical parameter taken from Oelkers and Helgeson (1990). This formalism is chosen because of consistency with the Helgeson-Kirkham-Flowers (HKF) (Helgeson et al., 1981; Sverjensky, 1997) equation-of-state (EOS), which is *de facto* the most widely used EOS in hydrothermal geochemistry (e.g., Miron et al. 2019).

Formation constants (K) are calculated from:

$$\Delta_r G^{\Theta} = -\mathrm{RT}\ln \mathrm{K} \quad (4)$$

where R is the gas constant and T is the absolute temperature.

The errors of the $\Delta_r G$ were estimated using the method proposed by Allen and Tildesley (1987, section 6.4), which takes into account both systematic and statistical errors. This method was successfully employed in measuring the uncertainties of thermodynamic integration by Rodinger et al. (2005), Mei et al. (2018, 2020) and Guan et al. (2020). The cumulative formation constants (logß) for the reaction

$$Y^{3+} + 2SO_4^{2-} = Y(SO_4)_2^{-} \quad (5)$$

were calculated by adding the logK(P,T) for the $Y^{3+} + SO_4^{2-} = Y(SO_4)^{+}$ and $Y(SO_4)^{+} + SO_4^{2-} = Y(SO_4)_2^{-}$ reactions, applying standard error propagation rules.

## 2.3 X-ray absorption spectroscopy (XAS)

### 2.3.1 Sample solutions and XAS measurements

MilliQ water and analytical grade yttrium sulfate ($Y_2(SO_4)_3$•$8H_2O$), $Na_2SO_4$, 96% $H_2SO_4$, and NaCl were used to prepare the experimental solutions for XAS measurements (Table 2). All solutions were prepared gravimetrically.

The speciation of yttrium in sulfate and mixed sulfate-chloride solutions was characterised via *in situ* XAS measurements using the high temperature-high pressure cell developed at the Institut Néel/ESRF (Testemale et al., 2005); the details of the experimental setup are described in Guan et al. (2020). The temperature of the fluid at the beam location was calibrated (e.g., Tooth et al., 2013; Louvel et al., 2017) by calculating the density of pure water from measurements of the absorbance and X-ray mass attenuation coefficients tabulated by Chantler (1995), and then compared to that from the equation of state of pure water (NIST database, Lemmon et al., 2000). This method provides a direct measurement of the temperature at the beam position; temperature accuracy is better than 5 ºC, and temperature varied within less that

1 ºC during the measurements. Pressure was read from a calibrated Bourdin gauge with a precision better than 5 bars; during the experiment, pressure was maintained within <1 bar by a proportional–integral–derivative (PID) controller system (Bruyère et al., 2008).

Yttrium K-edge (17,038 eV) Extended X-ray Absorption Fine Structure (EXAFS) spectra were collected up to 400 ºC at 800 bars at the FAME beamline at the European Synchrotron Research Facility (ESRF) in Grenoble, France. The ESRF is a 6.03 GeV ring; operating in 7/8 multi-bunch mode it has a maximum current of 200 mA. FAME is a bending magnet beamline (see Proux et al., 2005 for details), and its double crystal Si(220) monochromator provides an energy resolution of 0.87 eV at the Y K-edge energy. A focused beam size of FWHM 220 x 145 $\mu m^2$ was used. The incident and transmitted beam intensities $I_0$ and $I_1$ were measured with Si diodes, and a Canberra 30 element solid state fluorescence detector was used for detecting fluorescence data. The beam energy was calibrated with an Y foil, such that the maximum of the first derivative was at 17,038 eV.

### 2.3.2 XAS data processing

EXAFS data were analysed with the HORAE package (Ravel and Newville, 2005), using FEFF version 9 (Rehr et al., 2009); $E_0$ was defined as the maximum of the first derivative. Reported errors in EXAFS parameters (1-σ) are those calculated by the Artemis program (part of HORAE). The amplitude reduction factor ($S_0^2$) accounts for multi-electronic processes that impact the amplitude of the EXAFS signal (Roy et al., 1997), and is determined by fitting a compound with similar molecular structure as the unknown. In our case, $S_0^2$ was determined by fixing the coordination of a low salinity solution at 30 ºC to eight oxygen atoms (Guan et al., 2020), as the structure of the Y(III) aqua ion has been well characterized by previous studies (Ikeda et al., 2005a,b; Ohta et al., 2008; Liu et al., 2012; Lindqvist-Reis et al., 2000). A $S_0^2$ value of 0.73 was determined by refining the $S_0^2$, bond lengths and EXAFS Debye-Waller

factors for this solution; this value is consistent with theoretical constraints (Roy et al., 1997) and was used in all subsequent refinements.

For each solution, all spectra were fitted simultaneously, resulting in one $\Delta E_0$ and one set of goodness-of-fit parameters for each solution. The EXAFS Debye-Waller $\sigma^2$ was fitted at the lowest measured temperature for each solution, with the constraint that it typically doubles from 30 to 500 ºC, as determined from MD simulations (Guan et al., 2020). Note that the Debye-Waller values determined from the *ab initio* MD simulations are higher than the experimental ones, as a result of the short sampling times in *ab initio* MD, that tend to overestimate structural disorder. However, the relative changes in the MD Debye-Waller values are likely to be accurate, especially since the vibrational characteristics of the complexes are well reproduced by *ab initio* MD (e.g., Mei et al., 2013 and references therein). In practice, this was applied by increasing the EXAFS Debye-Waller by a factor of 1.2 for each ~100 ºC increase in temperature. The EXAFS Debye-Waller coefficients for sulfur and chlorine were assumed to be the same as that for O, in part to reduce the number of variables and in part due to the (usually) low (S±Cl):O ratio meaning that an independent measurement of these parameters was not possible.

# 3 Results

## 3.1 Geometry of Y(III)-sulfate complexes

The results of *ab initio* MD of Y sulfate complexes from CP2K are summarized in Table 3. The results from CP2K and CPMD for box 3 (Table 1) are compared in Supplementary Table S1. Both codes predict similar geometries (bond distances and coordination numbers) of the complexes at similar conditions, but more ligand exchange reactions were observed from the CPMD simulation than CP2K. Figure 1 shows snapshots of different Y(III)-sulfate and sulfate-chloride complexes.

297 In general, Y(III) can bond with 1 or 2 oxygen atoms from a $SO_4^{2-}$ group, forming
298 monodentate (Y-S distance at ~3.6 Å) or bidentate (Y-S distance at ~3.0 Å) structures
299 (Figures 1a, b). Figure 2 shows the distance between Y(III) and S as a function of simulation
300 time, which reflects the change in the structure of the Y-sulfate complexes. At 200 ˚C
301 (Figure 2a), simulation (1a) was launched with the $[Y(SO_4)(H_2O)_9]^+$ structure (in the following
302 text, square bracket are used when the full first-shell coordination is indicated, i.e. including
303 coordinated water molecules); for the first 20.5 ps, the complex stabilized as $[Y(SO_4)(H_2O)_{6.6}]^+$
304 with a monodentate $SO_4^{2-}$. After this, a second sulfate bonded with Y(III), and this $Y(SO_4)_2^-$
305 complex was stable for the rest of the simulation. The two sulfate ions were bonded with Y(III)
306 in a monodentate configuration for 41.6 ps, then in the last 19.9 ps one of the sulfate ligands
307 switched to bidentate bonding, which resulted in the loss of one of the coordinated water
308 molecules and decreased the average hydration number of the $Y(SO_4)_2^-$ complex from 5.2 to
309 4.2. At 300 ˚C (1b), the simulation started with the configuration $[Y(SO_4)(H_2O)_8]^+$, with
310 bidentate bonding of the sulfate ligands. This configuration remained stable for the whole
311 simulation time (43 ps), with an average hydration number of 7.2.
312 At 350 ˚C, in simulation (1c) (Figure 2b), the initial configuration $[Y(SO_4)_2(H_2O)_7]^-$
313 dehydrated rapidly to $[Y(SO_4)_2(H_2O)_{3.8}]^-$ and was then stable for 31.5 ps until another $SO_4^{2-}$
314 bonded with Y(III) and the hydration number decreased to 1.8. When bonded with two sulfate
315 ions, all three combinations of structures with two sulfate ions were observed (i.e. both sulfate
316 groups in monodentate configuration; both in bidentate configuration; and mixed mono- and
317 bidentate). When Y(III) was bonded to 3 sulfate ions after 30 ps, the 2x bidentate plus 1x
318 monodentate was the predominate configuration.
319 $Cl^-$ was then added to the simulation to test for mixed $SO_4^{2-}$-$Cl^-$ complexes (jobs 2a, 2b,
320 2c). Under these conditions, Y-Cl bonding was detected at temperatures over 200 ˚C (350 and
321 500 ˚C). At 200 ˚C, simulation (2a, Figure 2c) had a starting configuration of

322 $[Y(SO_4)Cl(H_2O)_7]^0$, which rapidly changed to $[Y(SO_4)(H_2O)_{5.8}]^+$ and then remained stable for
323 the rest of the simulation. The Y-$SO_4^{2-}$ complex was monodentate but became bidentate for the
324 last 2 ps of the simulation. At the higher temperatures of 350 and 500 ˚C (simulations 2b,
325 Figure 2d and 2c, Figure 2e, respectively), Y(III) was coordinated to both $Cl^-$ and $SO_4^{2-}$, with
326 Y-Cl bond lengths ranging from 2.60 Å to 2.63 Å. At 350 ˚C, the $SO_4^{2-}$ bonded to Y(III)
327 predominantly in a monodentate manner (Figure 2d), whereas it was bidentate at 500 ˚C
328 (Figure 2e). Deprotonation occurred in both simulations 2b and 2c, which resulted in the
329 formation of $[YCl(HSO_4)(OH)(H_2O)_3]^0$ and $[YCl_2(SO_4)(OH)(H_2O)]^{2-}$ at 350 ˚C and 500 ˚C,
330 respectively (Figure 1c,1d). The $H^+$ in simulation 2c bonded with the free sulfate and became
331 $HSO_4^-$ in the simulation box.

332 The hydration number of Y(III) decreased with increasing temperature, with Y-O($H_2O$)
333 distances ranging from 2.32 Å to 2.41 Å. These Y-O($H_2O$) distances are slightly longer than
334 the Y-O($SO_4^{2-}$) distances, which range from 2.23 – 2.32 Å. The transition from monodentate
335 to bidentate sulfate geometry is associated with the loss of one coordinated water, causing a
336 decrease in hydration number. Deprotonation and formation of Y-OH bonds were also
337 observed, with Y-OH distances at ~2.10 Å.

338 ## 3.2 *Ab initio* thermodynamic integration of Y(III)-sulfate complexes

339 Figure 3 shows the results of the free energy surface calculations for the ligand dissociation
340 reaction of the Y(III) mono-sulfate complex at 200 ˚C, 800 bar.

341 $$Y(SO_4)^+ = Y^{3+} + SO_4^{2-} \qquad (6)$$

342 The Helmholtz free energy $\Delta A_{I\rightarrow II}$ of reaction (6) was calculated by integrating the mean force
343 ($F_C$) required to constrain Y-S($SO_4^{2-}$) distances at fixed values from position I (average binding
344 distance for the sulfate in the bidentate $Y(SO_4)^+$ complex, derived from unconstrained MD) to
345 position II (negligible interactions between the Y(III) and sulfate ions). As expected, $F_C$ is near
346 zero at both position I ($r_I$ = 3 Å; $F_C$ = 6.4 ± 2.7 kJ/(mol•Å)) and II ($r_{II}$ = 6 Å; $F_C$ = -3.1

± 2.3 kJ/(mol•Å). A second (meta-stable) equilibrium point is found at the intermediate position III (3.6 Å; Figure 3), which corresponds to the monodentate $Y(SO_4)^+$ complex. Thus, a second Helmholtz free energy can be obtained from this calculation, which refers to the change of $Y(SO_4)^+$ from the monodentate to bidentate structures ($\Delta A_{I\rightarrow III}$). During the transition from bidendate (position I) to monodendate (position III), $F_C$ reaches a minimum of -64.6 ± 5.7 kJ/(mol•Å) at a Y-S($SO_4^{2-}$) distance $r$ = 3.2 Å. With the increasing Y-S distance from bidentate to monodentate, one of the oxygens from the $SO_4^{2-}$ remains at ~2.3 Å, however, the other oxygen moves away from Y(III). For example, at the Y-S($SO_4^{2-}$) distance of 3.3 Å (position a in Figure 3), the other oxygen is at 3 Å from Y(III) and the structure became monodentate afterwards, where the hydration number of Y(III) increased by 1 (total hydration number of 6) and reached equilibrium at $r_{III}$. The difference in the free energy between bi- and mono-dentate $Y(SO_4)^+$ is 6.1 ± 3.2 kJ/mol (from $r_I$ to $r_{III}$). From $r_{III}$ to $r_{II}$, the maximum energy barrier of dissociation was reached at 4.3 Å (38.1 ± 6.7 kJ/mol). The $F_C$ are close to zero when the Y-S($SO_4^{2-}$) distance is beyond ~5 Å (1.0 ± 2.8 kJ/(mol•Å) at 5.3 Å; 2.3 ± 3.0 kJ/(mol•Å) at 5.6 Å and ‑ 3.1 ± 2.3 kJ/(mol•Å) at 6.0 Å), indicating that there are no interactions between Y(III) and $SO_4^{2-}$. The integration of $F_C$ over the reaction path gives a free energy difference for reaction (6) of 23.8 ± 12.5 kJ/mol and 17.8 ± 8.9 kJ/mol for bidentate and monodentate $Y(SO_4)^+$ complexes, respectively.

To test the effect of the box size on the results of the thermodynamic integrations, the free energy surface calculation of reaction (6) at 300 ˚C was conducted using the box 1 composition (Table 1), which contains twice as many waters as box 3 (111 vs. 55). Since the CPMD calculations are prohibitively CPU intensive at this box size (~14,400 CPU hour for each ps of real time simulation), we reduced the minimum simulation time to ~5 ps (instead of 7 ps) at each distance. Still, this single thermodynamic integration run costed a total of ~1.76 M CPU hours. All free energy surfaces for the dissociations of the $Y(SO_4)^+$ and $Y(SO_4)_2^-$ complexes

obtained in this study are shown in Figure 4, and the resulting Gibbs free energy of reaction and equilibrium constants for the formation (logK) of these complexes are summarized in Table 4. The results from the two different box sizes are consistent after the concentration and activity correction.

Because of the large size of the Y(III)-sulfate complexes (Fig. 1), the symmetrically equivalent Y-sulfate complexes are separated by ~3 water molecules in the boxes containing 55 waters. Hence, finite size effects may be significant, but cannot be avoided given current computational capabilities for the *ab initio* approach chosen in this study. Yet, we can be confident that the results presented are valid because the energy of dissociation is expected to be dominated by first-shell effects (sulfate ligand bonding and hydration shell), that are well described via *ab initio* MD even in a small box. This assumption is validated by comparing (i) results of *ab initio* thermodynamic MD in boxes of different sizes, and (ii) results of classical and *ab initio* MD. (i) The thermodynamic properties derived from the simulations in boxes with 55 vs. 111 waters are equal within error. The doubling of the number of atoms results in a factor 10 increase in computational resources, but only 26% increase in the linear box size; however, the separation between the symmetrically equivalent Y-sulfate complexes increases significantly by at least one water molecule in the boxes containing 111 waters compared to 55 waters (Table 1; box length increases by 3.37 Å). Hence, the results from the larger box confirm the dominance of first shell effects on the energetics of the ligand formation reactions. (ii) Classical MD employing the potential mean force (PMF) can be conducted in large simulation boxes (1000's of water molecules), minimizing the effects of box size and ionic strength. However, empirical potential parameters are usually based on the experimental and *ab initio* results, and are poorly suited to quantify first-shell interactions, especially in systems with complex orbital shapes imposing strong constraints on the geometry of the complexes. In the case of REE, Zhang and Yan (2022) recently showed that these limitations

reduce the accuracy of thermodynamic predictions for ligand exchange reactions; for example, the logß of $La(SO_4)^+$ calculated from classical MD at 250 ˚C is 3.69 ± 0.06 higher than the experimentally-based value (Migdisov et al. 2016). Finally, direct comparison with experimental data is important to validate the predicted geometry and stoichiometry of the complexes; in this study, we find excellent qualitative agreement between *ab initio* simulations and *in-situ* XAS results.

### 3.3 Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS)

Two sets of solutions were measured (Table 2); sulfate-only (Sols 2,4,10) and mixed sulfate-chloride solutions (Sols 9,13,14). All R-space spectra have a peak at ~1.9 Å (phase uncorrected) due to Y-O bonding, and some solutions show a small peak at ~2.5 Å (phase uncorrected) due to Y-S bonding (Figure 5). The Y-O peak (i) shifted position slightly with temperature and (ii) showed the 'classic' dehydration effect for metal complexes, where the number of O atoms (i.e. waters of hydration) coordinated to Y(III) decreased with increasing temperature (Table 5, Figure 5; Brugger et al. 2016). In contrast, the Y-S($SO_4^{2-}$) peak position remained constant with temperature (Figure 5b).

EXAFS cannot distinguish between oxygen from water or from a sulfate group, as the Y-O contribution can be fitted with a single average distance (Figure 5), but the experimental Y-O distances (2.32 to 2.385 Å) are close to the average distances derived from MD, which results show that Y-O($H_2O$) distances generally range from 2.38 to 2.40 Å, whereas Y-O($SO_4^{2-}$) distances range from 2.23 to 2.32 Å. For example for Sol4 (~2 m $SO_4^{2-}$ Table 2, comparable to MD job 1a, Table 3) at 200 ºC, the experimental bond length (2.368(7) Å) is similar to the averaged MD Y-O($H_2O$) and Y-O($SO_4^{2-}$) bond lengths for the first 20 ps, ~2.37 Å; the MD water-sulfate Y-O bond length averaged over 80 ps is ~2.35 Å, which is within 3-σ of the experimentally derived bond length. At 350 ºC, the experimental Y-O bond length is 2.357(7) Å, which is within 2-σ of the average MD value ~2.35 Å.

EXAFS fits (Figure 5) of the sulfate-only solutions demonstrated that Y-S complexing only occurred for the higher pH solutions, i.e. where most of the sulfate was introduced as $Na_2SO_4$ with only minor $H_2SO_4$ to acidify the solution to avoid hydroxide complexing (Table 2). No Y(III) sulfate complexing was observed in low pH solutions, where $H_2SO_4$ was the only source of sulfate. As noted in section 3.1, MD simulations indicate that monodentate Y-S distances are ~3.6 Å and bidentate Y-S distances ~3.0 Å (Figure 1a,b). Thus, based on the experimentally fitted bond length (2.98 to 3.08 Å, Table 5), it can be determined that the Y(III)-sulfate complexes are predominantly bidentate. The bidentate coordination resulted in a relatively rigid structure, and while some Y-S($SO_4^{2-}$) bond lengths had to be fixed for the EXAFS refinement, it can be seen that the Y-S($SO_4^{2-}$) peak position does not shift with temperature (Figure 5b).

EXAFS fits of the mixed sulfate-chloride solutions indicated that Y(III) chloride complexing occurred in all solutions where $Cl^-$ was present (Sols9,13,14). In Sol9, there was no Y(III) sulfate complexing as $H_2SO_4$ was the only source of sulfate, and the number of chloride bonding to Y(III) increased slightly with increasing temperature [$Y(H_2O)_{7.1}Cl_{1.3}$ at 30 ˚C to $Y(H_2O)_{5.0}Cl_{1.6}$ at 350 ˚C], an observation that is consistent with many previous studies of metal-chloride complexing (e.g., Brugger et al. 2016; Crerar et al. 1985; Guan et al. 2020; Liu et al. 2011; Mei et al. 2015a). For solutions that had Y(III) complexing with both $SO_4^{2-}$ and $Cl^-$ (Sol13,14), the number of sulfate bonded to Y(III) increased slightly with increasing temperature, while the number of chlorides decreased [$Y(H_2O)_{4.8}Cl_{1.8}(SO_4)_{1.3}$ at 200 ºC to $Y(H_2O)_{4.3}Cl_{1.3}(SO_4)_{1.6}$ at 350-400 ˚C, Sol13]. This is in apparent contradiction to the MD results, which demonstrated increasing Y-Cl coordination with increasing temperature (no Y-Cl complexing at 200 ˚C, even when Cl was included in the initial configuration and increasing Y-Cl coordination at 500 ˚C, as described in section 3.1). However, direct comparison is difficult, because the pH in the experiments changes from acidic at room T to near neutral at

447 400˚C (Table 2), which is expected to decrease chloride complexing versus sulfate complexing.
448 With respect to the geometry of the predominant complexes, the experimental and MD results
449 agree well: the Y-Cl bond lengths are similar, being within 3σ of the experimental error (2.68(1)
450 to 2.76(7) Å experimental and 2.60 to 2.63 Å MD). Importantly, both experimental and MD
451 results agree that Y-sulfate coordination increases with increasing temperature in these mixed
452 sulfate-chloride solutions.

453 # 4 Discussion

454 ## 4.1 Y(III)-sulfate complexes : monodentate vs. bidentate

455 Ligands like sulfate and carbonate can form both monodentate or bidentate structures
456 (Brugger et al., 2016), which affects the geometry and stability of metal complexes in
457 hydrothermal fluids (e.g., $UO_2^{2+}$-sulfate, Kalintsev et al., 2019; and Eu(III)-sulfate, Liu et al.,
458 2017). The unconstrained MD results show that Y(III) can bond with $SO_4^{2-}$ in both
459 monodentate and bidentate modes; therefore, when bonding with two (or more) $SO_4^{2-}$, the
460 configuration can be any combination of monodentate, bidentate or mixed structures.
461 Thermodynamic integration provides an effective way to determine the formation constants
462 and the difference in Gibbs free energy between the two structures. The results are summarized
463 in Table 6. For the reactions:

464 $$Y^{3+} + SO_4^{2-} = Y(SO_4)^{+} \quad (7)$$

465 $$Y(SO_4)^{+} + SO_4^{2-} = Y(SO_4)_2^{-} \quad (8)$$

466 at the same conditions, the maximum absolute difference of the Gibbs free energy between the
467 two structures (mono and bidentate for reaction (7); 1x monodentate and 1xbidentate, and
468 2xbidentate for reaction (8), Table 6) is -14 .0 ±3.4 kJ/mol for reaction (8) at 300 ˚C (800 bar).
469 Previous theoretical calculations of uranyl sulfate (Vallet and Grenthe, 2007) at 25 ˚C had

similar differences in Gibbs free energies from monodentate to bidentate of -17 kJ/mol for $UO_2(SO_4)$ and -13 kJ/mol for $UO_2(SO_4)_2^{2-}$, respectively.

The studies of both Y(III)- and uranyl- mono-/bidentate sulfate complexes suggest that in general the bidentate structures are slightly more stable than the monodentate structure. However, for reaction (8) at 200 ˚C, calculations show that near-equal amounts of monodentate and bidentate Y-sulfate structures could exist in the solution. For the equilibrium:

$$Y(SO_4)_n(SO_4)(\mathbf{m})^{(1-2n)} = Y(SO_4)_n(SO_4)(\mathbf{b})^{(1-2n)} \quad (n=0,1) \qquad (9)$$

where (m) indicates monodentate, and (b) bidentate sulfate complexing; the corresponding mass action equation is

$$\ln(K_9) = -\frac{\Delta_r G}{RT} = \ln\frac{a_{Y(SO_4)_n(SO_4)(\mathbf{b})^{(1-2n)}}}{a_{Y(SO_4)_n(SO_4)(\mathbf{m})^{(1-2n)}}} = \ln\frac{c_{Y(SO_4)_n(SO_4)(\mathbf{b})^{(1-2n)}}\cdot\gamma_{Y(SO_4)_n(SO_4)(\mathbf{b})^{(1-2n)}}}{c_{Y(SO_4)_n(SO_4)(\mathbf{m})^{(1-2n)}}\cdot\gamma_{Y(SO_4)_n(SO_4)(\mathbf{m})^{(1-2n)}}} \quad (10)$$

Because the activity coefficients for both isomers are identical (same charges of the species), equation (10) provides the actual ratio of the two isomers ($\frac{c_{Y(SO_4)_n(SO_4)(\mathbf{b})^{(1-2n)}}}{c_{Y(SO_4)_n(SO_4)(\mathbf{m})^{(1-2n)}}}$) as a function of Gibbs free energy of reaction ($\Delta_r G$) and temperature (T, in kelvin); the ratio is 1 if $\Delta_r G$=0 at all temperature; at 200˚C, the ratio is 0.8 at $\Delta_r G$= -1 kJ/mol, and 4.6 at $\Delta_r G$= -6 kJ/mol; at 300˚C, the ratios is 1.5 at $\Delta_r G$ = -2 kJ/mol and 18.9 at $\Delta_r G$ = -14 kJ/mol; at 400˚C, the ratios are 6.0 at $\Delta_r G$ = -10 kJ/mol and 2.4 at $\Delta_r G$ = -5 kJ/mol (Table 6).

The EXAFS analysis confirms that at temperatures over 200 ˚C, Y(III) sulfate complexes are predominantly bidentate. A previous *in situ* XAS study on Eu(III) (Liu et al., 2017) found a similar bidentate configuration for the $Eu(SO_4)_2^{2-}$ complex, and it can thus be expected that all REE will form similar complexes in S-bearing hydrothermal fluids. The trends of higher translational entropy with increasing temperatures of the system (Mei et al., 2015a; Brugger et al., 2016) is one of the reasons to favour the bidentate structure of Y(III)-$(SO_4^{2-})_{1,2}$ complexes, as the second oxygen of the bonded sulfate will substitute for one water molecule when the structure changes from monodentate to bidentate, e.g.

$$[Y(SO_4)(H_2O)_n(\mathbf{m})]^+ = [Y^b(SO_4)(H_2O)_{n-1}(\mathbf{b})]^+ + H_2O \quad (11)$$

Therefore, considering the experimental results, the bidentate formation constants of each reaction are chosen as the final data for geochemical modelling. The cumulative formation constant (logß) of each reaction at different P-T are listed in Table 7.

## 4.2 Thermodynamic extrapolations

The thermodynamic properties of all predominant aqueous species are required over a wide range of temperatures and pressures to enable predictions of metal transport and precipitation under hydrothermal conditions, in particular simulations of complex processes such as fluid-rock interaction, fluid mixing, or cooling. The HKF equation-of-state is the most widely used semi-empirical EOS to extrapolate the thermodynamic properties of aqueous complexes from limited experiment points. The original HKF EOS is applicable to 1000 ˚C and 5 kbar, and recently the approach has been extended to 6.0 GPa and 1200 ˚C (Sverjensky et al. 2014; Huang and Sverjensky, 2019).

In this study, we fitted the HKF EOS for the standard Gibbs free energy of formation from the elements ($\Delta_f G^0(P,T)$) for the $YSO_4^+$ and $Y(SO_4)_2^-$ complexes described here, as well as for the $YCl_n^{3-n}$ (n=1-4) complexes studied by Guan et al. (2020). The fitting strategy was optimised to reflect most of the available constraints of Y-sulfate and Y-chloride complexing, and minimise the number of empirical fit parameters. The $\Delta_f G^0(P,T)$ each aqueous species were calculated from their formation constants and $\Delta_f G^0(P,T)$ values of $Y^{3+}$, $SO_4^{2-}$ and $Cl^-$ computed with HKF parameters compiled by Shock & Helgeson (1988) and Shock et al. (1997).

For Y-sulfate complexes, we fitted $\Delta_f G^0(P,T)$ at 200, 300 and 400 ˚C and 800 bar (Table 7) from MD; assuming that the REE-sulfate complexes behave coherently in hydrothermal fluids (Migdisov et al., 2016; Cangelosi et al., 2020), the experimental values of $Er(SO_4)_n^{3-2n}$ (n=1,2) from Migdisov and Williams-Jones (2008) at 25˚C, 100˚C, 150˚C, 200˚C and 250˚C (at $P_{sat}$) were also included in the fitting to provide a model that is internally consistent with REE. The

519 data at 200 ˚C, Psat of $Er(SO_4)_n^{3-2n}$ (n=1,2) from Migdisov and Williams-Jones (2008) is within
520 the error of the data of $Y(SO_4)_n^{3-2n}$ (n=1,2) in this study at 200 ˚C, 800 bar. Y+REE speciation
521 in seawater was recently reviewed by Schijf and Byrne (2021), who provided a $logK_{25°C}$ for
522 the formation of $YSO_4^+$ of 3.50, similar to the value of 3.59±0.11 for $ErSO_4^+$ of Migdisov and
523 Williams-Jones (2008).

524 For Y-chloride complexes, $\Delta_f G^0(25°C, 1bar)$) of $YCl_n^{3-n}$ (n= 1, 2) was set to the values
525 from the thermodynamic parameters of Ho-Cl complexes from the study of Migdisov et al.,
526 (2009); values for n=3,4 were estimated assuming a linear behaviour of the energetics of the
527 step-wise complex forming reactions. Similar to Y-sulfate, the formation constant for the $YCl^{2+}$
528 complex reported by Schijf and Byrne (2021) (0.65±0.03) is identical within error to the value
529 for $HoCl^{2+}$ of 0.71 derived from Migdisov et al. (2009). The partial molar volume
530 ($\bar{V}^0(25°C, 1bar)$ of the sulfate and chloride complexes were chosen from the linear
531 correlations as from Haas et al. (1995).

532 Within the HKF formalism, the pressure and temperature dependence of the partial molar
533 volume ($\bar{V}^0(25°C, 1bar)$) and molar heat capacity ($\bar{c_p}^0(25°C, 1bar)$) are described by the
534 empirical parameters *a1-a4* and *c1-c2*, respectively. We attempted to use the empirical
535 correlations proposed in the DEW model of Sverjensky et al. (2014) for these parameters, i.e.,
536 fitting only $\Delta_f G^0(25°C, 1bar)$, molar entropy ($\bar{S}^0(25°C, 1bar)$), $\bar{c_p}^0(25°C, 1bar)$, and, for
537 sulfate complexes, $\bar{V}^0(25°C, 1bar)$; however, we found that this approach did not reproduce
538 the selected data points within 2σ error. For the final fits, reported in Table 8, we therefore fit
539 the PT dependence of (i) molar volume using the *a1* parameter (*a2*=*a3*=*a4*=0; refining these
540 did not improve the results significantly), and (ii) molar heat capacity using *c1* and *c2*. The
541 Born coefficient $\omega$ was calculated using the correlations defined in the DEW model
542 (Sverjensky et al. 2014). Optimisation was conducted using a non-linear least square approach

to minimise the sum of the square of the predicted and experimental $\Delta_f G^0(P,T)$, weighted by the experimental errors of each datapoint.

The parameters of the HKF EOS provided in Table 8 should be considered as provisional and will be refined in subsequent publications.

### 4.3 Geological implications

Our *ab initio* thermodynamic integration provided formation constants of Y(III) sulfate complexes up to high temperatures (400 ˚C). Together with the thermodynamic data of Y(III) chloride (Table 8), Y(III) fluoride (Dos Santos et al., 2012; Loges et al., 2013) and $Y(OH)_3$(s) (Navrotsky et al., 2015), it is now possible to model the Y solubility and the predominant Y(III) species in hydrothermal sulfate, chlorine and fluorine fluids. The modelling was conducted with the CHNOSZ program (Dick, 2019). The thermodynamic data for aqueous species other than Y(III) are sourced from its default OBIGT database, which includes the aqueous species from Sverjensky et al. (1997). Thermodynamic data for $Y^{3+}$ and hydroxide Y(III) complexes in OBIGT are sourced from Shock and Helgeson (1998) and Shock et al. (1997).

Figure 6 shows the predominant species of Y(III) in the $Cl^-$-$SO_4^{2-}$-$F^-$-$Na^+$ system as a function of pH and temperature, for oxidised (sulfate stable), chloride-rich fluids (Cl:S = 10). Fluorine is also present, at concentrations typical of F-rich hydrothermal systems (Cl:F = 200 and 2000; Banks et al., 1994; Xing et al. 2019; Yardley, 2005). $Y^{3+}$ is predominant only at low temperature and at low pH, at both $P_{sat}$ (Figures 6a, b) and 1000 bar (Figures 6c, d). Yttrium forms strong complexes with fluorine (Loges et al., 2013), although the mobility of Y+REE in F-rich fluids is limited by the low solubility of fluoride-bearing minerals (e.g., Migdisov, et al., 2019), such as simple fluorides (used as proxies in our simple diagrams) and fluoro-carbonates. In all diagrams, $YF_3$(s) and $Y(OH)_3$(s) are the solubility-limiting phases (shown for 1 ppb Y). The stability of Y(III)-Cl complexes increases with increasing temperature, and Y(III) exists predominantly as $YCl_3$(aq) in the modelled brines (2 molal chloride). Y(III) sulfate complexes

568 may play an important role in Y transport when there is relatively low concentration of fluorine
569 in the fluids, and $Y(SO_4)_2^-$ is predicted to predominate at temperature from 100 to 300˚C over
570 a pH range of ~1.5 – 4 at $P_{sat}$ (Figure 6b). At pressure of 1 kbar, $Y(SO_4)^+$ is predicted to
571 predominate at intermediate acidic pH at temperatures from 100 ˚C to ~180 ˚C, and at higher
572 temperature the $Y(SO_4)_2^-$ complex becomes predominant to temperatures of ~280 ˚C; at higher
573 temperature, Y-chloride complexes take over (Figure 6d).
574 Hence, the presence of sulfate increases the solubility of Y(III) under specific conditions.
575 Since the stability of sulfate is redox sensitive, Y(III) solubility becomes highly redox-sensitive,
576 with rapid precipitation of Y minerals upon destabilisation of aqueous sulfate. Though mix
577 ligand Y(III)-sulfate-chloride complexes were not included in the geochemical model due to
578 lack of quantitative data, Y(III) solubility may be further increased by the formation of Y(III)-
579 sulfate-chloride.
580 An interesting feature of the diagrams in Figures 6 is the strong effect of pressure on
581 mineral solubility and aqueous Y(III) speciation. For example, the predominance field of the
582 aqueous Y-F complex increases dramatically at 1 kbar versus $P_{sat}$, resulting in a significant
583 increase in Y solubility via reaction (12b) compared to (12a). This difference suggests that
584 reactions (12a) and (12b) are associated with large changes in molar volumes:
585 $$YF_3(s) + 2\ SO_4^{2-} = Y(SO_4)_2^- + 3\ F^- \quad (12a)$$
586 $$\Delta_r\bar{V}^0_{25^\circ C,1bar} = -53.8\ cm^3\ mol^{-1};\ \Delta_r\bar{V}^0_{200^\circ C,1000bar} = -71.0\ cm^3\ mol^{-1}$$
587 $$YF_3(s) = YF_2^+ + F^- \quad (12b)$$
588 $$\Delta_r\bar{V}^0_{25^\circ C,1bar} = -130.1\ cm^3\ mol^{-1};\ \Delta_r\bar{V}^0_{200^\circ C,1000bar} = -136.73\ cm^3\ mol^{-1}$$
589 The main reason for these differences is that the fluoride and sulfate ions have different
590 hydration spheres (e.g., Patel et al., 2011). Such strong pressure effects on aqueous speciation
591 are rarely reported in the literature, and usually expected over larger pressure differences (e.g.,
592 Brugger et al. 2016; Ohoa, et al., 2015). Hence, the simulation results suggest that in cases

involving ligand exchange among halides and oxyanion ligands such as sulfate and carbonate, pressure may have a significant effect at mid- to upper-crustal depths, and that pressure-induced precipitation may be a significant ore-forming process in some cases.

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