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# Yttrium speciation in sulfate-rich hydrothermal ore-forming fluids

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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 °C and 800 bar. The MD results were complemented by *in situ* X-ray absorption spectroscopy (XAS) measurements. Both MD and XAS show that

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

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

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

45

## 46 1 Introduction

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

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

62 In order to develop more effective exploration methods for REE deposits and to optimise  
63 the applications of REE as petrogenetic tools, it is beneficial to understand the mechanism of  
64 REE transport in hydrothermal fluids. REE transport is a function of solution composition  
65 (transporting and precipitating ligands, including Cl<sup>-</sup>, F<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, CO<sub>3</sub><sup>2-</sup>, etc...), other  
66 chemical parameters such as pH, temperature (T) and pressure (P), and the stability of REE-  
67 bearing minerals. As a ligand, sulfate is known to play a critical role in many geological  
68 environments, including seafloor vent fluids (Bach et al., 2003; Wang et al., 2020); volcano-  
69 hydrothermal systems (Inguaggiato et al., 2015); subduction fluids (Debret and Sverjensky,  
70 2017; Rielli et al., 2017); and many magmatic hydrothermal systems (Panina, 2005). REE form  
71 strong sulfate complexes under ambient conditions (Gimeno Serrano et al., 2000; Lozano et al.  
72 2020) and a direct link between sulfate-rich fluids and REE mineralization has been reported  
73 in a variety of deposits. Sulfate is for instance abundant in fluid inclusions associated with REE  
74 mineralisation in the granite-related Capitan Pluton, New Mexico (Banks et al., 1994; up to  
75 24,210 ppm SO<sub>4</sub><sup>2-</sup>) and in the quartz syenite-hosted bastnaesite deposits of the Gallinas  
76 Mountains, New Mexico (Williams-Jones et al., 2000; McLemore, 2011). Though most REE  
77 deposits are associated with magmatic carbonatites (González-Álvarez et al., 2021), late-  
78 magmatic mobilisation by hydrothermal fluids played an important role in upgrading the ores,

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

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

104 spectroscopy to determine the Y(III)-Cl complexes present at temperature up to 500 °C and  
105 their formation constants, and [Stefanski and Jahn \(2020\)](#) used *ab initio* molecular dynamics to  
106 characterise the geometry and thermodynamics of Y(III)-Cl and Y(III)-F complexes under  
107 subduction zone conditions (800 °C, 13 and 45 kbar). To date, no quantum chemical study of  
108 Y(III)-sulfate (or any other REE-sulfate) complexes are reported, and experiments are limited  
109 to temperatures of 250 °C. Recently, [Zhang and Yan \(2022\)](#) used classical MD simulations to  
110 show that heavy REE (Lu) form more stable aqueous complexes than light REE (La) with a  
111 number of ligands, including sulfate; however, the classical MD method used in their study  
112 provides relatively large discrepancy between MD-derived and experimental stability constants  
113 (3-4 log units for sulfate).

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

124

## 125 2 Method

### 126 2.1 *Ab initio* molecular dynamics

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

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

150 pseudopotentials (Goedecker et al., 1996; Hartwigsen et al., 1998; Krack, 2005) and double-  
151 zeta valence polarized (DZVP) basis sets (VandeVondele and Hutter 2007) together with the  
152 BLYP exchange correlation functional (Becke, 1988; Lee et al., 1988). In CPMD, the BLYP  
153 exchange correlation functional was also used but in combination with the most-commonly  
154 used Troullier-Martins norm-conserving pseudopotentials (Troullier and Martins, 1991).  
155 Previous studies (e.g., Lin et al., 2012; Mei et al., 2015a) have shown that the BLYP functional  
156 can accurately describe aqueous metal-ligand interactions, especially at high temperature. In  
157 CP2K, a timestep 0.5 femtosecond (fs) was chosen, but a shorter simulation timestep of  
158 0.073 fs was required in CPMD. The shorter time step required by the Car-Parrinello MD in  
159 CPMD is responsible for most of the increase in processing resources relative to CP2K.

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

169

## 170 2.2 *Ab initio* thermodynamic integrations

171 *Ab initio* MD provides information on the geometric and stoichiometric properties of Y-  
172 sulfate complexes; however, in most cases the ligand exchange rates are longer than the time  
173 scale of the *ab initio* MD simulations achievable with current high performance computing  
174 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 ( $\text{SO}_4^{2-}$ ) from the equilibrium distance ( $r_I$ ) to a distance  
187 ( $r_{II}$ ) where there are no interactions between Y(III) and  $\text{SO}_4^{2-}$ . This is achieved by constraining  
188 the Y-S distance. The average force ( $f(r)$ ) required to constrain the Y(III)-S( $\text{SO}_4^{2-}$ ) 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  $r$ :

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

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  $\Delta A_{I \rightarrow II}$  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

200 simulation in such a big box, we reduced the minimum simulation time to ~5 ps (instead of  
201 7 ps) at each distance in this calculation.

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

$$204 \quad \Delta_r G^\ominus = \Delta_r G + RT \ln \frac{c_{AY_A} \cdot c_{BY_B}}{c_C \gamma_C \cdot c_D \gamma_D} \quad (2)$$

205 where  $c_i$  is the concentration of the  $i^{\text{th}}$  compound in the reaction  $A + B \rightarrow C + D$ , and  $\gamma_i$  is  
206 the activity coefficient of each species;  $\Delta_r G^{\ominus,c}$  is calculated assuming  $\gamma_i = 1$ , and  $\Delta_r G^\ominus$  using  
207 activity coefficients described in the following paragraph. The concentrations  $c_i$  were defined  
208 using the initial (at distance  $r_{\text{I}}$ ; reactants) and final ( $r_{\text{II}}$ ; products) configurations in the *ab initio*  
209 thermodynamic integration. For example, for the reaction  $Y^{3+} + SO_4^{2-} = Y(SO_4)^+$ , the initial  
210 equilibrated simulation box contains 1 m  $Y^{3+} + 2$  m  $SO_4^{2-}$ ; the final contains 1 m  $Y(SO_4)^+ +$   
211 1  $SO_4^{2-}$ . For the reaction  $Y(SO_4)^+(b) + SO_4^{2-} = Y(SO_4)_2^-$ , the concentrations of all species are  
212 equal to 1; hence, in this case, no correction is required if activity coefficients are neglected  
213 (equation (2)).

214 A more accurate estimate of the standard Gibbs free energy for the complex-forming  
215 reactions was obtained using the B-dot extension of the Debye-Hückel theory (Helgeson et al.,  
216 1981) to estimate the activity coefficients of the ions in the reaction:

$$217 \quad \log \gamma_i = -\frac{z_i^2 A_\gamma I^{1/2}}{1 + a_i B_\gamma I^{1/2}} + \dot{B}_\gamma I \quad (3)$$

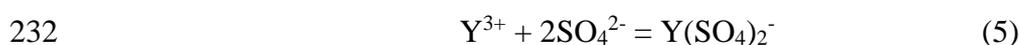
218 where;  $z_i$  is the charge of ion  $i$ ;  $I$  is the ionic strength in molality;  $a_i$  is the ion size parameter  
219 ( $\text{\AA}$ );  $A_\gamma$  and  $B_\gamma$  are defined in Tables 1 and 2 in Helgeson and Kirkham (1974),  $\dot{B}_\gamma$  is an  
220 empirical parameter taken from Oelkers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

224 Formation constants (K) are calculated from:

$$225 \quad \Delta_r G^\ominus = -RT \ln K \quad (4)$$

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

227 The errors of the  $\Delta_r G$  were estimated using the method proposed by [Allen and Tildesley](#)  
228 [\(1987, section 6.4\)](#), which takes into account both systematic and statistical errors. This method  
229 was successfully employed in measuring the uncertainties of thermodynamic integration by  
230 [Rodinger et al. \(2005\)](#), [Mei et al. \(2018, 2020\)](#) and [Guan et al. \(2020\)](#). The cumulative  
231 formation constants ( $\log\beta$ ) for the reaction



233 were calculated by adding the  $\log K(P,T)$  for the  $\text{Y}^{3+} + \text{SO}_4^{2-} = \text{Y}(\text{SO}_4)^+$  and  $\text{Y}(\text{SO}_4)^+ + \text{SO}_4^{2-}$   
234  $= \text{Y}(\text{SO}_4)_2^-$  reactions, applying standard error propagation rules.

## 235 2.3 X-ray absorption spectroscopy (XAS)

### 236 2.3.1 Sample solutions and XAS measurements

237 MilliQ water and analytical grade yttrium sulfate ( $\text{Y}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ ),  $\text{Na}_2\text{SO}_4$ , 96%  $\text{H}_2\text{SO}_4$ ,  
238 and NaCl were used to prepare the experimental solutions for XAS measurements ([Table 2](#)).  
239 All solutions were prepared gravimetrically.

240 The speciation of yttrium in sulfate and mixed sulfate-chloride solutions was characterised  
241 via *in situ* XAS measurements using the high temperature-high pressure cell developed at the  
242 Institut Néel/ESRF ([Testemale et al., 2005](#)); the details of the experimental setup are described  
243 in [Guan et al. \(2020\)](#). The temperature of the fluid at the beam location was calibrated (e.g.,  
244 [Tooth et al., 2013](#); [Louvel et al., 2017](#)) by calculating the density of pure water from  
245 measurements of the absorbance and X-ray mass attenuation coefficients tabulated by [Chantler](#)  
246 [\(1995\)](#), and then compared to that from the equation of state of pure water (NIST database,  
247 [Lemmon et al., 2000](#)). This method provides a direct measurement of the temperature at the  
248 beam position; temperature accuracy is better than 5 °C, and temperature varied within less than

249 1 °C during the measurements. Pressure was read from a calibrated Bourdin gauge with a  
250 precision better than 5 bars; during the experiment, pressure was maintained within <1 bar by  
251 a proportional–integral–derivative (PID) controller system (Bruyère et al., 2008).

252 Yttrium K-edge (17,038 eV) Extended X-ray Absorption Fine Structure (EXAFS) spectra  
253 were collected up to 400 °C at 800 bars at the FAME beamline at the European Synchrotron  
254 Research Facility (ESRF) in Grenoble, France. The ESRF is a 6.03 GeV ring; operating in 7/8  
255 multi-bunch mode it has a maximum current of 200 mA. FAME is a bending magnet beamline  
256 (see Proux et al., 2005 for details), and its double crystal Si(220) monochromator provides an  
257 energy resolution of 0.87 eV at the Y K-edge energy. A focused beam size of FWHM  
258 220 x 145  $\mu\text{m}^2$  was used. The incident and transmitted beam intensities  $I_0$  and  $I_1$  were measured  
259 with Si diodes, and a Canberra 30 element solid state fluorescence detector was used for  
260 detecting fluorescence data. The beam energy was calibrated with an Y foil, such that the  
261 maximum of the first derivative was at 17,038 eV.

### 262 2.3.2 XAS data processing

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

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

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

## 289 3 Results

### 290 3.1 Geometry of Y(III)-sulfate complexes

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

297 In general, Y(III) can bond with 1 or 2 oxygen atoms from a  $\text{SO}_4^{2-}$  group, forming  
298 monodentate (Y-S distance at  $\sim 3.6 \text{ \AA}$ ) or bidentate (Y-S distance at  $\sim 3.0 \text{ \AA}$ ) 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  $200 \text{ }^\circ\text{C}$   
301 (Figure 2a), simulation (1a) was launched with the  $[\text{Y}(\text{SO}_4)(\text{H}_2\text{O})_9]^+$  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  $[\text{Y}(\text{SO}_4)(\text{H}_2\text{O})_{6.6}]^+$   
304 with a monodentate  $\text{SO}_4^{2-}$ . After this, a second sulfate bonded with Y(III), and this  $\text{Y}(\text{SO}_4)_2^-$   
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  $\text{Y}(\text{SO}_4)_2^-$  complex from 5.2 to  
309 4.2. At  $300 \text{ }^\circ\text{C}$  (1b), the simulation started with the configuration  $[\text{Y}(\text{SO}_4)(\text{H}_2\text{O})_8]^+$ , 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  $350 \text{ }^\circ\text{C}$ , in simulation (1c) (Figure 2b), the initial configuration  $[\text{Y}(\text{SO}_4)_2(\text{H}_2\text{O})_7]^-$   
313 dehydrated rapidly to  $[\text{Y}(\text{SO}_4)_2(\text{H}_2\text{O})_{3.8}]^-$  and was then stable for 31.5 ps until another  $\text{SO}_4^{2-}$   
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  $\text{Cl}^-$  was then added to the simulation to test for mixed  $\text{SO}_4^{2-}\text{-Cl}^-$  complexes (jobs 2a, 2b,  
320 2c). Under these conditions, Y-Cl bonding was detected at temperatures over  $200 \text{ }^\circ\text{C}$  ( $350$  and  
321  $500 \text{ }^\circ\text{C}$ ). At  $200 \text{ }^\circ\text{C}$ , simulation (2a, Figure 2c) had a starting configuration of

322  $[\text{Y}(\text{SO}_4)\text{Cl}(\text{H}_2\text{O})_7]^0$ , which rapidly changed to  $[\text{Y}(\text{SO}_4)(\text{H}_2\text{O})_{5.8}]^+$  and then remained stable for  
 323 the rest of the simulation. The  $\text{Y}-\text{SO}_4^{2-}$  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  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , with  
 326 Y-Cl bond lengths ranging from 2.60 Å to 2.63 Å. At 350 °C, the  $\text{SO}_4^{2-}$  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  $[\text{YCl}(\text{HSO}_4)(\text{OH})(\text{H}_2\text{O})_3]^0$  and  $[\text{YCl}_2(\text{SO}_4)(\text{OH})(\text{H}_2\text{O})]^{2-}$  at 350 °C and 500 °C,  
 330 respectively (**Figure 1c,1d**). The  $\text{H}^+$  in simulation **2c** bonded with the free sulfate and became  
 331  $\text{HSO}_4^-$  in the simulation box.

332 The hydration number of Y(III) decreased with increasing temperature, with Y-O( $\text{H}_2\text{O}$ )  
 333 distances ranging from 2.32 Å to 2.41 Å. These Y-O( $\text{H}_2\text{O}$ ) distances are slightly longer than  
 334 the Y-O( $\text{SO}_4^{2-}$ ) 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.



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( $\text{SO}_4^{2-}$ ) distances at fixed values from position I (average binding  
 344 distance for the sulfate in the bidentate  $\text{Y}(\text{SO}_4)^+$  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;  $F_C = 6.4 \pm 2.7$  kJ/(mol·Å)) and II ( $r_{II} = 6$  Å;  $F_C = -3.1$

347  $\pm 2.3$  kJ/(mol $\cdot$ Å). A second (meta-stable) equilibrium point is found at the intermediate  
348 position III (3.6 Å; [Figure 3](#)), which corresponds to the monodentate Y(SO<sub>4</sub>)<sup>+</sup> complex. Thus,  
349 a second Helmholtz free energy can be obtained from this calculation, which refers to the  
350 change of Y(SO<sub>4</sub>)<sup>+</sup> from the monodentate to bidentate structures ( $\Delta A_{I \rightarrow III}$ ). During the  
351 transition from bidentate (position I) to monodentate (position III),  $F_C$  reaches a minimum of  
352  $-64.6 \pm 5.7$  kJ/(mol $\cdot$ Å) at a Y-S(SO<sub>4</sub><sup>2-</sup>) distance  $r = 3.2$  Å. With the increasing Y-S distance  
353 from bidentate to monodentate, one of the oxygens from the SO<sub>4</sub><sup>2-</sup> remains at  $\sim 2.3$  Å, however,  
354 the other oxygen moves away from Y(III). For example, at the Y-S(SO<sub>4</sub><sup>2-</sup>) distance of 3.3 Å  
355 (position a in [Figure 3](#)), the other oxygen is at 3 Å from Y(III) and the structure became  
356 monodentate afterwards, where the hydration number of Y(III) increased by 1 (total hydration  
357 number of 6) and reached equilibrium at  $r_{III}$ . The difference in the free energy between bi- and  
358 mono-dentate Y(SO<sub>4</sub>)<sup>+</sup> is  $6.1 \pm 3.2$  kJ/mol (from  $r_I$  to  $r_{III}$ ). From  $r_{III}$  to  $r_{II}$ , the maximum energy  
359 barrier of dissociation was reached at 4.3 Å ( $38.1 \pm 6.7$  kJ/mol). The  $F_C$  are close to zero when  
360 the Y-S(SO<sub>4</sub><sup>2-</sup>) distance is beyond  $\sim 5$  Å ( $1.0 \pm 2.8$  kJ/(mol $\cdot$ Å) at 5.3 Å;  $2.3 \pm 3.0$  kJ/(mol $\cdot$ Å) at  
361 5.6 Å and  $-3.1 \pm 2.3$  kJ/(mol $\cdot$ Å) at 6.0 Å), indicating that there are no interactions between  
362 Y(III) and SO<sub>4</sub><sup>2-</sup>. The integration of  $F_C$  over the reaction path gives a free energy difference for  
363 reaction (6) of  $23.8 \pm 12.5$  kJ/mol and  $17.8 \pm 8.9$  kJ/mol for bidentate and monodentate  
364 Y(SO<sub>4</sub>)<sup>+</sup> complexes, respectively.

365 To test the effect of the box size on the results of the thermodynamic integrations, the free  
366 energy surface calculation of reaction (6) at 300 °C was conducted using the box 1 composition  
367 ([Table 1](#)), which contains twice as many waters as box 3 (111 vs. 55). Since the CPMD  
368 calculations are prohibitively CPU intensive at this box size ( $\sim 14,400$  CPU hour for each ps of  
369 real time simulation), we reduced the minimum simulation time to  $\sim 5$  ps (instead of 7 ps) at  
370 each distance. Still, this single thermodynamic integration run costed a total of  $\sim 1.76$  M CPU  
371 hours. All free energy surfaces for the dissociations of the Y(SO<sub>4</sub>)<sup>+</sup> and Y(SO<sub>4</sub>)<sub>2</sub><sup>-</sup> complexes

372 obtained in this study are shown in [Figure 4](#), and the resulting Gibbs free energy of reaction  
373 and equilibrium constants for the formation ( $\log K$ ) of these complexes are summarized in  
374 [Table 4](#). The results from the two different box sizes are consistent after the concentration and  
375 activity correction.

376 Because of the large size of the Y(III)-sulfate complexes ([Fig. 1](#)), the symmetrically  
377 equivalent Y-sulfate complexes are separated by  $\sim 3$  water molecules in the boxes containing  
378 55 waters. Hence, finite size effects may be significant, but cannot be avoided given current  
379 computational capabilities for the *ab initio* approach chosen in this study. Yet, we can be  
380 confident that the results presented are valid because the energy of dissociation is expected to  
381 be dominated by first-shell effects (sulfate ligand bonding and hydration shell), that are well  
382 described via *ab initio* MD even in a small box. This assumption is validated by comparing  
383 (i) results of *ab initio* thermodynamic MD in boxes of different sizes, and (ii) results of  
384 classical and *ab initio* MD. (i) The thermodynamic properties derived from the simulations in  
385 boxes with 55 vs. 111 waters are equal within error. The doubling of the number of atoms  
386 results in a factor 10 increase in computational resources, but only 26% increase in the linear  
387 box size; however, the separation between the symmetrically equivalent Y-sulfate complexes  
388 increases significantly by at least one water molecule in the boxes containing 111 waters  
389 compared to 55 waters ([Table 1](#); box length increases by 3.37 Å). Hence, the results from the  
390 larger box confirm the dominance of first shell effects on the energetics of the ligand formation  
391 reactions. (ii) Classical MD employing the potential mean force (PMF) can be conducted in  
392 large simulation boxes (1000's of water molecules), minimizing the effects of box size and  
393 ionic strength. However, empirical potential parameters are usually based on the experimental  
394 and *ab initio* results, and are poorly suited to quantify first-shell interactions, especially in  
395 systems with complex orbital shapes imposing strong constraints on the geometry of the  
396 complexes. In the case of REE, [Zhang and Yan \(2022\)](#) recently showed that these limitations

397 reduce the accuracy of thermodynamic predictions for ligand exchange reactions; for example,  
398 the  $\log\beta$  of  $\text{La}(\text{SO}_4)^+$  calculated from classical MD at 250 °C is  $3.69 \pm 0.06$  higher than the  
399 experimentally-based value (Migdisov et al. 2016). Finally, direct comparison with  
400 experimental data is important to validate the predicted geometry and stoichiometry of the  
401 complexes; in this study, we find excellent qualitative agreement between *ab initio* simulations  
402 and *in-situ* XAS results.

### 403 3.3 Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS)

404 Two sets of solutions were measured (Table 2); sulfate-only (Sols 2,4,10) and mixed  
405 sulfate-chloride solutions (Sols 9,13,14). All R-space spectra have a peak at  $\sim 1.9$  Å (phase  
406 uncorrected) due to Y-O bonding, and some solutions show a small peak at  $\sim 2.5$  Å (phase  
407 uncorrected) due to Y-S bonding (Figure 5). The Y-O peak (i) shifted position slightly with  
408 temperature and (ii) showed the ‘classic’ dehydration effect for metal complexes, where the  
409 number of O atoms (i.e. waters of hydration) coordinated to Y(III) decreased with increasing  
410 temperature (Table 5, Figure 5; Brugger et al. 2016). In contrast, the Y-S( $\text{SO}_4^{2-}$ ) peak position  
411 remained constant with temperature (Figure 5b).

412 EXAFS cannot distinguish between oxygen from water or from a sulfate group, as the Y-  
413 O contribution can be fitted with a single average distance (Figure 5), but the experimental Y-  
414 O distances (2.32 to 2.385 Å) are close to the average distances derived from MD, which results  
415 show that Y-O( $\text{H}_2\text{O}$ ) distances generally range from 2.38 to 2.40 Å, whereas Y-O( $\text{SO}_4^{2-}$ )  
416 distances range from 2.23 to 2.32 Å. For example for Sol4 ( $\sim 2$  m  $\text{SO}_4^{2-}$  Table 2, comparable to  
417 MD job 1a, Table 3) at 200 °C, the experimental bond length (2.368(7) Å) is similar to the  
418 averaged MD Y-O( $\text{H}_2\text{O}$ ) and Y-O( $\text{SO}_4^{2-}$ ) bond lengths for the first 20 ps,  $\sim 2.37$  Å; the MD  
419 water-sulfate Y-O bond length averaged over 80 ps is  $\sim 2.35$  Å, which is within 3- $\sigma$  of the  
420 experimentally derived bond length. At 350 °C, the experimental Y-O bond length is  
421 2.357(7) Å, which is within 2- $\sigma$  of the average MD value  $\sim 2.35$  Å.

422 EXAFS fits (Figure 5) of the sulfate-only solutions demonstrated that Y-S complexing  
423 only occurred for the higher pH solutions, i.e. where most of the sulfate was introduced as  
424 Na<sub>2</sub>SO<sub>4</sub> with only minor H<sub>2</sub>SO<sub>4</sub> to acidify the solution to avoid hydroxide complexing  
425 (Table 2). No Y(III) sulfate complexing was observed in low pH solutions, where H<sub>2</sub>SO<sub>4</sub> was  
426 the only source of sulfate. As noted in section 3.1, MD simulations indicate that monodentate  
427 Y-S distances are ~3.6 Å and bidentate Y-S distances ~3.0 Å (Figure 1a,b). Thus, based on the  
428 experimentally fitted bond length (2.98 to 3.08 Å, Table 5), it can be determined that the Y(III)-  
429 sulfate complexes are predominantly bidentate. The bidentate coordination resulted in a  
430 relatively rigid structure, and while some Y-S(SO<sub>4</sub><sup>2-</sup>) bond lengths had to be fixed for the  
431 EXAFS refinement, it can be seen that the Y-S(SO<sub>4</sub><sup>2-</sup>) peak position does not shift with  
432 temperature (Figure 5b).

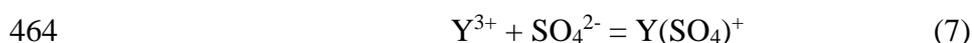
433 EXAFS fits of the mixed sulfate-chloride solutions indicated that Y(III) chloride  
434 complexing occurred in all solutions where Cl<sup>-</sup> was present (Sols9,13,14). In Sol9, there was  
435 no Y(III) sulfate complexing as H<sub>2</sub>SO<sub>4</sub> was the only source of sulfate, and the number of  
436 chloride bonding to Y(III) increased slightly with increasing temperature [Y(H<sub>2</sub>O)<sub>7.1</sub>Cl<sub>1.3</sub> at  
437 30 °C to Y(H<sub>2</sub>O)<sub>5.0</sub>Cl<sub>1.6</sub> at 350 °C], an observation that is consistent with many previous studies  
438 of metal-chloride complexing (e.g., Brugger et al. 2016; Crerar et al. 1985; Guan et al. 2020;  
439 Liu et al. 2011; Mei et al. 2015a). For solutions that had Y(III) complexing with both SO<sub>4</sub><sup>2-</sup> and  
440 Cl<sup>-</sup> (Sol13,14), the number of sulfate bonded to Y(III) increased slightly with increasing  
441 temperature, while the number of chlorides decreased [Y(H<sub>2</sub>O)<sub>4.8</sub>Cl<sub>1.8</sub>(SO<sub>4</sub>)<sub>1.3</sub> at 200 °C to  
442 Y(H<sub>2</sub>O)<sub>4.3</sub>Cl<sub>1.3</sub>(SO<sub>4</sub>)<sub>1.6</sub> at 350-400 °C, Sol13]. This is in apparent contradiction to the MD  
443 results, which demonstrated increasing Y-Cl coordination with increasing temperature (no Y-  
444 Cl complexing at 200 °C, even when Cl was included in the initial configuration and increasing  
445 Y-Cl coordination at 500 °C, as described in section 3.1). However, direct comparison is  
446 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 3 $\sigma$  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

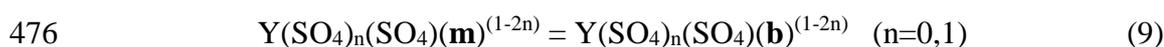
455 Ligands like sulfate and carbonate can form both monodentate or bidentate structures  
456 (Brugger et al., 2016), which affects the geometry and stability of metal complexes in  
457 hydrothermal fluids (e.g., UO<sub>2</sub><sup>2+</sup>-sulfate, Kalintsev et al., 2019; and Eu(III)-sulfate, Liu et al.,  
458 2017). The unconstrained MD results show that Y(III) can bond with SO<sub>4</sub><sup>2-</sup> in both  
459 monodentate and bidentate modes; therefore, when bonding with two (or more) SO<sub>4</sub><sup>2-</sup>, 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:



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  $\pm$ 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

470 similar differences in Gibbs free energies from monodentate to bidentate of -17 kJ/mol for  
471  $\text{UO}_2(\text{SO}_4)$  and -13 kJ/mol for  $\text{UO}_2(\text{SO}_4)_2^{2-}$ , respectively.

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

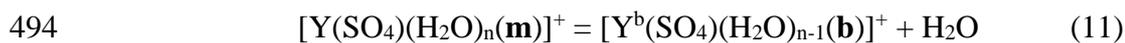


477 where (m) indicates monodentate, and (b) bidentate sulfate complexing; the corresponding  
478 mass action equation is

$$479 \quad \ln(K_9) = -\frac{\Delta_r G}{RT} = \ln \frac{a_{\text{Y}(\text{SO}_4)_n(\text{SO}_4)(\mathbf{b})^{(1-2n)}}}{a_{\text{Y}(\text{SO}_4)_n(\text{SO}_4)(\mathbf{m})^{(1-2n)}}} = \ln \frac{c_{\text{Y}(\text{SO}_4)_n(\text{SO}_4)(\mathbf{b})^{(1-2n)}} \gamma_{\text{Y}(\text{SO}_4)_n(\text{SO}_4)(\mathbf{b})^{(1-2n)}}}{c_{\text{Y}(\text{SO}_4)_n(\text{SO}_4)(\mathbf{m})^{(1-2n)}} \gamma_{\text{Y}(\text{SO}_4)_n(\text{SO}_4)(\mathbf{m})^{(1-2n)}}} \quad (10)$$

480 Because the activity coefficients for both isomers are identical (same charges of the  
481 species), equation (10) provides the actual ratio of the two isomers  $\left(\frac{c_{\text{Y}(\text{SO}_4)_n(\text{SO}_4)(\mathbf{b})^{(1-2n)}}}{c_{\text{Y}(\text{SO}_4)_n(\text{SO}_4)(\mathbf{m})^{(1-2n)}}}\right)$  as a  
482 function of Gibbs free energy of reaction ( $\Delta_r G$ ) and temperature (T, in kelvin); the ratio is 1 if  
483  $\Delta_r G=0$  at all temperature; at 200°C, the ratio is 0.8 at  $\Delta_r G= -1$  kJ/mol, and 4.6 at  $\Delta_r G= -$   
484 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,  
485 the ratios are 6.0 at  $\Delta_r G = -10$  kJ/mol and 2.4 at  $\Delta_r G = -5$  kJ/mol (Table 6).

486 The EXAFS analysis confirms that at temperatures over 200 °C, Y(III) sulfate complexes  
487 are predominantly bidentate. A previous *in situ* XAS study on Eu(III) (Liu et al., 2017) found  
488 a similar bidentate configuration for the  $\text{Eu}(\text{SO}_4)_2^{2-}$  complex, and it can thus be expected that  
489 all REE will form similar complexes in S-bearing hydrothermal fluids. The trends of higher  
490 translational entropy with increasing temperatures of the system (Mei et al., 2015a; Brugger et  
491 al., 2016) is one of the reasons to favour the bidentate structure of Y(III)- $(\text{SO}_4^{2-})_{1,2}$  complexes,  
492 as the second oxygen of the bonded sulfate will substitute for one water molecule when the  
493 structure changes from monodentate to bidentate, e.g.



495 Therefore, considering the experimental results, the bidentate formation constants of each  
496 reaction are chosen as the final data for geochemical modelling. The cumulative formation  
497 constant ( $\log\beta$ ) of each reaction at different P-T are listed in [Table 7](#).

#### 498 4.2 Thermodynamic extrapolations

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

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

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

519 data at 200 °C,  $P_{\text{sat}}$  of  $\text{Er}(\text{SO}_4)_n^{3-2n}$  ( $n=1,2$ ) from Migdisov and Williams-Jones (2008) is within  
520 the error of the data of  $\text{Y}(\text{SO}_4)_n^{3-2n}$  ( $n=1,2$ ) 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  $\log K_{25^\circ\text{C}}$  for  
522 the formation of  $\text{YSO}_4^+$  of 3.50, similar to the value of  $3.59 \pm 0.11$  for  $\text{ErSO}_4^+$  of Migdisov and  
523 Williams-Jones (2008).

524 For Y-chloride complexes,  $\Delta_f G^0(25^\circ\text{C}, 1\text{bar})$  of  $\text{YCl}_n^{3-n}$  ( $n=1,2$ ) 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  $\text{YCl}^{2+}$   
528 complex reported by Schijf and Byrne (2021) ( $0.65 \pm 0.03$ ) is identical within error to the value  
529 for  $\text{HoCl}^{2+}$  of 0.71 derived from Migdisov et al. (2009). The partial molar volume  
530 ( $\bar{V}^0(25^\circ\text{C}, 1\text{bar})$ ) 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 ( $\bar{V}^0(25^\circ\text{C}, 1\text{bar})$ ) and molar heat capacity ( $\bar{c}_p^0(25^\circ\text{C}, 1\text{bar})$ ) 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  $\Delta_f G^0(25^\circ\text{C}, 1\text{bar})$ , molar entropy ( $\bar{S}^0(25^\circ\text{C}, 1\text{bar})$ ),  $\bar{c}_p^0(25^\circ\text{C}, 1\text{bar})$ , and, for  
537 sulfate complexes,  $\bar{V}^0(25^\circ\text{C}, 1\text{bar})$ ; however, we found that this approach did not reproduce  
538 the selected data points within  $2\sigma$  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

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

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

### 547 4.3 Geological implications

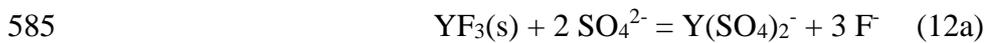
548 Our *ab initio* thermodynamic integration provided formation constants of Y(III) sulfate  
549 complexes up to high temperatures (400 °C). Together with the thermodynamic data of Y(III)  
550 chloride (Table 8), Y(III) fluoride (Dos Santos et al., 2012; Loges et al., 2013) and Y(OH)<sub>3</sub>(s)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

557 Figure 6 shows the predominant species of Y(III) in the Cl<sup>-</sup>-SO<sub>4</sub><sup>2-</sup>-F<sup>-</sup>-Na<sup>+</sup> system as a  
558 function of pH and temperature, for oxidised (sulfate stable), chloride-rich fluids (Cl:S = 10).  
559 Fluorine is also present, at concentrations typical of F-rich hydrothermal systems (Cl:F = 200  
560 and 2000; Banks et al., 1994; Xing et al. 2019; Yardley, 2005). Y<sup>3+</sup> is predominant only at low  
561 temperature and at low pH, at both P<sub>sat</sub> (Figures 6a, b) and 1000 bar (Figures 6c, d). Yttrium  
562 forms strong complexes with fluorine (Loges et al., 2013), although the mobility of Y+REE in  
563 F-rich fluids is limited by the low solubility of fluoride-bearing minerals (e.g., Migdisov, et al.,  
564 2019), such as simple fluorides (used as proxies in our simple diagrams) and fluoro-carbonates.  
565 In all diagrams, YF<sub>3</sub>(s) and Y(OH)<sub>3</sub>(s) are the solubility-limiting phases (shown for 1 ppb Y).  
566 The stability of Y(III)-Cl complexes increases with increasing temperature, and Y(III) exists  
567 predominantly as YCl<sub>3</sub>(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:



586 
$$\Delta_r \bar{V}_{25^\circ C, 1bar}^0 = -53.8 \text{ cm}^3 \text{ mol}^{-1}; \Delta_r \bar{V}_{200^\circ C, 1000bar}^0 = -71.0 \text{ cm}^3 \text{ mol}^{-1}$$



588 
$$\Delta_r \bar{V}_{25^\circ C, 1bar}^0 = -130.1 \text{ cm}^3 \text{ mol}^{-1}; \Delta_r \bar{V}_{200^\circ C, 1000bar}^0 = -136.73 \text{ cm}^3 \text{ mol}^{-1}$$

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

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

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