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2 **Multiple sulfur isotope fractionation in hydrothermal**  
3 **systems in the presence of radical ions and molecular**  
4 **sulfur**

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**Keywords:**

Trisulfur radical ion; disulfur radical ion, molecular sulfur; hydrothermal fluid; experiment; sulfur isotopes; mass dependent fractionation (MDF); mass independent fractionation (MIF).

**Abstract:**

This study is aimed to evaluate the role played by the sulfur radical ions ( $S_3^{\cdot-}$  and  $S_2^{\cdot-}$ ) and molecular sulfur ( $S^0$ ) on sulfur isotope fractionation and to investigate if these species may leave an isotope fingerprint in hydrothermal systems. For this purpose, we combined i) experiments using a hydrothermal reactor with aqueous  $S_3^{\cdot-}$ ( $S_2^{\cdot-}$ )- $S^0$ -sulfate-sulfide fluids and pyrite across a wide range of temperatures (300-450°C), pressures (300-800 bar), fluid acidity (4<pH<8) and with elevated total sulfur concentrations (0.1-1.0 mol/kg fluid) favorable for formation of those polymeric sulfur species, ii) precise quadruple S isotope analyses of the different S-bearing aqueous species in sampled fluids and in-situ precipitated pyrite, and iii) thermodynamic modeling of sulfur aqueous speciation and solubility. Our results quantitatively confirm both equilibrium and kinetic  $SO_4$ - $H_2S$  and pyrite- $H_2S$  mass dependent fractionation (MDF) factors previously established using extensive experimental and natural data from more dilute fluids in which polymeric sulfur species are negligible. MDF signatures of  $S^0$  measured in the sampled fluids of this study reveal different  $S^0$ -forming pathways such as i) breakdown on cooling of  $S_3^{\cdot-}$  (and  $S_2^{\cdot-}$ ) and other chain-like  $S^0$  polymers only stable at high temperature and being isotopically identical to  $H_2S$ ; ii) cyclooctasulfur ( $S_8^0$ , liquid or solid) precipitating by recombination of sulfate and sulfide and/or by exchange with polysulfide dianions ( $S_n^{2-}$ ) on cooling and being slightly  $^{34}S$ -enriched compared to  $H_2S$  (by ~2 ‰ of  $\delta^{34}S$ ); and iii) a different type of  $S^0$  resulting from thiosulfate irreversible breakdown and being highly  $^{34}S$ -depleted (by ~12 ‰) relative to  $H_2S$ . Our data do not show any significant mass independent fractionation (MIF) of  $^{33}S$  and  $^{36}S$ , with  $\Delta^{33}S$  and  $\Delta^{36}S$  values of any S aqueous species and pyrite being within  $\pm 0.1$  ‰ and  $\pm 1.0$  ‰, respectively. Therefore, under the investigated experimental conditions, the radical  $S_3^{\cdot-}$  ion is unlikely to generate significant MIF in the hydrothermal fluid phase and in pyrite and native sulfur precipitated therefrom. Our study supports the existing interpretations of small  $\Delta^{33}S$  and  $\Delta^{36}S$  variations between sulfide/sulfate-bearing fluid and pyrite as MDF in terms of reaction kinetics, different reaction pathways, and mass conservation effects such as mixing of S reservoirs or Rayleigh distillation. Our data extend, across a wider range of sulfur concentration and chemical speciation, the existing multiple S isotopes models that exploit such variations as a complement to the traditional  $\delta^{34}S$  tracer to monitor the approach to equilibrium and evolution of hydrothermal fluids.

**Highlights:**

- Isotope signatures of sulfur species and pyrite have been studied in hydrothermal fluids.
- MDF equilibrium and kinetic  $SO_4$ - $H_2S$  and pyrite- $H_2S$  factors are quantified.
- No MIF anomalies are detected in the presence of sulfur radical ions.
- Isotope signature of molecular sulfur fingerprints the different mechanisms of  $S^0$  formation.
- Several environments offer potential for MIF generation in fluid-mineral systems.

65

**1. INTRODUCTION**

66

67 Fractionation among the four stable isotopes of sulfur ( $^{32}\text{S}$ ,  $^{33}\text{S}$ ,  $^{34}\text{S}$ , and  $^{36}\text{S}$ ) has been used for tracing  
 68 various geological processes since 1960's (e.g., Thode et al., 1961; Hulston and Thode, 1965). In most  
 69 chemical and biological reactions, the sulfur isotope ratios obey mass-dependent fractionations (MDF);  
 70 however, significant mass-independent fractionation (MIF) anomalies ( $\Delta^{33}\text{S} > 0.2\text{‰}$ )<sup>1</sup> were identified in  
 71 pyrite and barite from Archean sedimentary rocks likely caused by  $\text{SO}_2$  photolysis in the atmosphere (e.g.,  
 72  $\Delta^{33}\text{S} \approx -4$  to  $+14\text{‰}$ ; Farquhar et al., 2000; Johnston, 2011; Philippot et al., 2012), and also in sulfide minerals  
 73 from a number of younger magmatic, hydrothermal and metamorphic rocks (e.g., Farquhar et al., 2002;  
 74 Bekker et al., 2009; Thomassot et al., 2009; Cabral et al., 2013; Young et al., 2013; Delavault et al., 2016;  
 75 Ripley and Li, 2017; LaFlamme et al., 2018a,b; Smit et al., 2019), which were interpreted as the  
 76 reworking/recycling of Archean supracrustal rocks. These anomalies contrast with very small  $\Delta^{33}\text{S}$  values,  
 77 which are likely generated through MDF processes in low-temperature biological and inorganic sulfur redox  
 78 reactions in solution or at the mineral surfaces (typically  $< 0.15\text{‰}$ , Farquhar and Wing, 2003; Ono et al.,  
 79 2006, 2007; Farquhar et al., 2007; Johnston, 2011). These MDF processes are quite well understood and  
 80 result from mass-conservation effects (mostly mixing and Rayleigh distillation). Earlier theoretical work  
 81 using quantum-chemistry modeling suggested that MIF could be generated by heterogeneous reactions  
 82 (Lasaga et al., 2008), which was, however, not supported by a subsequent study (Balan et al., 2009).

83 In most hydrothermal fluids studied so far in nature (e.g., Kamysny et al., 2014; Stefansson et al.,  
 84 2015; McDermott et al., 2015) and laboratory (e.g., Ohmoto and Lasaga, 1982; Syverson et al., 2015;  
 85 Meshoulam et al., 2016), relevant to active seafloor or surface geothermal systems and different shallow-  
 86 crust hydrothermal deposits, sulfur isotope fractionation between the different inorganic sulfur species such  
 87 as sulfate, sulfide, native sulfur, thiosulfate, and some organic thiol species has been interpreted by both  
 88 equilibrium and kinetic MDF. This type of fractionation can only generate small deviations of  $^{33}\text{S}$  isotope  
 89 abundance from the classical MDF dependence ( $\Delta^{33}\text{S} < 0.05\text{‰}$ ). In contrast, large  $\Delta^{33}\text{S}$  anomalies (from  $-1.1$   
 90 to  $+13.0\text{‰}$ ) were reported in thermochemical sulfate reduction (TSR) reactions in hydrothermal experiments  
 91 in the presence of amino-acids (Watanabe et al., 2009; Oduro et al., 2011). TSR phenomena were also  
 92 invoked to explain the  $\Delta^{33}\text{S}$  record in Paleoproterozoic black shales at Talvivarra, Finland ( $-0.6 < \Delta^{33}\text{S} < 1.3\text{‰}$ ,  
 93 Young et al., 2013).

94 In the light of the large variety of sulfur isotope fractionation patterns exemplified above, detailed  
 95 knowledge of sulfur chemical speciation in the fluid phase is required for understanding sulfur isotope

<sup>1</sup> Variations of S isotope ratios (normalized to the most abundant  $^{32}\text{S}$  isotope) are conventionally expressed in the  $\delta$ -notation relative to the V-CDT standard (Vienna-Cañon Diablo Troilite meteorite; Ding et al., 2001):

$\delta^{3x}\text{S}$  (in ‰) =  $[(^{3x}\text{S}/^{32}\text{S})_{\text{sample}} / (^{3x}\text{S}/^{32}\text{S})_{\text{V-CDT}} - 1] \times 1000$ , where x denotes 3, 4 or 6 for  $^{33}\text{S}$ ,  $^{34}\text{S}$ , and  $^{36}\text{S}$ , respectively.

MDF means that isotope ratios are proportional to the mass difference between isotopes yielding the relationships:  $\delta^{33}\text{S} \approx (0.515 \pm 0.005) \times \delta^{34}\text{S}$ , and  $\delta^{36}\text{S} \approx (1.89 \pm 0.02) \times \delta^{34}\text{S}$  (e.g., Urey, 1947). MDF refers to isotope compositions deviating from this mass scaling law (i.e.  $\Delta^{33}\text{S} \approx \delta^{33}\text{S} - 0.515 \times \delta^{34}\text{S}$ ; see section 2.5 for details and rigorous equations).

96 fractionation, both MDF and MIF, in natural processes involving fluids. The major chemical forms of sulfur  
97 are known to be sulfate and sulfide (and sulfur dioxide and hydrogen sulfide in gas phase), which have been  
98 extensively studied over the last decades. However, recent discoveries of the sulfur radical ions  $S_3^{\cdot-}$  and  $S_2^{\cdot-}$   
99 in geological fluids (Pokrovski and Dubrovinsky, 2011; Pokrovski and Dubessy, 2015) may lead to re-  
100 evaluate our vision of a number of geochemical processes in which sulfur is involved. For example, sulfur  
101 radicals enhance gold and platinum solubility in hydrothermal fluids involved in porphyry and orogenic  
102 deposit genesis (Pokrovski et al., 2015; 2019; Laskar et al., 2019). These radicals could also contribute to  
103 redox changes in the subcontinental lithospheric mantle by slab-liberated S-bearing fluids in subduction  
104 zones thereby affecting the sulfur release and metallogenic potential of the arc magmas (e.g., Rielli et al.,  
105 2017; Frimmel, 2018; Colin et al., 2020). At shallow-crust conditions, the  $S_3^{\cdot-}$  ion was hypothesized to be a  
106 reaction intermediate controlling the kinetics of TSR processes and associated sulfur isotope fractionations  
107 (Truche et al., 2014; Pokrovski and Dubessy, 2015; Barré et al., 2017). The particular properties of  $S_3^{\cdot-}$  make  
108 it different from the ‘traditional’ sulfur species and, therefore, might be responsible for MIF  $^{33}S$  anomalies  
109 found in sulfides from hydrothermal settings and during TSR phenomena evoked above. This is because  $S_3^{\cdot-}$   
110 exhibits a magnetic moment due to a free electron, potentially enabling MIF, contrary to traditional sulfur  
111 molecules and ions (Buchachenko, 2001). Furthermore,  $S_3^{\cdot-}$  is a structural and electronic analog of ozone  
112 ( $O_3$ ) and its radicals exhibiting large  $^{17}O$  MIF anomalies due to symmetry effects (e.g.,  $^{16}O^{16}O^{16}O$  vs  
113  $^{16}O^{17}O^{18}O$ ), which is a general quantum-level control potentially applicable to other triatomic molecules and  
114 radicals (Gao and Marcus, 2001; Babikov et al., 2003; Chakraborty et al., 2013; Reinhardt and Robert, 2013).  
115 The major challenge in studying  $S_3^{\cdot-}$  and  $S_2^{\cdot-}$  is that they are only stable and sufficiently abundant in aqueous  
116 solution at elevated temperatures and are not preserved on cooling/quench by very rapidly decomposing into  
117 traditional sulfur species such as sulfide, sulfur, polysulfides, and/or sulfate (Chivers and Elder, 2013;  
118 Pokrovski and Dubessy, 2015 and references therein).

119 Along with  $S_3^{\cdot-}$  and  $S_2^{\cdot-}$ , another previously disregarded sulfur species in hydrothermal fluids, is a  
120 form of polymeric molecular sulfur ( $S_n^0$ , where  $n$  is undetermined number of uncharged S atoms in chain-  
121 like polymers), which has been identified by solubility and in-situ Raman spectroscopy measurements in S-  
122 rich solutions at  $>200^\circ C$  (Dadze and Sorokin, 1993; Pokrovski and Dubessy, 2015; Barré et al., 2017), but  
123 its effect on both sulfur redox kinetics and isotope fractionation remains unexplored. This form of molecular  
124 sulfur is different from the previously recognized aqueous cyclo-octasulfur  $S_8^0$  (e.g., Kamyshny, 2008;  
125 Pokrovski and Dubessy, 2015). Similarly to  $S_3^{\cdot-}$ ,  $S_n^0$  is not preserved on cooling in its original state, by  
126 transforming to native sulfur, molten or solid ( $S_{(s,l)}$ , composed of  $S_8$  rings), which is a common low-  
127 temperature ( $<150^\circ C$ ) product of S-bearing fluids both in laboratory and natural hydrothermal-volcanic  
128 settings. Therefore, native sulfur may potentially record, through its isotope signature, processes of sulfur  
129 species transformation in fluids under elevated  $T$ - $P$  conditions inaccessible to direct observation/sampling.  
130 Such processes include disproportionation of magmatic  $SO_2$  (e.g., Kusakabe et al., 2000; Kouzmanov and  
131 Pokrovski, 2012), TSR reactions (Barré et al., 2017), or  $S_3^{\cdot-}$  and  $S_n^0$  transformations on cooling (e.g.,

132 Pokrovski and Dubessy, 2015). In this article, these different uncharged polymeric molecular sulfur forms  
133 are collectively termed as ‘S<sup>0</sup>’.

134 In an attempt to bring quantitative constraints on the role played by the trisulfur (and disulfur) radical  
135 ion and polymeric molecular sulfur on S isotope fractionation in hydrothermal environments, we combined  
136 *i*) experiments in S<sub>3</sub><sup>-</sup>(S<sub>2</sub><sup>-</sup>)-S<sup>0</sup>-sulfate-sulfide hydrothermal fluids, *ii*) precise analyses of the multiple sulfur  
137 isotope ratios in the different sulfur aqueous forms (sulfate, sulfide and S<sup>0</sup>) and coexisting pyrite, and *iii*)  
138 thermodynamic modeling of sulfur aqueous speciation and solubility. The results contribute to better  
139 understanding of complex sulfur isotope fractionation processes in both ancient and modern hydrothermal  
140 systems relevant to various types of metal ore deposits formed by S-bearing fluids within the Earth’s crust.

141

142

## 2. MATERIALS AND METHODS

### 2.1. Experimental strategy and conditions

143

144

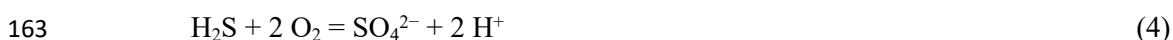
145 Four experiments were conducted in synthetic aqueous sulfate-sulfide fluids from 300 to 450°C and  
146 from ~300 to ~700 bar to investigate both kinetic and equilibrium sulfur isotope fractionation over a wide  
147 range of S<sub>3</sub><sup>-</sup> concentrations (from <0.0001 to ~0.1 moles S per kg of fluid (m), Table 1). Aqueous thiosulfate  
148 solutions K<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (-HCl-KOH) served as the source of sulfur, following the same approach as recent in-situ  
149 Raman spectroscopy studies that identified S<sub>3</sub><sup>-</sup>, S<sub>2</sub><sup>-</sup> and S<sup>0</sup> (Pokrovski and Dubessy, 2015). Potassium was  
150 preferred to Na which forms at elevated temperatures a poorly soluble Na<sub>2</sub>SO<sub>4</sub> solid compared to K<sub>2</sub>SO<sub>4</sub>  
151 (Linke and Seidell, 1965). Thiosulfate breaks down in aqueous solution on heating above 150°C, producing  
152 dominantly sulfate and sulfide



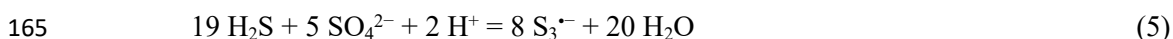
154 Adding acid (HCl) or base (KOH) allows enhanced formation of protonated (HSO<sub>4</sub><sup>-</sup>) or deprotonated (HS<sup>-</sup>)  
155 species, respectively, enabling acidity buffering



158 Alternatively, acidity buffering at slightly acidic pH values may also be achieved by using alkali  
159 aluminosilicate mineral assemblages, such as quartz-muscovite-microcline, which was used in one of our  
160 experiments (m22, see below). Furthermore, equilibria between sulfate and sulfide at elevated temperatures  
161 impose oxygen fugacity (*f*<sub>O<sub>2</sub></sub>), which typically ranges, depending on pH, from HM-2 to HM+2 (where HM  
162 denotes the log*f*<sub>O<sub>2</sub></sub> value of the conventional hematite-magnetite mineral buffer):



164 The formation of S<sub>3</sub><sup>-</sup> in such sulfate-sulfide solutions can be formally described by the reaction



166 This reaction implies that the abundance of S<sub>3</sub><sup>-</sup> is controlled by total S concentration (S<sub>tot</sub>, which is  
167 proportional to the sum of the dominant sulfate and sulfide), solution pH, and the H<sub>2</sub>S/SO<sub>4</sub> ratio (and therefore



168 oxygen fugacity), with a maximum abundance at a given set of  $T$ ,  $S_{\text{tot}}$  and  $\text{pH}$  at a  $\text{H}_2\text{S}/\text{SO}_4^{2-}$  ratio of 19/5.  
169 Note that this formal reaction in no way reflects the mechanisms of  $\text{S}_3^{*-}$  formation and breakdown, but only  
170 illustrates the fundamental thermodynamic controls on the  $\text{S}_3^{*-}$  equilibrium concentration in solution. In  
171 addition to the above S species produced by reactions (1) to (5), and depending on S and K total content,  $\text{pH}$   
172 and  $T$ - $P$  conditions, variable amounts of sulfate and sulfide ion pairs with  $\text{K}^+$ ,  $\text{SO}_2$ ,  $\text{S}_8^0$  (both aqueous and  
173 molten), disulfur ion  $\text{S}_2^{*-}$ , and polysulfide dianions  $\text{S}_n^{2*-}$  will also form.

174 The concentrations of all these species can be estimated using available thermodynamic data (see  
175 section 2.6 and Table A2.1 for discussion and data sources). Figure 1 shows the calculated equilibrium  
176 distribution of the different sulfur species, using the best up-to-date thermodynamic data (but see section  
177 2.6), in  $\text{K}_2\text{S}_2\text{O}_3$  aqueous solutions over the  $T$ - $P$ - $S_{\text{tot}}$ - $\text{pH}$ -redox range of this study, and Table 1 overviews the  
178 composition and different steps of the conducted experiments. In this manuscript, all  $\text{pH}$  values are  
179 thermodynamically calculated at the corresponding  $T$ - $P$ -composition. Two exploratory runs (m22 and m29)  
180 at  $350^\circ\text{C}$  in acidic ( $\text{pH} \sim 4.5$  at experimental  $T$ - $P$ ) and alkaline ( $\text{pH} \sim 7.3$ ) solutions were designed to examine  
181 S isotope fractionation in a  $\text{S}_3^{*-}$ -rich ( $\sim 0.07$  m S in the form of  $\text{S}_3^{*-}$ ) and  $\text{S}_3^{*-}$ -poor ( $< 0.001$  m S) fluids,  
182 respectively. A more elaborated experiment (m32) consisted of two succeeding steps in slightly alkaline  $\text{S}_3^{*-}$   
183 - poor conditions ( $\sim 0.005$  m S) at two contrasting temperatures,  $300$  and  $450^\circ\text{C}$ , followed by an acidification  
184 of the fluid at  $450^\circ\text{C}$  to increase  $\text{S}_3^{*-}$  concentration by a factor of 10 ( $\sim 0.04$  m S). In addition, the  $\text{S}_2^{*-}$  may  
185 also be present at such elevated temperatures (Fig. 1b; Pokrovski and Dubessy, 2015; Pokrovski et al., 2019).  
186 The last step of the three experiments above was conducted in the presence of pyrite (plus barite in m22)  
187 whose precipitation was induced by injecting, in-situ into the reactor, an  $\text{FeCl}_2$  (plus  $\text{BaCl}_2$  in m22) aqueous  
188 solution, thus simulating pyrite precipitation in natural hydrothermal fluids. Finally, a fourth experiment  
189 (m33) was conducted at  $300^\circ\text{C}$  at near-neutral  $\text{pH}$  ( $\sim 5.3$ ) by progressively diluting with water the initial  
190  $\text{K}_2\text{S}_2\text{O}_3$ -bearing fluid leading to a decrease of  $\text{S}_3^{*-}$  concentration by a factor of 10 (from  $\sim 0.07$  to  $0.008$  m S),  
191 to examine the effect of changing of  $\text{S}_3^{*-}$  abundance on sulfur isotope fractionation.

192 Our experimental systems offer a good analog for natural S-rich fluids in arc-related magmatic-  
193 hydrothermal systems hosting porphyry, skarn and epithermal Cu-Au-Mo deposits, which are characterized  
194 by typical temperatures of  $250$ - $500^\circ\text{C}$ , pressures of  $100$ - $1000$  bar, a wide  $\text{pH}$  ( $3$ - $8$ ) and redox ( $\text{HM} \pm 2$ ) ranges,  
195 typical salinities of  $5$ - $15$  wt% of  $\text{NaCl} + \text{KCl}$ , the coexistence of sulfate and sulfide in a wide range of  
196 concentrations (from  $\sim 0.01$  to a few wt% S), and the ubiquitous presence of pyrite (Einaudi et al., 2003;  
197 Kouzmanov and Pokrovski, 2012). Furthermore, the isotope fractionation patterns obtained in this study are  
198 also relevant to other hydrothermal settings and ore-deposit contexts that are all characterized by the presence  
199 of S-bearing fluids and iron sulfide minerals (e.g., seafloor geothermal systems, orogenic and sedimentary  
200 basin metal deposits).

201

## 202 2.2. Experimental setup

203



204 The runs were conducted using a Coretest reactor (Fig. 2) equipped with a flexible gold inner cell  
205 with a Ti 2- $\mu\text{m}$  frit filter in its head, i.e. analogous to Seyfried et al. (1987) and Rosenbauer et al. (1993) and  
206 recently adapted to multicomponent and S-rich systems as described previously (Pokrovski et al., 2015; Kokh  
207 et al., 2017). The gold cell (120-180  $\text{cm}^3$  of initial volume) is inserted into a high-pressure vessel ( $\sim 1000$   $\text{cm}^3$   
208 volume, type 316 SS, stainless steel), which is filled with water as a pressure medium controlled by a gas-  
209 driven pump, and placed into an electrically heated ( $\pm 1^\circ\text{C}$ ) rocking furnace. An ultrafast sampling device,  
210 analogous to that of Seewald and Seyfried (1990), consists of a titanium tube attached to two high-pressure  
211 titanium valves and a rigid titanium vial ( $\sim 2.5$   $\text{cm}^3$ ) tightly assembled to the second valve. The device enables  
212 an almost instantaneous ( $< 1$  s) transfer into the vial of a portion of the fluid phase pushed by the internal  
213 pressure from the reactor. This design prevents sulfur precipitation or degassing (see Kokh et al., 2017 for  
214 details), which would have inevitably occurred in S-bearing systems using traditional sampling procedures.  
215 Prior to experiments, the gold cell was cleaned with  $\text{HNO}_3$  and annealed at  $380^\circ\text{C}$  for 1 h to allow for a  
216 greater malleability and deformation.

217 During an experiment, fluids were periodically sampled and processed as described in sections 2.3  
218 and 2.4. In the course of experiments m32 and m33, aqueous HCl or pure water were injected into the cell,  
219 initially loaded with a thiosulfate solution, using a calibrated capstan pump (total volume = 12  $\text{cm}^3$ ). This  
220 injection allows controlled changes of the fluid pH and  $S_{\text{tot}}$  concentration and, consequently, the sulfur  
221 speciation (in particular, the amount of  $S^0$  and  $S_3^{2-}$ , see Table 1 and Fig. 1). Precipitation of pyrite (together  
222 with barite in m22), in the final stage of three experiments (m22, m29 and m32), was induced by injection  
223 into the reactor of an  $\text{FeCl}_2$  (- $\text{BaCl}_2$ ) aqueous solution in amounts not exceeding those of aqueous sulfide.  
224 Then the fluid composition continued to be monitored by periodic sampling, and the solid was finally  
225 recovered upon complete cooling of the reactor.

226

### 227 **2.3. Chemical analyses of sampled fluids**

228

229 Because the complex sulfur speciation at elevated  $T$ - $P$  strongly evolves upon fluid cooling (Fig. 1d),  
230 the original species identity and distribution cannot be adequately recovered in quenched samples. Therefore,  
231 special procedures are required for separation and preservation of the different sulfur forms for chemical and  
232 isotope analyses. These procedures are based on improved methods developed in our previous studies of S-  
233 rich fluid systems (e.g., Pokrovski et al., 2008; Kokh et al., 2016). Each sampling session comprised multiple  
234 samples of the fluid phase (usually 5, amounting 0.5 to 1.0 g each), directly taken into specific aqueous  
235 reagents (concentrated solutions of  $\text{I}_2$ ,  $\text{Cd}(\text{CH}_3\text{COO})_2$ ,  $\text{Zn}(\text{CH}_3\text{COO})_2$ ,  $\text{NH}_3$ ) placed in the sampling vial to  
236 allow for quantitative recovery and preservation of the different forms of sulfur, as well as dissolved chloride,  
237 potassium, iron and gold (Table A1.1). Total aqueous sulfur ( $S_{\text{tot}}$ ) was analyzed in samples taken into aqueous  
238 ammonia (28 wt%  $\text{NH}_3$ ) by inductively coupled plasma - atomic emission spectrometry (ICP-AES) and high-  
239 performance liquid chromatography (HPLC) after complete oxidation by hydrogen peroxide (30 wt%  
240 aqueous  $\text{H}_2\text{O}_2$ ) of all S forms to sulfate. Total aqueous chloride was also analyzed by HPLC in the same  $\text{NH}_3$

241 and H<sub>2</sub>O<sub>2</sub>-treated samples. Total reduced sulfur (S<sub>red</sub>, comprising H<sub>2</sub>S/HS<sup>-</sup>/KHS, S<sub>n</sub><sup>2-</sup> and, eventually, SO<sub>2</sub>  
242 and unreacted thiosulfate) was trapped in HCl aqueous solution containing an excess of iodine over sampled  
243 sulfur, and quantified by titration of the remaining I<sub>2</sub> by a standard thiosulfate solution, since all these reduced  
244 S species react with I<sub>2</sub> (e.g., Charlot, 1966; Dadze and Sorokin, 1993). Sulfide-type sulfur (S<sub>sulfide</sub>, comprising  
245 H<sub>2</sub>S, HS<sup>-</sup> and KHS) was separated from the other sulfur forms by sampling the fluid into a cadmium acetate  
246 solution of near-neutral pH (~6), which results in quantitative precipitation of all sulfide species as poorly  
247 soluble Cd sulfide (CdS solubility is <μmol Cd/kg fluid), followed by iodometric titration in an I<sub>2</sub>-HCl  
248 solution. Oxygen gas in the air space of the vial before sampling is less than 0.001 mmol/L, compared to 10s  
249 to 100s mmol/L of potentially oxidizable S species in the fluid (e.g., H<sub>2</sub>S), so that oxidation by air is  
250 negligible. Sulfate-type aqueous sulfur (S<sub>sulfate</sub>, comprising SO<sub>4</sub><sup>2-</sup>, HSO<sub>4</sub><sup>-</sup>, and their K<sup>+</sup> ion pairs, existing at  
251 experimental *T-P* conditions, Fig. 1) was quantified by HPLC as the SO<sub>4</sub><sup>2-</sup> ion in water-diluted near-neutral  
252 pH acetate solutions, after removal of sulfide as CdS precipitate by centrifugation. The presence of thiosulfate  
253 in the supernatant was also checked by HPLC, but could not be quantified.

254 Molecular sulfur was separated from other S species as hexane extracts (hereafter S<sup>0</sup><sub>hexane</sub>) collected  
255 from samples trapped into Cd acetate solution followed by removal of CdS via centrifugation. The hexane  
256 fraction was then analyzed for S<sup>0</sup> by UV spectrometry at a wavelength of 264 nm calibrated using reference  
257 solutions prepared by dissolving a given amount of native sulfur in hexane. The analytical uncertainty on the  
258 S<sup>0</sup> concentration determination in our systems is typically ±50%, mostly because impurities common in our  
259 chemically complex samples (including acetate and its decomposition products that may partition into  
260 hexane) absorb in the same UV range. All vials and tubes were also rinsed with hexane after recovery of each  
261 sampled solution, and analyzed for S<sup>0</sup>, which has always been found below the detection limit (<0.0001 m  
262 S). An independent way for estimating S<sup>0</sup> concentrations in the sampled fluid was using sulfur mass balance  
263 between S<sub>tot</sub> and the sum of sulfate and reduced sulfur (hereafter S<sup>0</sup><sub>balance</sub>), because S<sup>0</sup> does not react with  
264 iodine and does not precipitate with Cd or Ba acetate.

265 Concentrations of potassium, gold and iron were determined by ICP-AES and, selectively, by flame  
266 atomic absorption spectrometry (FAAS), after the NH<sub>3</sub> sample treatment with aqua regia. This treatment  
267 consists of i) gentle evaporation of the sample on hot plate (60-80°C) in a cleaned Teflon vial (Savilex ®),  
268 ii) reaction of the residue with 2 g of hot aqua regia in the closed vial (at 120°C for 2h), followed by iii)  
269 gentle evaporation of solution (at 60-70°C) to 0.2-0.3 g, and iv) dilution of the remaining solution by ultra-  
270 pure 0.5 wt% HCl - 1.5wt% HNO<sub>3</sub> in water. More details on the chemical procedures and associated  
271 uncertainties are given in Kokh et al. (2016, 2017). The results of fluid analyses are reported in Table 2 and  
272 shown as a function of run duration in Fig. 3.

273

## 274 **2.4. Processing of sampled fluids for sulfur isotope analyses**

275

276 The sulfur isotope ratios were analyzed (depending on the experiment) in the initial thiosulfate and  
277 sampled aqueous sulfate, sulfide and molecular sulfur (if available), and in the precipitated pyrite recovered

278 after the run. Like for the chemical analyses described above, the challenge was to accurately separate the  
279 different sulfur forms on sampling to avoid, as much as possible, both chemical recombination and isotope  
280 exchange/mixing among these forms in our S-rich systems on cooling. The fluid sample treatment is  
281 described as follows and summarized in Table A1.1.

282 In an exploratory experiment (m22), sulfur samples were taken into an aqueous solution of zinc and  
283 barium acetate, resulting in simultaneous precipitation of ZnS and BaSO<sub>4</sub> in the sampling vial. However,  
284 difficulties were encountered when converting ZnS to H<sub>2</sub>S from the fine-grained ZnS-BaSO<sub>4</sub> mixture that  
285 prevented ZnS, being armored by BaSO<sub>4</sub>, to quantitatively react with the HCl solution, resulting in low yields.  
286 Consequently, the experimental protocol was changed in the subsequent experiments. In runs m29, m32, and  
287 m33, aqueous sulfide was trapped as ZnS by placing 1.0-1.5 mL of 1 m zinc acetate solution into the sampling  
288 vial. The formed ZnS precipitate was centrifuged (3800 rpm for 15 min) to separate it from the solution,  
289 washed with deionized water and dried at 90°C for subsequent isotope analyses. After centrifugation, the  
290 supernatant solution was reacted with 1.5 mL of 1 m barium acetate to precipitate BaSO<sub>4</sub>, which was then  
291 centrifuged, washed, dried similarly to the ZnS precipitate, and reserved for isotope analyses.

292 Molecular sulfur S<sup>0</sup> was separated by extraction into hexane after precipitating H<sub>2</sub>S as CdS when  
293 sampling the fluid directly into a 1 mL of 1 m cadmium acetate solution. This procedure prevents *i*) isotope  
294 exchange between S<sup>0</sup> and H<sub>2</sub>S/HS<sup>-</sup> prone to rapid re-equilibration, and *ii*) possible recombination of sulfate  
295 and sulfide to form additional S<sup>0</sup>. Despite all these precautions, native sulfur might still partly precipitate,  
296 especially in S-rich acidic solutions, during the fluid passage through the sampling tubes and valves before  
297 reaching the vial with the trapping reagent, and thus get transferred into the vial together with the fluid.  
298 Although the different origins and formation mechanisms of S<sup>0</sup> in the sampled fluid cannot be distinguished  
299 by bulk S<sup>0</sup> chemical analyses, their isotopic composition is expected to reflect those mechanisms. The  
300 supernatant containing sulfate and S<sup>0</sup> was separated from the CdS precipitate by centrifugation (3800 rpm  
301 for 15 min), filtered (0.45 μm) and placed into a glass flask with 30 mL of hexane and 10 mL of glycerol (the  
302 latter was used to protect the eventually remaining thiosulfate from oxidation that might lead to additional  
303 formation of molecular sulfur; Dadze and Sorokin, 1993). The aqueous solution and the hexane phase were  
304 allowed to react for at least 48 h to enable the complete extraction of S<sup>0</sup> into the hexane phase, as checked by  
305 time-dependent analyses. The S<sup>0</sup>-bearing hexane fraction was then recovered and analyzed for S<sup>0</sup> by UV-Vis  
306 spectrometry (section 2.3). After the UV analysis, the hexane was gently evaporated at 50°C and the  
307 precipitated sulfur was saved for isotope analyses.

308 The sulfur isotope composition of the initial thiosulfate was measured separately in its sulfane (S<sup>2-</sup>)  
309 and sulfonate (S<sup>6+</sup>) parts according to the slightly modified protocols of Uyama et al. (1985) and Syverson et  
310 al. (2015). An aqueous 0.1 m AgNO<sub>3</sub> solution was used to precipitate the sulfane sulfur as Ag<sub>2</sub>S from an  
311 aqueous 0.05 m K<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. The supernatant was separated from the precipitate by centrifugation and  
312 reacted with an excess of barium acetate to precipitate the sulfonate part as BaSO<sub>4</sub>, which was then recovered  
313 after centrifugation.

314

## 315 2.5. Quadruple sulfur isotope analyses and isotope standardization and notation

316

317 Measurements of the four stable sulfur isotope ratios were realized with a gas source Ion Ratio Mass  
 318 Spectrometer (IRMS) Thermo Finnigan MAT 253 at the Institut de Physique du Globe de Paris (IPGP) as  
 319 described by Labidi et al. (2012). Samples of ZnS, BaSO<sub>4</sub> and S<sup>0</sup> were converted to solid silver sulfide (Ag<sub>2</sub>S)  
 320 using established techniques (Thode et al., 1961; Canfield et al., 1986; Labidi et al., 2012). The obtained  
 321 Ag<sub>2</sub>S was in turn quantitatively converted to sulfur hexafluoride gas (SF<sub>6</sub>) purified cryogenically by  
 322 distillation and by gas chromatography before being introduced into the spectrometer (Appendix A1 for  
 323 details). Procedural blanks, associated with sulfur conversion into Ag<sub>2</sub>S and subsequent Ag<sub>2</sub>S fluorination  
 324 and purification, are too low to be quantified (nano-molal levels). The S isotope composition of SF<sub>6</sub>(g) was  
 325 analyzed at mass-to-charge ratio values of 127, 128, 129, and 131 corresponding to the S<sup>32</sup>F<sub>5</sub><sup>+</sup>, S<sup>33</sup>F<sub>5</sub><sup>+</sup>, S<sup>34</sup>F<sub>5</sub><sup>+</sup>,  
 326 and S<sup>36</sup>F<sub>5</sub><sup>+</sup> ions, respectively (note that fluorine has a single stable isotope, <sup>19</sup>F, which avoids any mass  
 327 interference). Typical analytical errors of our measurements in a single session (2 standard deviations, 2 SD)  
 328 are 0.05 ‰, 0.01 ‰, and 0.18 ‰ for δ<sup>34</sup>S, Δ<sup>33</sup>S and Δ<sup>36</sup>S, respectively. Typical external reproducibility on  
 329 δ<sup>34</sup>S, Δ<sup>33</sup>S, and Δ<sup>36</sup>S among different sessions (conducted over >1 year and by several analysts) and parallel  
 330 chemical treatments of the same sampled fluid are 0.6 ‰, 0.02 ‰, and 0.35 ‰ (2 SD), respectively, as  
 331 estimated by four independent measurements of the pyrite sample from experiment m29.

332 All δ<sup>34</sup>S, Δ<sup>33</sup>S and Δ<sup>36</sup>S data obtained in this study are reported relative to the V-CDT standard, which  
 333 is a virtual S isotope reference adopted instead of the previously used natural Cañon Diablo Troilite (CDT)  
 334 meteorite, that was found to be slightly isotopically heterogeneous (Ding et al., 2001). The V-CDT standard  
 335 was defined on the base of a homogeneous synthetic standard, IAEA-S-1 (Ag<sub>2</sub>S), with a δ<sup>34</sup>S value of -0.30‰  
 336 relative to V-CDT (Ding et al., 2001; references therein). Because there is presently no international standard  
 337 for δ<sup>33</sup>S and δ<sup>36</sup>S, in this study we anchored our <sup>33</sup>S and <sup>36</sup>S data to the V-CDT reference scale, for consistency  
 338 with the recent studies (Ono et al., 2007) assuming that δ<sup>33</sup>S<sub>V-CDT</sub> = -0.055±0.14 ‰, δ<sup>36</sup>S<sub>V-CDT</sub> = -1.37±0.5 ‰,  
 339 Δ<sup>33</sup>S<sub>V-CDT</sub> = 0.100±0.003 ‰, and Δ<sup>36</sup>S<sub>V-CDT</sub> = -0.8±0.1 ‰ (see also Geng et al., 2019 for a recent inter-  
 340 comparison). Note that this normalization has no consequences on calculations of isotope fractionation  
 341 factors between different sulfur species. Values of Δ<sup>33</sup>S and Δ<sup>36</sup>S were calculated according to Farquhar and  
 342 Wing (2003):

$$343 \Delta^{33}\text{S}_{\text{V-CDT}} = \delta^{33}\text{S}_{\text{V-CDT}} - 1000 \times [(1 + \delta^{34}\text{S}_{\text{V-CDT}}/1000)^{\lambda^{33}} - 1] \quad (6)$$

$$344 \Delta^{36}\text{S}_{\text{V-CDT}} = \delta^{36}\text{S}_{\text{V-CDT}} - 1000 \times [(1 + \delta^{34}\text{S}_{\text{V-CDT}}/1000)^{\lambda^{36}} - 1] \quad (7)$$

345 where λ<sup>33</sup> and λ<sup>36</sup> are adopted as 0.515 and 1.889, respectively (note that these values may vary by a few  
 346 ‰ in different equilibrium and kinetic isotope exchange reactions, Young et al., 2012). Isotope fractionation  
 347 between the different sulfur forms (here given for δ<sup>34</sup>S) is expressed relative to aqueous sulfide analyzed as  
 348 ZnS:

$$349 1000 \times \ln \alpha_i \approx \delta^{34}\text{S}_i - \delta^{34}\text{S}_{\text{sulfide}} \quad (8)$$

350 where  $i$  denotes sulfate sulfur (collectively termed as  $\text{SO}_4$ ), molecular sulfur ( $\text{S}^0$ ) or pyrite (Py), and  $\alpha_i$  is the  
351 conventional isotope fractionation factor between  $i$ -species and sulfide,  $(^{34}\text{S}/^{32}\text{S})_i / (^{34}\text{S}/^{32}\text{S})_{\text{sulfide}}$ . The results  
352 of S isotope analyses obtained in this study are reported in Tables 3 and 4 and plotted in Figs 5 to 8.

353

## 354 2.6. Chemical equilibrium calculations of aqueous sulfur speciation and solubility

355

356 Sulfur speciation and solubility in the fluid phase of the experimental systems were modelled using  
357 available thermodynamic data, and the results were compared with the measured S species concentrations.  
358 Calculations were performed using the HCh software package and associated Unitherm database, allowing  
359 chemical equilibrium simulations in fluid-mineral systems (Shvarov, 2008; 2015), and accounting for non-  
360 ideality of the fluid using the extended Debye-Hückel equation (Helgeson et al., 1981). The selection of  
361 thermodynamic data sources was discussed in detail elsewhere (Pokrovski et al., 2015, 2019; Kokh et al.,  
362 2017), and will be only briefly summarized here.

363 The thermodynamic properties of the minerals, major fluid components, and most aqueous ionic  
364 sulfur species were taken from the updated SUPCRT (Johnson et al., 1992), JANAF (Chase, 1998), and  
365 USGS (Robie and Hemingway, 1995) databases, complemented by recent data for ionic sulfur forms  
366 including  $\text{S}_3^-$  (Pokrovski and Dubessy, 2015; references therein) using the revised and extended HKF  
367 (Helgeson-Kirkham-Flowers) equation of state (Oelkers et al., 2009; Sverjensky et al., 2014; references  
368 therein). The thermodynamic properties of the aqueous ‘gas-like’ sulfur nonelectrolytes,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ , as well  
369 as  $\text{H}_2$  and  $\text{O}_2$ , were adopted from Akinfiev and Diamond (2003) whose model provides a more accurate  
370 description of such species over the  $T$ - $P$  range relevant to our study (300-450°C; <1 kbar) than the SUPCRT  
371 database, which was based on a more limited experimental dataset for derivation of the HKF model  
372 coefficients for those species. The thermodynamic properties of the polysulfide ions ( $\text{S}_n^{2-}$ , where  $n$  is between  
373 2 and 6) and aqueous  $\text{S}_8^0$  at 300-450°C were taken from Pokrovski and Dubessy (2015); both types of species  
374 were found to be negligible in the fluid at the elevated temperatures of our experiments (<0.001 m S; Fig. 1).  
375 The  $\text{S}_2^-$  radical ion, with a stability constant at 450°C and 700 bar from Pokrovski et al. (2019), was predicted  
376 to account for ~0.01 m S in experiment m32, which is comparable to  $\text{S}_3^-$  (Fig. 1b). However, the uncertainties  
377 on such predictions are large (of an order of magnitude); furthermore, the  $\text{S}_2^-$  ion is expected to be negligible  
378 in our lower- $T$  experiments since it has not been detected by Raman resonance spectroscopy below 450°C  
379 (Pokrovski and Dubessy, 2015). The sources of thermodynamic properties of solid phases and aqueous  
380 species used in the modeling are summarized in Table A2.1 and the results of calculations for typical  
381 conditions of our experiments are shown in Fig. 1.

382 The missing species in these calculations are molecular sulfur polymers  $\text{S}_n^0$  forming around 300°C  
383 as detected by in-situ Raman spectroscopy (Pokrovski et al. Dubessy, 2015; Barré et al., 2017) and protonated  
384 polysulfides ( $\text{HS}_n^-$ ), for which no thermodynamic data are currently available at elevated temperatures.  
385 Estimations of Pokrovski and Dubessy (2015) suggest that  $\text{S}_n^0$  equilibrium concentrations in thiosulfate  
386 solutions more concentrated than those of our study ( $\text{S}_{\text{tot}} \sim 2$  m), attain maximum values of the order of 0.1-



387 0.2 m S around 300°C, and show sharply decreasing amounts with increasing  $T$  and/or decreasing  $S_{\text{tot}}$   
388 concentration. However, considering the large errors of such estimates and possible multiple and likely out-  
389 of-equilibrium origins of molecular sulfur found in the experiments of this study, quantification of  $S^0$   
390 equilibrium concentrations cannot confidently be made at present. Similarly, the amount of  $\text{HS}_n^-$  cannot be  
391 quantitatively assessed, but the absence of H-S vibrations in the Raman spectra of Pokrovski and Dubessy  
392 (2015) and Barré et al. (2017) strongly suggests that their concentrations at  $T$ - $P$ -pH conditions of our  
393 experiments are likely to be too small to affect sulfur mass and isotope balance.

394 New data obtained in the course of this study allowed estimations of the amount and origin of  $S^0$  at  
395 elevated temperatures based of  $S^0$  isotope signatures, and a revision of the stability of the major sulfate-  
396 bearing species,  $\text{KSO}_4^-$  (Fig. 1) based on the observation of  $\text{K}_2\text{SO}_4(\text{s})$  precipitation in one experiment at  
397 450°C (m32; section 4.1.1 and Appendix A3). The revised calculations, with corrected  $\text{KSO}_4^-$  stability  
398 constants, of equilibrium aqueous sulfate and sulfide concentrations for each experimental step will be  
399 compared with their experimental counterparts (Fig. 4) and help to better constrain the interpretation of the  
400 S isotope patterns.

401

402

### 3. RESULTS

403

#### 3.1. Sulfur chemical speciation in the fluid phase

404

##### 3.1.1. Experiments at 350°C (m22, m29)

407 Two experiments have been conducted at 350°C and 300-400 bar in acidic (0.5 m  $\text{K}_2\text{S}_2\text{O}_3$ -0.14 m  
408 HCl,  $\text{pH}_{350^\circ\text{C}} \sim 4.5$ , run m22) and less concentrated slightly alkaline (0.2 m  $\text{K}_2\text{S}_2\text{O}_3$ -0.09 m KOH,  $\text{pH}_{350^\circ\text{C}} \sim 7.3$ ,  
409 run m29) solutions, corresponding to  $\text{S}_3^{2-}$ -rich ( $\sim 0.07$  m S) and  $\text{S}_3^{2-}$ -poor ( $\sim 0.002$  m S) compositions,  
410 respectively. The concentrations of S species measured in these experiments are reported in Table 2 and their  
411 evolution with time is shown in Fig. 3a,b. In both experiments, before  $\text{FeCl}_2$  injection, sulfate and sulfide  
412 represent the major fraction of dissolved sulfur. Reduced sulfur ( $S_{\text{red}}$ ) is slightly higher than sulfide, by 0.01  
413 to 0.04 m S, in the acidic experiment (m22); the difference might be due to the presence of minor quantities  
414 of  $\text{SO}_2$  which is titrated by iodine together with sulfide. Reduced sulfur concentrations in the alkaline  
415 experiment (m29) are identical to those of sulfide. There are no discernable changes of the species  
416 concentration with time, suggesting that a chemical steady state is reached at this temperature within less  
417 than a few days. Total S concentrations ( $S_{\text{tot}}$ ) analyzed in the less concentrated alkaline-pH run (m29) match  
418 the sum of  $S_{\text{sulfate}}$  and  $S_{\text{red}}$  concentrations, implying an insignificant contribution of other S species that might  
419 have been omitted by our analytical protocols ( $< 0.03$  m S). In contrast, significant imbalance (up to 0.3 m S)  
420 between  $S_{\text{tot}}$  and the sum of  $S_{\text{red}}$  and  $S_{\text{sulfate}}$  is apparent in the more concentrated acidic run (m22). This  
421 imbalance ( $S^0_{\text{balance}}$ ) is attributed to the presence of molecular sulfur  $S^0$  in the sampled fluid, which can react  
422 neither with iodine nor with cadmium or barium acetate. This  $S^0_{\text{balance}}$  may have multiple origins that will be

423 discussed in section 4. In the next step of both experiments, after the injection of FeCl<sub>2</sub> (m29) and KCl-FeCl<sub>2</sub>-  
424 BaCl<sub>2</sub> (in m22), S<sub>tot</sub> becomes largely dominated by sulfate given that a major part of reduced sulfur  
425 precipitated as pyrite. Concentrations of S<sub>tot</sub> are similar within errors to S<sub>sulfate</sub> in m29, and are slightly higher  
426 than S<sub>sulfate</sub> in m22, likely due to the presence of minor amounts of SO<sub>2</sub> favored by acidic pH (Fig. 1).

427

### 428 3.1.2. Experiment at 300 and 450°C (m32)

429 More complete information about sulfur speciation has been gained in a subsequent experiment  
430 conducted at 300 and 450°C (m32), with the development of a protocol for molecular sulfur analysis (see  
431 section 2.3). This experiment was started in alkaline solution (0.5 m K<sub>2</sub>S<sub>2</sub>O<sub>3</sub>-0.3 m KOH pH<sub>300°C</sub> ~7) at 300°C,  
432 500 bar and run for 13 days (step m32/1); then the temperature was raised to 450°C and kept for 14 days  
433 (pH<sub>450°C</sub> ~8, m32/2). In a next step lasting 8 days (m32/3), an HCl solution was injected into the reactor  
434 resulting in acidification (pH<sub>450°C</sub> ~7), allowing a better identification of S<sub>3</sub><sup>-</sup> whose abundance is predicted  
435 to increase at more acidic pH (Table 1, Fig. 1). In the final step (m32/4, lasting 8 days), a FeCl<sub>2</sub> solution was  
436 injected, resulting in pyrite precipitation and further fluid acidification (pH<sub>450°C</sub> ~6). Total K and S  
437 concentrations steadily decrease at a molar K/S ratio close to 2 with time during the 300°C step (Fig. 3c and  
438 A3.1). This decrease suggests the precipitation of K<sub>2</sub>SO<sub>4</sub>(s), which is known to have a retrograde solubility  
439 with temperature (Pokrovski and Dubessy, 2015). Further decrease of S and K concentrations is observed as  
440 the temperature was raised to 450°C, following by stabilization for ~1 week, suggesting an attainment of  
441 steady state concentrations. The retrograde solubility of K<sub>2</sub>SO<sub>4</sub>(s) was apparent at the 450°C stage during a  
442 temporary heating regulation problem before sample #6 (Table 2, Fig. 3c), causing the temperature to  
443 decrease to ~260°C, and before sample #7, causing the temperature to increase to ~460°C. The solubility of  
444 K<sub>2</sub>SO<sub>4</sub>(s) rapidly responded to these temperature changes by increasing above and then decreasing below the  
445 steady-state values obtained in 2 previous samples #4 and #5 (Table 2; Fig. 3c, A3.1).

446 During the 300°C stage (m32/1), measured concentrations of sulfate and sulfide remained constant  
447 over ~1 week, but their sum was inferior to that of S<sub>tot</sub> by a factor of ~2 (Table 2, Fig. 3c), demonstrating the  
448 presence of analytically unreactive molecular sulfur (S<sup>0</sup><sub>balance</sub>). Concentrations of S<sup>0</sup><sub>balance</sub> decreased by ~50%  
449 accompanied by an increase in both sulfate and sulfide (in the 2<sup>nd</sup> week), reflecting a slow and complex  
450 kinetics of thiosulfate transformation. A fourth species contributing to aqueous S is the thiosulfate ion, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>,  
451 which was detected by HPLC analyses in sample #1 solution after separation of ZnS. The presence of  
452 undecomposed S<sub>2</sub>O<sub>3</sub><sup>2-</sup> and/or its possible intermediate decomposition products (SO<sub>3</sub><sup>2-</sup>) at this stage is also  
453 independently confirmed by the systematically higher measured concentrations of S<sub>red</sub> compared to S<sub>sulfide</sub>,  
454 since both thiosulfate and sulfite are titratable by iodine, but do not precipitate with Cd or Zn.

455 The *T* rise to 450°C after that step resulted in a drop of S<sup>0</sup><sub>balance</sub> concentrations by a factor of 5 to 10  
456 as compared to the preceding sampling at 300°C (Fig. 3c). It should be noted that the S<sup>0</sup> values exhibit a large  
457 scatter due to both analytical difficulties for measuring S<sup>0</sup> in hexane extracts (S<sup>0</sup><sub>hexane</sub>) and the use of mass-  
458 balance relations (S<sup>0</sup><sub>balance</sub>) for deriving close-to-zero values (~0.01 m S). Yet, despite the scatter, the S<sup>0</sup><sub>hexane</sub>  
459 concentrations appear, on average, quite similar to the S<sup>0</sup><sub>balance</sub> ones (Fig. A4.3), yielding a mean value of



460 0.04±0.02 m S (1 SD) for S<sup>0</sup> concentration for the whole set of datapoints over the three steps at 450°C  
 461 (m32/2, 3, 4). Both types of S<sup>0</sup> data do not show any clear tendency as a function of elapsed time (Fig. 3c).

462

### 463 3.1.3. Experiment at 300°C and near-neutral pH (m33)

464 A fourth experiment was conducted at 300°C and 500 bar in 0.5 to 0.2 m K<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution at near-  
 465 neutral pH (pH<sub>300°C</sub> ~5.3). This experiment was designed to better explore the effect of dilution resulting in  
 466 large changes in S<sub>3</sub><sup>-</sup> (and S<sup>0</sup>) concentrations without much changing the overall solution chemistry and  
 467 acidity. At the initial stage (~0.5 m K<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, m33/1), sulfate and sulfide account for >60% of S<sub>tot</sub> (Table 2).  
 468 There are no systematic changes within errors of their concentrations with time, suggesting that a chemical  
 469 steady state is reached. Likewise, there is no systematic difference between measured S<sub>red</sub> and S<sub>sulfide</sub>  
 470 concentrations, suggesting the absence of significant amounts (>0.02 m S) of reduced species other than  
 471 H<sub>2</sub>S/HS<sup>-</sup> (e.g., polysulfide ions, SO<sub>2</sub>, or undecomposed thiosulfate). In contrast, there is yet significant  
 472 imbalance (up to 30% S<sub>tot</sub>) between S<sub>tot</sub> and the sum of S<sub>sulfide</sub> and S<sub>sulfate</sub>, due to the presence of molecular  
 473 sulfur (S<sup>0</sup><sub>balance</sub>, Table 2), as was also confirmed by direct analyses of S<sup>0</sup><sub>hexane</sub>. After the first injection of water,  
 474 this imbalance is significantly reduced as a result of dilution (to ~15% S<sub>tot</sub>). After the second injection of  
 475 water, the S<sup>0</sup> fraction further decreased to become <5% S<sub>tot</sub> after 1 week (Table 2, Fig. 3d). Like in experiment  
 476 m32, both types of S<sup>0</sup> datapoints (S<sub>hexane</sub> and S<sub>balance</sub>) are quite scattered, but without any systematic trends  
 477 between them (Fig. A4.3).

478

## 479 3.2. Sulfur isotope ratios in the fluid phase and pyrite

480

481 In two exploratory experiments (m22 and m29), only a limited dataset could be obtained on S isotope  
 482 ratios of the different species (Table 3, Fig. A4.1 and A4.2). Most isotope data have been obtained on S<sub>sulfide</sub>  
 483 (trapped as ZnS) and S<sup>0</sup> (analyzed by the CRS treatment of the ZnS-BaSO<sub>4</sub> mixture in m22; Appendix A1).  
 484 Only few data points could be collected from S<sub>sulfate</sub> (trapped as BaSO<sub>4</sub>) due to imperfections in separating  
 485 ZnS from BaSO<sub>4</sub>. The δ<sup>34</sup>S<sub>sulfide</sub> and δ<sup>34</sup>S<sub>S<sup>0</sup></sub> values are consistently more negative, by 14-21 ‰, than the  
 486 δ<sup>34</sup>S<sub>sulfate</sub> values; however, the paucity of the BaSO<sub>4</sub> data does not allow the identification of any systematic  
 487 trends with time.

488 A more extensive sulfur isotope data set has been obtained in experiment m32 (Table 3, Fig. 5a and  
 489 6). The isotope composition of sulfonate (O<sub>3</sub>-S-) and sulfane (-S) sulfur of the initial thiosulfate (which  
 490 decompose respectively to sulfate and sulfide according to reaction 1), evolves upon heating to 300°C, with  
 491 sulfate and sulfide becoming through time <sup>34</sup>S-enriched and <sup>34</sup>S-depleted, respectively. In other words, the  
 492 difference in 1000×lnα<sub>SO<sub>4</sub></sub> (δ<sup>34</sup>S<sub>sulfate</sub> - δ<sup>34</sup>S<sub>sulfide</sub>) at each given moment increases with time, yet without  
 493 reaching a steady state at 300°C (Fig. 5c). This evolution is mainly controlled by the increase in δ<sup>34</sup>S<sub>sulfate</sub>,  
 494 whereas δ<sup>34</sup>S<sub>sulfide</sub> remains constant within errors (Fig. 5a); this clearly indicates that at least a third S isotope  
 495 pool is being formed. After the temperature rise to 450°C, δ<sup>34</sup>S<sub>sulfide</sub> values stay constant while δ<sup>34</sup>S<sub>sulfate</sub> values

496 increase slightly (by  $<2\%$  over 30 days), yielding a value  $1000 \times \ln \alpha_{\text{SO}_4}$  of  $15.0 \pm 1.0 \%$  for the two last data  
497 points after pyrite precipitation. Only three isotope compositional data points could be obtained for  $\text{S}^0_{\text{hexane}}$   
498 in this experiment. One data point from the first sample taken just after  $T$  change to  $450^\circ\text{C}$  (sample #4, Table  
499 3) has an anomalously light isotope signature relative to sulfide ( $1000 \times \ln \alpha_{\text{S}^0} = -11.6 \%$ ). Such a low value  
500 is unlikely to be an analytical artifact, since it is in good agreement with that calculated using sulfur mass  
501 and isotope balance on sulfate and sulfide (Fig. 5a, Appendix A5). The two other  $\text{S}^0$  isotope data points,  
502 obtained in samples #8 and #9 taken respectively 2 and 5 days after the HCl injection at  $450^\circ\text{C}$  (stage m32/3),  
503 show  $1000 \times \ln \alpha_{\text{S}^0}$  values tending to zero. The isotope composition of the precipitated pyrite in this experiment  
504 is similar to that of the aqueous sulfide fraction within  $0.4 \%$  of  $\delta^{34}\text{S}$  (Table 4).

505 Sulfur isotope data obtained in experiment m33 (Table 3, Fig. 5b,d) confirm the major isotope trends  
506 for the  $\text{SO}_4\text{-H}_2\text{S}$  pair observed in m32. The isotope composition of sulfonate ( $\text{O}_3\text{-S-}$ ) and sulfane ( $\text{-S}$ ) sulfur  
507 of the initial thiosulfate rapidly evolves upon heating to  $300^\circ\text{C}$ , with sulfate and sulfide becoming with time  
508  $^{34}\text{S}$ -enriched and  $^{34}\text{S}$ -depleted, respectively. The resulting  $1000 \times \ln \alpha_{\text{SO}_4}$  value is almost constant over the run  
509 duration, yielding a steady state value of  $20.1 \pm 1.5 \%$  (Fig. 5d).

510 In all performed experiments, the values of  $\Delta^{33}\text{S}$  for all species vary between  $-0.02 \%$  and  $+0.08 \%$ ,  
511 and do not show any systematic trends (Fig. 6, 7, A4.2). The values of  $\Delta^{36}\text{S}$  vary between  $-1\%$  and  $+1\%$   
512 without displaying any systematic trends amongst sulfide, sulfate and  $\text{S}^0$ , and overlapping with those of the  
513 initial thiosulfate. The scatter is mostly due to analytical issues because the analysis of  $\delta^{36}\text{S}$  would commonly  
514 be affected by a small contribution of fluorocarbon compounds that shifts measured  $\delta^{36}\text{S}$  towards more  
515 positive values (Rumble and Hoering, 1994). Nevertheless, these relatively small variations imply that there  
516 is no significant sulfur mass independent fractionation on both  $^{33}\text{S}$  and  $^{36}\text{S}$ ; however, they do provide  
517 additional insight into both equilibrium and kinetic processes affecting mass-dependent fractionation among  
518 the sulfur species as will be discussed in section 4.2.4.

519

520

## 4. DISCUSSION

### 4.1. Solubility and chemical speciation of sulfur

522

523 Sulfur solubility and species concentrations measured in this study can be compared with equilibrium  
524 thermodynamic calculations. In all experiments, four major types of S chemical forms predicted by the  
525 available thermodynamics (Table A2.1) are aqueous sulfate ( $\text{SO}_4^{2-}$ ,  $\text{HSO}_4^-$ ,  $\text{KSO}_4^-$ , and  $\text{KHSO}_4^0$ ), sulfide  
526 ( $\text{H}_2\text{S}$ ,  $\text{HS}^-$ , and  $\text{KHS}^0$ ), radical ions ( $\text{S}_3^{\cdot-}$  at all  $T$ , and  $\text{S}_2^{\cdot-}$  at  $450^\circ\text{C}$ ), and pyrite ( $\text{FeS}_2$ ). In addition, in m22  
527 aqueous  $\text{SO}_2$  and three other phases,  $\text{S}_{(\text{s,l})}$ , at step m22/1, and barite ( $\text{BaSO}_4$ ) and alunite ( $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ )  
528 at step m22/2 after pyrite precipitation were predicted to form (Table 1). All other known solid phases are  
529 predicted to be largely undersaturated in our experiments. Other types of aqueous species, such as thiosulfate,  
530  $\text{S}_8^0$ , and traditional polysulfide ions, represent a negligibly small amount of  $\text{S}_{\text{tot}}$  at equilibrium ( $<0.1\%$ ).

531 Comparisons between calculated and measured concentrations of sulfate, sulfide,  $\text{SO}_2$  and  $\text{S}^0/\text{S}_3^{2-}/\text{S}_2^{2-}$  are  
532 shown in Fig. 4; they reveal several interconnected points of discrepancy regarding the precipitation of the  
533  $\text{K}_2\text{SO}_4$  solid (in m32), sulfate-sulfide-pyrite equilibration, and the formation of  $\text{S}^0$ , which are discussed  
534 below.

535

#### 536 4.1.1. $\text{K}_2\text{SO}_4(\text{s})$ precipitation

537 The precipitation of  $\text{K}_2\text{SO}_4(\text{s})$  was inferred in run m32 (0.5 m  $\text{K}_2\text{S}_2\text{O}_3$ -KOH-HCl, at 300 and 450°C  
538 with in-situ changes in pH induced by HCl injection), through observation of concomitant decrease of total  
539 dissolved potassium and sulfur concentrations through time (Fig. 3c, Appendix A3). The precipitation of  
540  $\text{K}_2\text{SO}_4(\text{s})$  is, however, not consistent with equilibrium calculations using the thermodynamic properties of  
541  $\text{K}_2\text{SO}_4(\text{s})$ ,  $\text{K}^+$  and sulfate aqueous species from available data sources (Table A2.1). The calculations predict  
542  $\text{K}_2\text{SO}_4(\text{s})$  to be undersaturated in the fluid by a factor of 10. The likely reason for this discrepancy is poor  
543 constraints on the thermodynamic parameters of the dominant  $\text{KSO}_4^-$  ion pair (Fig. 1), which are based on  
544 HKF-model extrapolations relying on limited experimental data at low temperatures. To account for  
545  $\text{K}_2\text{SO}_4(\text{s})$  formation, a correction to the value of the formation constant of  $\text{KSO}_4^-$  from  $\text{K}^+$  and  $\text{SO}_4^{2-}$  at 450°C  
546 and 700 bar has been made to match the measured solubility of  $\text{K}_2\text{SO}_4(\text{s})$  at each 450°C step of experiment  
547 m32 ( $\log K_{450^\circ\text{C}, 700 \text{ bar}} = 3.4 \pm 0.5$ ; Appendix A3). This correction does not exceed 1 log unit compared to the  
548 SUPCRT original value ( $\log K_{450^\circ\text{C}, 700 \text{ bar}} = 4.4$ ). The difference is within realistic uncertainties of HKF model  
549 predictions for such ion pairs at elevated temperatures (e.g., Pokrovski et al., 1995; Scheuermann et al., 2019).  
550 The 300°C step of this experiment does not allow direct reliable corrections for  $\text{KSO}_4^-$  formation constant,  
551 because no steady state has been attained (Fig. 3c). Therefore, we have corrected the fluid composition at the  
552 300°C step of m32 by subtracting manually the mass-balance deduced amount of precipitated  $\text{K}_2\text{SO}_4$ , but  
553 this correction has again a minor effect (Fig. A3.2). Nevertheless, to maintain consistency, in the following  
554 discussion both 300°C and 450°C corrections were included when modeling equilibrium S speciation in  
555 experiment m32 (Fig. 4c).

556

#### 557 4.1.2. Aqueous sulfate and sulfide and pyrite

558 Before the pyrite precipitation stage, a decent agreement between measured and calculated  $\text{S}_{\text{sulfide}}$   
559 values is observed for the least-concentrated experimental compositions in m29/1 (0.2 m  $\text{K}_2\text{S}_2\text{O}_3$ , pH ~7.3,  
560 350°C) and m33/3 (0.2m  $\text{K}_2\text{S}_2\text{O}_3$ , pH ~5.3, 300°C). The other experimental compositions show  
561 systematically lower measured  $\text{S}_{\text{sulfide}}$ , which is due to the presence of  $\text{S}^0$ , as directly confirmed by mass  
562 balance calculations and analyses of hexane extracts (discussed in section 4.1.3 below). Another potential  
563 cause of the difference between measured and calculated  $\text{S}_{\text{sulfide}}$  in the highest-temperature run (450°C,  
564 m32/2,3) might be an underestimation of the thermodynamically predicted amount of  $\text{S}_2^{2-}$  forming at the  
565 expense of  $\text{H}_2\text{S}$ . The measured  $\text{S}_{\text{sulfate}}$  concentrations in experiments m22, m29, m33 (and m32 at 450°C, after  
566 correction for  $\text{K}_2\text{SO}_4(\text{s})$ ) agree within errors with the calculated ones, which further confirms that  $\text{S}^0$  forms  
567 more at the expense of sulfide than sulfate. An exception to this trend is stage m32/1 at 300°C and alkaline

568 pH that still shows significant underestimation of measured  $S_{\text{sulfate}}$ , which is due to lack of equilibrium and  
 569 the slowness of thiosulfate decomposition.

570 In the final stages of experiments m22, m29 and m32 with precipitated pyrite (and barite and alunite  
 571 in m22), calculations predict almost complete scavenging of the injected Fe (and Ba) amounts by the solid  
 572 phase, which is in excellent agreement with both low Fe dissolved concentrations ( $<0.002\text{-}0.02$  m, Table 2)  
 573 and the differences in  $S_{\text{sulfide}}$  concentrations measured before and after the  $\text{FeCl}_2$  injection. However, for all  
 574 three experiments in the presence of pyrite, the measured aqueous  $S_{\text{sulfide}}$  concentrations are somewhat lower  
 575 than those predicted using equilibrium thermodynamics (Fig. 4a-c). The difference between measured and  
 576 predicted  $S_{\text{sulfide}}$  concentration values in equilibrium with pyrite (0.05-0.1 m S) suggests that pyrite, once  
 577 precipitated, may not fully chemically re-equilibrate with the solution within the short time frame of these  
 578 experimental stages ( $<10$  days).

#### 579 4.1.3. Molecular sulfur formation

581 Molecular sulfur was clearly identified in three from the four runs conducted in this study. The  
 582 exception is run m29 at  $350^\circ\text{C}$  with the lowest  $S_{\text{tot}}$  concentration (0.4 m S), which was the simplest from the  
 583 point of view of aqueous S speciation, with dominant sulfate and sulfide and negligible amounts of  $\text{S}_3^{2-}$   
 584 ( $<0.001$  m S). The small imbalance between  $S_{\text{tot}}$  and  $[S_{\text{sulfide}} + S_{\text{sulfate}}]$  in this experiment before pyrite  
 585 precipitation ( $<0.03$  m S, Table 2) is comparable with the uncertainties of the species concentrations. In  
 586 contrast, experiment m22, conducted at the same temperature but in a more concentrated and more acid  
 587 solution, is predicted to contain at equilibrium, along with sulfate and sulfide, significant  $\text{S}_3^{2-}$  concentrations  
 588 (0.067 m S; Table 1, Fig. 4a). The major difference between the analytical data and thermodynamic  
 589 predictions for this experiment is the presence of large amounts of  $\text{S}^0$  ( $\sim 0.3$  m S) as clearly apparent from  
 590 mass balance between measured  $S_{\text{tot}}$  and the sum of  $S_{\text{sulfate}}$  and  $S_{\text{sulfide}}$  (Table 2). Such elevated  $\text{S}^0$   
 591 concentrations are not accounted for by thermodynamics, which predicts  $<0.001$  m of  $\text{S}_8^0$  (aq) at equilibrium  
 592 using the thermodynamic data sources from Table A2.1 (Fig. 1). The contribution from breakdown of  $\text{S}_3^{2-}$  to  
 593 molecular sulfur on cooling during sampling can be estimated by the reaction:



595 Molecular sulfur and  $\text{H}_2\text{S}$  are the most reactive S species that are known to easily form during rapid cooling  
 596 of hydrothermal fluids (Giggenbach, 1997; Pokrovski and Dubessy, 2015). The formation of sulfate is  
 597 kinetically too slow to occur during the sampling in our experiments (e.g., Ohmoto and Lasaga, 1982). The  
 598 formation of polysulfide dianions, such as  $\text{S}_6^{2-}$  that is known to form by recombination of two  $\text{S}_3^{2-}$  in non-  
 599 aqueous solvents (e.g., Chivers and Elder, 2013; Steudel and Chivers, 2019), is negligible at our acidic pH  
 600 (Fig. 1a). Therefore reaction (9) is likely to control the  $\text{S}_3^{2-}$  breakdown in this experiment. Yet, the maximum  
 601 produced amount of  $\text{S}^0$  by  $\text{S}_3^{2-}$  breakdown in experiment m22, according to reaction (9), is 0.056 m S, which  
 602 is not enough to account for the difference  $[S_{\text{tot}} - (S_{\text{sulfate}} + S_{\text{sulfide}})]$  in this experiment ( $\sim 0.3$  m S, Fig. 4a). It  
 603 is thus very likely that the major part of  $\text{S}^0$  observed in sampled fluids from this experiment has a different  
 604 origin. As shown by Pokrovski and Dubessy (2015) by in-situ Raman spectroscopy on similar solutions,

605 another type of  $S^0$  is present at the  $T$ - $P$  conditions of this experiment and is likely represented by chain-like  
 606 polymeric molecules in equilibrium with sulfate, sulfide and  $S_3^{2-}$  ion. Furthermore, part of  $S^0$  found in  
 607 sampled solutions in this experiment may be produced by a very fast precipitation of the native sulfur phase  
 608 ( $S^0$  liquid at  $>115^\circ\text{C}$  and solid at lower  $T$ ) during the sampling when the fluid is transferred from the hot  
 609 reactor ( $350^\circ\text{C}$ ) to the cold sampling vial ( $<100^\circ\text{C}$ ). Indeed, thermodynamic predictions suggest that, if solid-  
 610 solution equilibrium for sulfur is attained at  $100^\circ\text{C}$  during sampling,  $>30\%$  of  $S_{\text{tot}}$  would precipitate as native  
 611 sulfur before reaching the trapping iodine or zinc acetate solution in the vial. Even through such rapid  
 612 attainment of equilibrium at low temperatures within the sampling time frame is unlikely (e.g., Ohmoto and  
 613 Lasaga, 1982), this potential artifact of S precipitation could not be completely excluded, in particular in  
 614 acidic systems in which sulfur solubility is lower (Fig. 1a,d), and thus may also contribute to the  $S^0$   
 615 concentrations found in this experiment.

616 Further insight into the origin of molecular sulfur is gained from step m32/1 at lower  $T$  ( $300^\circ\text{C}$ ) and  
 617 more alkaline pH (7.2). Under these conditions, sulfur solid/liquid phase precipitation during sampling on  
 618 cooling is not favorable because of the greater S solubility in alkaline solutions (Fig. 1a) and much slower  
 619 redox kinetics (e.g., Ohmoto and Lasaga, 1982). Thermodynamic calculations predict negligible amounts of  
 620  $S_8^0$  ( $<0.001$  m S) and fairly small amounts of  $S_3^{2-}$  (0.004 m S). These relatively small concentrations cannot  
 621 account for the major fraction of  $S^0$  observed at this stage (50% of  $S_{\text{tot}}$ , Table 2, Fig. 3c). This different type  
 622 of  $S^0$  is likely to originate from irreversible thiosulfate breakdown on heating:



624 This reaction is the most straightforward and kinetically easiest one, since it requires only breaking the S-S  
 625 bond of the thiosulfate ion with minimal electron transfer between the two S atoms. With time, both  $S^0$  and  
 626  $SO_3^{2-}$  undergo transformation to  $H_2S$  and  $SO_4^{2-}$ , which are thermodynamically stable at these conditions:



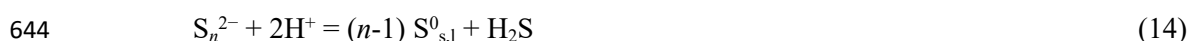
629 This interpretation is supported by *i*) systematic positive difference between  $S_{\text{red}}$  and  $S_{\text{sulfide}}$  at this stage (Table  
 630 2) pointing to the presence of an iodine-titratable S form such as  $SO_3^{2-}$ , in line with reaction (10); *ii*) decrease  
 631 of the  $S^0_{\text{balance}}$  concentration; and *iii*) increase of  $S_{\text{sulfate}}$  and  $S_{\text{sulfide}}$  with time at  $300^\circ\text{C}$  (Table 2, Fig. 3c) in line  
 632 with reactions (11) and (12). With the  $T$  rise to  $450^\circ\text{C}$ , this type of  $S^0$  becomes negligible, since both analyzed  
 633 and mass-balance derived  $S^0$  (0.045 m S on average, Table 2) is in excellent agreement with the amount that  
 634 may be produced via collective breakdown of  $S_3^{2-}$  according to reaction (9) and  $S_2^{2-}$  according to an analogous  
 635 reaction:



637 In contrast, in experiment m33 at lower  $T$  ( $300^\circ\text{C}$ ) and near-neutral pH,  $S^0$  concentration that could  
 638 be produced by  $S_3^{2-}$  breakdown is  $\sim 5$  times lower than the concentration obtained using mass balance between  
 639 measured  $S_{\text{tot}}$  and sulfate plus sulfide (0.065 vs 0.3-0.5 m S at stage m33/1). This imbalance indicates the  
 640 presence of far more significant amounts of  $S^0$ , confirmed by direct analyses of hexane extracts (Table 2;  
 641 Fig. 4d). This additionally formed  $S^0$  observed in the sampled fluids may potentially be due to precipitation



642 of liquid/solid  $S^0$  on cooling via partial recombination of sulfate and sulfide via the reversal of reaction (12),  
 643 and/or via the breakdown of the polysulfide dianions ( $S_n^{2-}$ ):



645 Indeed,  $S_n^{2-}$  ions, being negligible at our experimental temperatures of  $\geq 300^\circ\text{C}$  ( $<0.001\text{ m S}$ ), are predicted  
 646 to form in increasing amounts upon equilibrium cooling for this experimental composition (up to  $0.1\text{ m S}$  at  
 647  $<100^\circ\text{C}$ , Fig. 1d). It is impossible, however, to evaluate the exact extent of both reactions (12) and (14),  
 648 which are unlikely to attain equilibrium during the fast sampling and cooling of the fluid. Subsequent dilution  
 649 with water yielded a significant decrease in both  $S_{\text{hexane}}^0$  and  $S_{\text{balance}}^0$  concentrations, but they are still  
 650 systematically higher than the  $S^0$  concentrations that may be produced on cooling from thermodynamically  
 651 predicted  $S_3^{*-}$  amounts (reaction 9). The second dilution with water further decreased the observed  $S^0$   
 652 concentrations that became with time almost identical to those predicted from  $S_3^{*-}$  at the end of the last stage  
 653 of this experiment ( $\sim 0.01\text{ m S}$ , Table 1).

654 In summary, molecular sulfur found in our experiments is only significant at rather high  $S_{\text{tot}}$   
 655 concentrations ( $>0.4\text{--}0.5\text{ m}$ ) and moderate temperatures ( $<350^\circ\text{C}$ ). It may stem from multiple contributions,  
 656 as summarized in Fig. 9: *i*) equilibrium chain-like  $S^0$  forming at elevated temperatures as found by in-situ  
 657 Raman spectroscopy; *ii*)  $S^0$  formed by the fast breakdown of  $S_3^{*-}$  (and  $S_2^{*-}$ ) during cooling (reactions 9 and  
 658 13); *iii*) liquid or solid  $S_{s,l}^0$  directly precipitated during fluid extraction from the reactor before reaching the  
 659 sample vial, probably by reverse of reaction (12) and/or by reaction (14); and *iv*)  $S^0$  as an intermediate  
 660 forming at the initial stages of the thiosulfate breakdown (reaction 10). In contrast, at lower  $S_{\text{tot}}$  concentrations  
 661 ( $<0.4\text{ m}$ ) and/or higher temperatures ( $450^\circ\text{C}$ ), the  $S_3^{*-}$  (and potentially  $S_2^{*-}$ ) is the major source of the  
 662 measured  $S^0$  in our quenched samples (reactions 9 and 13). These different types of  $S^0$  may be expected to  
 663 have distinct isotope signatures, which may allow their better identification, as discussed below.

664

## 665 4.2. Sulfur isotope fractionation and comparison with literature data

666

667 The experimental and modelled data on S speciation in our experiments allow the interpretation of S  
 668 isotope fractionation between the major aqueous and solid species, and the evaluation of the effect of the  
 669 radical ions and  $S^0$  on this fractionation.

670

### 671 4.2.1. Sulfate and sulfide

672 In all experiments, sulfate is systematically enriched in  $^{34}\text{S}$  compared to the coexisting sulfide, in  
 673 agreement with general concepts of isotope fractionation that more oxidized S atoms such as in  $\text{SO}_4^{2-}$  having  
 674 stronger chemical bonds are enriched in the heavier isotope compared to more reduced and more weakly  
 675 bonded S atoms such as  $\text{H}_2\text{S}$  (e.g., Urey, 1947). Isotope fractionation between sulfate and sulfide,  
 676  $1000 \times \ln \alpha_{\text{SO}_4} = \delta^{34}\text{S}_{\text{sulfate}} - \delta^{34}\text{S}_{\text{sulfide}}$ , is  $20.3 \pm 1.5\text{ ‰}$  (m33,  $300^\circ\text{C}$ ), between 14 and  $21\text{ ‰}$  (m22 and m29,  
 677  $350^\circ\text{C}$ ), and  $15.1 \pm 0.2\text{ ‰}$  (m32/2-4,  $450^\circ\text{C}$ ). These values are in agreement with literature data at equilibrium

678 from both theory and experiment (Ohmoto and Rye, 1979; Ohmoto and Lasaga, 1982; Ono et al., 2007; Otake  
679 et al., 2008; Syverson et al., 2015; Eldridge et al., 2016; references therein), which are in the range 20-24  
680 (300°C), 17-20 (350°C), and 13-16 ‰ (450°C). In contrast, at 300°C and alkaline conditions (m32/1,  
681 pH=6.9) after 13 days of reaction, the value of  $1000 \times \ln \alpha_{\text{SO}_4}$  is only ~12 ‰, which is much smaller than its  
682 equilibrium counterpart of 20-24 ‰. Whereas the  $\delta^{34}\text{S}_{\text{sulfide}}$  (ZnS) value becomes constant after 3 days of  
683 reaction, the corresponding  $\delta^{34}\text{S}_{\text{sulfate}}$  ( $\text{BaSO}_4$ ) value continues to steadily increase over the duration of this  
684 step (Table 3), causing  $1000 \times \ln \alpha_{\text{SO}_4}$  values to increase (Fig. 5a,c). A similar trend is observed at the same  $T$   
685 (m33) but more acidic pH (5.3), with a faster reach of a steady state (Fig. 5b,d). The increasing  $\delta^{34}\text{S}_{\text{sulfate}}$   
686 values through time while  $\delta^{34}\text{S}_{\text{sulfide}}$  remained constant imply another S isotope reservoir in this system that  
687 is being depleted in  $^{34}\text{S}$ . Such a reservoir is consistent with the detection of significant amounts of  $\text{S}^0$ . The  
688 kinetic isotope patterns observed here are in agreement with the generally slow rates of isotopic equilibration  
689 of sulfate (Ohmoto and Lasaga, 1982; references therein), and attest for much higher chemical and isotope  
690 reactivity of  $\text{H}_2\text{S}$  and the associated reduced S species ( $\text{S}^0$ ,  $\text{S}_3^{2-}$ ; Pokrovski and Dubessy, 2015). Using the  
691 rate law of Ohmoto and Lasaga (1982), the rate constant  $\log_{10} k_r$  (in  $\text{hour}^{-1}$ ) for an isotope exchange reaction  
692 between sulfide and sulfate at 300°C in these experiments was estimated to be  $-2.4 \pm 0.2$  and  $-1.9 \pm 0.3$  at pH  
693 6.9 and 5.3, respectively (Fig. 5c,d and Appendix A5). The small difference in the  $k_r$  values with pH is  
694 consistent with faster kinetics of sulfate-sulfide redox exchange rates in more acidic solutions (Ohmoto and  
695 Lasaga, 1982; Kusakabe et al., 2000). Furthermore, our absolute  $k_r$  values are similar, within the uncertainties,  
696 to those predicted by Ohmoto and Lasaga (1982) based on a large set of compiled experimental data from  
697 dilute  $\text{H}_2\text{S}$ - $\text{SO}_4$  solutions ( $<0.2 \text{ m S}_{\text{tot}}$ ) at 300°C and near-neutral pH ( $\text{pH}_{300^\circ\text{C}} \sim 5$  to 7) in which both  $\text{S}^0$  and  
698  $\text{S}_3^{2-}$  are negligible ( $\log_{10} k_r \sim -3 \pm 1$ ). Despite rather large errors associated with both measured and predicted  
699  $k_r$  values that depend on the fluid pH, ionic strength, and the presence of alkalis, this comparison does not  
700 reveal any significant effect of  $\text{S}^0$  and  $\text{S}_3^{2-}$  on the sulfate-sulfide chemical and isotope exchange rates.

701

#### 702 4.2.2. Molecular sulfur and radical ions

703 This study reports the first experimental data on the S isotope composition, including both major ( $^{32}\text{S}$   
704 and  $^{34}\text{S}$ ) and minor ( $^{33}\text{S}$  and  $^{36}\text{S}$ ) isotopes, of intermediate-valence aqueous sulfur species, radical sulfur ions  
705 and molecular sulfur of different origin in hydrothermal fluids. We will hereafter discuss the  $\text{S}^0$  isotope data  
706 in terms of  $\text{S}^0$ - $\text{H}_2\text{S}$  fractionation, which is expected to be much less affected by kinetic constraints than  
707 fractionations involving sulfate (e.g., Robinson et al., 1973; Kusakabe et al., 2000; Pokrovski and Dubessy,  
708 2015).

709 In experiments at acidic to neutral pH (m33/2,3 at 300°C, m22/1 at 350°C, and m32/3,4 at 450°C),  
710 the measured  $\delta^{34}\text{S}_{\text{S}^0}$  values are fairly close to those of sulfide (despite some data scatter caused by analytical  
711 uncertainties of the measurements of micro quantities of  $\text{S}^0$ , Table 3), yielding a mean isotope fractionation  
712 factor  $1000 \times \ln \alpha_{\text{S}^0}$  of  $0 \pm 1$  ‰ for the most robust data points. The absence of significant fractionation between  
713  $\text{S}^0$  and sulfide is confirmed by the few available literature data for both solid/liquid and aqueous  $\text{S}^0$ . For



714 example, Robinson (1973) did not observe any significant  $\delta^{34}\text{S}$  changes ( $<0.4\%$ ) during hydrolysis of  
715 orthorhombic sulfur ( $\alpha\text{-S}_8$ ) in water at 200-320°C, with the resulting  $\text{H}_2\text{S}$  being only slightly enriched in  $^{34}\text{S}$   
716 (by  $<2\%$ ). Kamishny et al. (2014) investigated multiple sulfur isotope fractionations in Yellowstone  
717 hydrothermal springs ( $<100^\circ\text{C}$ ) and found that  $\text{S}^0$  had values of  $\delta^{34}\text{S}$  and  $\delta^{33}\text{S}$  identical to or slightly heavier  
718 than those of  $\text{H}_2\text{S}$  (by  $<1\%$ ). Rare existing theoretical studies and data compilations predict equilibrium  
719 values of  $1000 \times \ln \alpha_{\text{S}^0}$  close to zero at our high-temperature conditions ( $-0.3 \pm 0.5\%$ , Ohmoto and Rye, 1979;  
720  $-0.7 \pm 0.1\%$ , Otake et al., 2008), as would be expected considering the small differences in redox state and  
721 bonding between the two compounds. Higher-order polysulfide dianions  $\text{S}_n^{2-}$  with  $n > 4$  were reported to be  
722  $^{34}\text{S}$ -enriched compared to  $\text{HS}^-$  in alkaline solutions at ambient  $T$ - $P$  (by up to 7%; Amrani et al., 2006).  
723 However, these anions are very minor at our conditions (Fig. 1) and the amplitude of fractionation is expected  
724 to tend closer to zero at the elevated temperatures of our experiments. More recently, the  $\text{S}_3^{2-}$  fractionation  
725 factor compared to  $\text{H}_2\text{S}$  ( $\delta^{34}\text{S}_{\text{S}_3^{2-}} - \delta^{34}\text{S}_{\text{H}_2\text{S}}$ ), has been reported to be about  $-1.0\%$  at  $450^\circ\text{C}$  from quantum-  
726 chemical calculations on gas phase (Tossell, 2012). Even though associated with some simplifications, these  
727 calculations support the idea that the isotope signatures of  $\text{S}_3^{2-}$ ,  $\text{S}^0$  and  $\text{H}_2\text{S}$  would be similar within 1 ‰ at  
728 hydrothermal conditions. Thus, molecular sulfur produced in the sampled fluids from these experiments is  
729 consistent with being derived from  $\text{S}_3^{2-}$  (and  $\text{S}_2^{2-}$  and chain-like  $\text{S}^0$  detected by Raman spectroscopy at high  
730  $T$ ).

731 An exception to this pattern is molecular sulfur produced via slow irreversible thiosulfate breakdown  
732 in experiment m32 at  $300^\circ\text{C}$  and early stages at  $450^\circ\text{C}$  in alkaline solution. This particular type of  $\text{S}^0$  exhibits  
733 an anomalously low fractionation factor,  $1000 \times \ln \alpha_{\text{S}^0}$ , of  $-11.6\%$  (Table 3, Fig. 5a). Despite the single  $\text{S}^0$   
734 isotope compositional value that could directly be measured at the early stages of this experiment, the trend  
735 of  $\delta^{34}\text{S}_{\text{S}^0}$  to depletion with time shown in in Fig. 5a is confirmed by sulfur mass and isotope balance  
736 (Appendix A5). At present, we do not have a sound physical-chemical explanation of this unique isotope  
737 signature, very different from the close-to-zero  $\text{S}^0$ - $\text{H}_2\text{S}$  isotope equilibrium fractionation value supported so  
738 far by the few available experimental and theoretical data. Thus, the anomalously light  $\text{S}^0$  observed during  
739 thiosulfate breakdown is a new finding that may be related to previously un-recognized kinetic controls  
740 operating at far-from-equilibrium conditions and favoring enrichment of  $\text{S}^0$  produced by irreversible reaction  
741 (10) in the lighter, i.e. generally more reactive, isotope  $^{32}\text{S}$ . We note also that  $\Delta^{33}\text{S}$  values show large  
742 variations at this step (Fig. 8a) confirming an out-of-equilibrium regime. In contrast, molecular sulfur from  
743 later stages of this experiment at more acidic pH (m32/3, samples #8 and #9, Table 3, Fig. 5a) has a  $\delta^{34}\text{S}$   
744 value identical within 1 ‰ to that of the coexisting aqueous sulfide. As it was shown above, the latter type  
745 of  $\text{S}^0$  fraction is likely to originate from  $\text{S}_3^{2-}$  (and  $\text{S}_2^{2-}$ ) breakdown to  $\text{S}^0$  and  $\text{H}_2\text{S}$  upon fluid quench according  
746 to reactions (9) and (13). Indeed, if no isotope exchange occurs during these fast reactions, the resulting  
747 measured  $\text{S}^0$  should carry a  $\delta^{34}\text{S}$  value similar to that of the radical ions.

748 Finally, an additional contribution to  $\text{S}^0$  might result from direct precipitation of solid/liquid sulfur  
749 on cooling via recombination of  $\text{H}_2\text{S}$  and  $\text{SO}_4^{2-}$  according to the reverse of reaction (12) and/or via  $\text{S}_n^{2-}$

750 breakdown via reaction (14), both leading to formation of  $S^0_{s,l}$ . This was likely the case for the early stage of  
751 experiment m33 before dilution with water (m33/1, samples #2 and #3, Tables 2 and 3, Fig. 5d). The two  
752 measured  $1000 \times \ln \alpha_{S^0}$  values are  $\sim 2.7$  ‰, which may suggest a contribution from the isotopically heavier  
753 sulfate to the  $S^0$  formation in this run. Indeed, combining an average value for  $\delta^{34}S_{H_2S}$  and  $\delta^{34}S_{SO_4}$  of  $-7$  and  
754  $+15$  ‰, respectively, for these samples with the stoichiometry of reaction (12), and assuming that no isotope  
755 exchange has time to occur during quenching, yields  $1000 \times \ln \alpha_{S^0} = +2$  ‰, in fair agreement with the measured  
756 values (Fig. 5d). Similarly, polysulfide ions that were shown to be  $^{34}S$  enriched compared to  $H_2S$  and  $S^0$  at  
757 ambient conditions (by  $\sim 3$  ‰, Amrani and Aizenshtat, 2004; Amrani et al., 2006) may partly be responsible  
758 for the slightly heavier  $S^0$  isotope signatures, but their exact contribution is impossible to quantify because  
759 the extent of reaction (14) during the fast fluid sampling is not known. With further dilution by water in this  
760 experiment, the degree of supersaturation with respect to  $S^0_{(s,l)}$  in the sampled fluid is significantly reduced,  
761 making both reactions (12) and (14) less favorable. Consequently, the measured  $1000 \times \ln \alpha_{S^0}$  values (for most  
762 robust analytical data points) tend to zero at these steps (m33/2,3), since this type of  $S^0$  is mostly produced  
763 by decomposition of  $S_3^{2-}$  on cooling, similar to experiment m32 at  $450^\circ C$  discussed above. A schematic  
764 summary of  $S^0$  isotope signatures resulting from different formation pathways is shown in Fig. 9. Thus, the  
765 isotope signature of  $S^0$  formed in a cooling hydrothermal fluid may directly reflect sulfur chemical speciation  
766 at high  $T-P$  and the dynamics of speciation changes upon fluid evolution.

767

#### 768 4.2.3. Pyrite

769 Sulfur isotope systematics of the precipitated pyrite exhibits a significant variability among the  
770 experiments, which may reflect the differences in aqueous S speciation, fluid acidity, temperature and  
771 duration. All these factors potentially affect both equilibrium and kinetic fractionation and pathways of  $FeS_2$   
772 precipitation, even though the interpretation is complicated by the impossibility to sample precipitated pyrite  
773 for simultaneous measurement of both aqueous sulfur and pyrite isotope values. Other issues add to this  
774 complexity such as *i*) relatively short durations of the post-precipitation stage (6-14 days), *ii*) paucity of  
775 isotope data for early experiments (m29), and *iii*) variations of  $\delta^{34}S_{sulfide}$  in the course of the runs likely due  
776 to analytical issues. In the light of these limitations, we have chosen to use the average value of the  $\delta^{34}S_{sulfide}$   
777 data points analyzed in sampled fluids before and after pyrite precipitation (where available) in the discussion  
778 of the pyrite-aqueous sulfide fractionation factors in each experiment, as summarized in Table 4.

779 The average values of the pyrite-sulfide fractionation factor  $1000 \times \ln \alpha_{py}$  found in the two  $350^\circ C$   
780 experiments, range from  $-0.5 \pm 1.3$  ‰ (m22, pH change upon pyrite precipitation from 4.5 to 3.7) to  $1.5 \pm 0.9$   
781 ‰ (m29, pH change upon pyrite precipitation from 7.3 to 5.3), whereas in the  $450^\circ C$  experiment (m32, pH  
782 change from 6.8 to 5.9) it is close to zero,  $0.3 \pm 0.7$  ‰ (Table 4). Equilibrium  $1000 \times \ln \alpha_{py}$  values reported in  
783 the literature on the basis of theoretical estimations within the range  $350-450^\circ C$  (Ohmoto and Rye, 1979;  
784 Otake et al., 2008; Blanchard et al., 2009; Eldridge et al., 2016) are in the range  $0.5-1.0$  ‰ for the  $Py-H_2S$   
785 pair and  $2.4-3.3$  ‰ for the pyrite- $HS^-$  pair, with aqueous  $H_2S$  being slightly enriched in  $^{34}S$  compared to  $HS^-$ ,

786 as also confirmed by recent direct experiments at ambient temperatures (Sim et al., 2019). Thus, our measured  
787  $1000 \times \ln \alpha_{\text{py}}$  value of 1.5 ‰ from the higher-pH experiment at 350°C (m29) with comparable fractions of H<sub>2</sub>S  
788 and HS<sup>-</sup> in the fluid before pyrite precipitation, is in reasonable agreement with those predictions. In contrast,  
789 for a more acidic (i.e. H<sub>2</sub>S-dominated) and S<sup>0</sup> and S<sub>3</sub><sup>-</sup>-richer experiment at the same temperature (m22), the  
790 mean  $1000 \times \ln \alpha_{\text{py}}$  value of -0.5 ‰ is by ~2 ‰ lower than the theoretical estimations above for the pyrite-  
791 H<sub>2</sub>S pair. However, these differences should be interpreted with caution because of the large uncertainty  
792 caused by variations of the  $\delta^{34}\text{S}_{\text{sulfide}}$  values in the fluid before and after pyrite precipitation (Tables 3 and 4).  
793 For the 450°C experiment (m32) at near-neutral pH, our  $1000 \times \ln \alpha_{\text{py}}$  value of 0.3 ‰ is identical within  
794 analytical errors to the theoretical predictions (0.5±0.5 ‰).

795 The  $1000 \times \ln \alpha_{\text{py}}$  values of -0.5 to 0.3 ‰ for the H<sub>2</sub>S-dominated runs (m22, m32) are only ~1 ‰  
796 higher on average than those reported by Syverson et al. (2015) from long-duration (>100 days) fluid-pyrite  
797 exchange experiments in more dilute and more acidic (pH<2) H<sub>2</sub>S-HSO<sub>4</sub><sup>-</sup> solutions, in which both S<sup>0</sup> and  
798 S<sub>3</sub><sup>-</sup> are negligible. Their experimental approach used 3-isotope systematics, convincingly demonstrating  
799 attainment of isotope equilibrium between pyrite and H<sub>2</sub>S, with  $1000 \times \ln \alpha_{\text{py}}$  of -1.9±0.8 ‰ at 350°C and -  
800 1.0±0.5 ‰ at 450°C (the latter value is estimated in this study by extrapolation assuming a *T*-dependence for  
801  $1000 \times \ln \alpha_{\text{py}}$  as in Ohmoto and Rye, 1979). The 1 ‰ difference between our and Syverson et al.'s (2015)  
802 experimental values may be due to multiple factors, such as *i*) lack of pyrite-fluid isotope equilibrium in our  
803 short-duration experiments, and *ii*) different reaction pathways of pyrite formation caused by differences in  
804 S aqueous speciation and fluid pH (this study and Ohmoto and Lasaga, 1982), or degree of solution  
805 oversaturation with respect to pyrite that may lead to different crystal morphology (e.g., Murowchick and  
806 Barnes, 1986, 1987) and, potentially, S isotope fractionation during crystal growth of different  
807 crystallographic faces. All these factors may potentially cause variations of isotope signatures in pyrite  
808 compared to the coexisting fluid from which it forms. Unfortunately, our dataset is too meagre to draw more  
809 definitive conclusions or to attempt to discriminate amongst the different pyrite formation pathways amply  
810 debated in the literature (e.g., Schoonen and Barnes, 1991; Butler et al., 2004; Ono et al., 2007; Rouxel et  
811 al., 2008; Saunier et al., 2011).

812 Likewise, the existing theoretical estimates of pyrite-aqueous sulfide fractionation factors may be  
813 affected by limitations arising from the use of different approaches for calculating  $\beta$ -factors of aqueous  
814 species from one hand and of solid phases from the other hand (Saunier et al., 2011 and references therein).  
815 An additional limiting factor is imperfections of the theoretical models for estimating hydration energies of  
816 ions versus uncharged aqueous species (e.g., HS<sup>-</sup> versus H<sub>2</sub>S; Syverson et al., 2015) and, more generally, by  
817 inaccuracies in assessing thermodynamic properties of aqueous non-electrolytes, such as H<sub>2</sub>S, in high *T-P*  
818 fluids (e.g., Oelkers et al., 2009; Akinfiev et al., 2015; references therein). Nevertheless, despite those  
819 experimental and theoretical limitations and the paucity of direct pyrite-fluid isotope exchange data over a  
820 wide range of temperature, acidity, and solution compositions, the main conclusion arising from this

821 discussion is that our results do not reveal any detectable effect of  $S_3^-$  and  $S^0$  on pyrite-fluid isotope exchange  
 822 rates and resulting pyrite isotope signatures.

823

#### 824 4.2.4. $\Delta^{33}S$ and $\Delta^{36}S$ systematics

825 The data obtained on the minor S isotopes,  $^{33}S$  and  $^{36}S$ , in S-rich hydrothermal fluid-pyrite systems  
 826 of this study do not provide evidence for significant mass-independent fractionation. First, our  $\delta^{33}S$  vs  $\delta^{34}S$   
 827 data plot on a commonly reported MDF fractionation line with a slope of  $0.515 \pm 0.001$  (95% confidence  
 828 level) for all experimental compositions and temperatures (Fig. 6a, 7a, A4.2a). Second, the majority of our  
 829  $\Delta^{33}S$  values plot within the area outlining potential variations of the  $\lambda_{33}$  value (Fig. 6b, 7b, A4.2b) predicted  
 830 among different sulfur aqueous species at equilibrium using Density Functional Theory (DFT) calculations  
 831 ( $0.505 < \lambda_{33} < 0.517$ , Otake et al., 2008; Eldridge et al., 2016) and those recorded in biological and inorganic  
 832 reactions among traditional S species both in nature and experiments ( $0.508 < \lambda_{33} < 0.519$ ; LaFlamme et al.,  
 833 2018a and references therein). Similarly, the most reliable  $\Delta^{36}S$  values plot within the area of the theoretical  
 834  $\lambda_{36}$  slopes for MDF fractionation among S aqueous species (Fig. 6c, 7c, A4.2c;  $1.88 < \lambda_{33} < 1.96$ ; Otake et  
 835 al., 2008; Eldridge et al., 2016). Third, our  $\Delta^{36}S$ - $\Delta^{33}S$  data do not plot on the MIF Archean array (Fig. 6d, 7d  
 836 and A4.2d).

837 Thus, within the experimental uncertainties, our data on  $^{33}S$  and  $^{36}S$  may be treated in terms of MDF,  
 838 and therefore may provide additional constraints on both kinetics and equilibrium of sulfur isotope exchange  
 839 reactions. We followed the approach based on the assumption that the difference of  $\Delta^{33}S$  and  $\Delta^{36}S$  values  
 840 between the different S species, being initially at disequilibrium, should tend to close-to-zero values when  
 841 approaching equilibrium (Ono et al., 2007; Syverson et al., 2015; Dauphas and Schauble, 2016), provided  
 842 there is no additional MIF contributions. Indeed, the most recent theoretical work of Eldridge et al. (2016)  
 843 predicts equilibrium  $\Delta^{33}S < 0.01$  ‰ for the  $SO_4^{2-}$ - $HS^-$  pair at 300°C and even smaller values ( $< 0.001$  ‰) for  
 844 other ionic S species. Our analysis here is limited by consideration of sulfate and sulfide, since no such  
 845 theoretical predictions exists for  $S^0$ , radical ions or pyrite.

846 Figure 8 shows the difference in  $\Delta^{33}S$  and  $\Delta^{36}S$  values between aqueous sulfate and sulfide (defined  
 847 hereafter as  $\Delta^{33}S_{\text{sulfate-sulfide}}$  and  $\Delta^{36}S_{\text{sulfate-sulfide}}$ ) as a function of time in each stage of experiments m32 and  
 848 m33. It can be seen that at 300°C during the initial thiosulfate breakdown (m32), the  $\Delta^{33}S_{\text{sulfate-sulfide}}$  and  
 849  $\Delta^{36}S_{\text{sulfate-sulfide}}$  values increase with time, consistent with the absence of equilibrium at this first stage as shown  
 850 by the temporal changes of both S chemical speciation and  $1000 \times \ln \alpha_{SO_4}$  values (Fig. 5). The temperature rise  
 851 to 450°C (m32) results in a decrease of  $\Delta^{33}S_{\text{sulfate-sulfide}}$  and  $\Delta^{36}S_{\text{sulfate-sulfide}}$  values, most of which being between  
 852 0.00 and 0.02 ‰ (Fig. 8a,b). Even though our first data are not precise enough to fully support those  
 853 calculated by Eldridge et al. (2016), our trend is in line with the tendency for isotope equilibration at higher  
 854  $T$  shown by the  $1000 \times \ln \alpha_{SO_4}$  evolution during the following stages (Fig. 5). Thus, our  $\Delta^{33}S$  data provide  
 855 additional support for the attainment of sulfate-sulfide (-pyrite) equilibrium in this experiment as  
 856 independently inferred from the  $\delta^{34}S$  data (Fig. 5a, A4.2). The values of  $\Delta^{36}S_{\text{sulfate-sulfide}}$ , which have been

857 obtained for the first time on such S-bearing hydrothermal systems, also indicate a tendency of approaching  
858 zero with time in the 450°C stages of experiment m32, in spite of the intrinsically large uncertainties (Fig.  
859 8b).

860 Values of  $\Delta^{33}\text{S}$  in the experiment at 300°C at near-neutral pH (m33) show roughly similar amplitude  
861 and pattern as in run m32, by tending towards zero during breakdown of the initial thiosulfate within the first  
862 2 weeks (Fig. 8c). Injection of water results in a ‘perturbation’ of  $\Delta^{33}\text{S}$  values, likely caused by partial  
863 decomposition of  $\text{S}_3^{2-}$  and  $\text{S}^0$  upon dilution. Values of  $\Delta^{36}\text{S}$  in this experiment are more scattered, but yet  
864 indicate a similar pattern upon water injection. Thus, our study confirms previous experimental and natural  
865 findings (e.g., Ono et al., 2007; Syverson et al., 2015; McDermott et al., 2015) that  $\Delta^{33}\text{S}$  and, potentially,  
866  $\Delta^{36}\text{S}$  systematics may reflect the dynamics of sulfur species transformation and exchange in hydrothermal  
867 fluids.

868

## 869 5. GEOCHEMICAL SIGNIFICANCE AND PERSPECTIVES

870

### 871 5.1. Implications for tracing hydrothermal processes

872 The present study is the first experimental investigation of the effect of intermediate-valence  
873 polymeric sulfur species on S isotope fractionation involving the four stable S isotopes at conditions typical  
874 of hydrothermal S-bearing fluid circulation and metal ore formation in the shallow crust (<2-3 km) leading  
875 to various types of deposits. Our findings have several implications for using S isotopes as tracers of  
876 hydrothermal processes in the Earth’s crust.

877 *First*, our data on S-rich fluids in the system pyrite-sulfide-sulfate quantitatively confirm the mass-  
878 dependent equilibrium fractionation amplitudes and kinetic patterns among these major sulfur chemical  
879 forms, previously established on the basis of extensive experimental and natural data obtained from more  
880 dilute S-poor fluids in which these polymeric sulfur species are negligible. Thus, with the available dataset,  
881 our results do not support recent hypotheses that the presence of  $\text{S}_3^{2-}$  (and  $\text{S}^0$ ) could increase the rates of  
882 thermochemical sulfate reduction (Truche et al., 2014) or control kinetic mechanisms of sulfate-sulfide  
883 exchange reactions in hydrothermal solution at acidic and neutral pH (Pokrovski and Dubessy, 2015).

884 *Second*, our study highlighted different origins of molecular sulfur in hydrothermal fluids, which  
885 may result not only from breakdown of  $\text{S}_3^{2-}$  (and  $\text{S}_2^{2-}$ ), but also from partial recombination of sulfate and  
886 sulfide or isotope exchange between polysulfide dianions and  $\text{H}_2\text{S}$  on cooling out of equilibrium yielding  
887 formation of liquid or solid sulfur ( $\text{S}_{(s,l)}$ ), or by irreversible thermal decomposition of thiosulfate ( $\text{S}^0_{\text{thios}}$ ). The  
888 sulfur radical ions and  $\text{S}^0$  have isotopic signatures indistinguishable from aqueous  $\text{H}_2\text{S}$ . The  $\text{S}_{(s,l)}$  phase may  
889 be slightly  $^{34}\text{S}$ -enriched (by 2-4 ‰) compared to  $\text{H}_2\text{S}$  thereby reflecting the contribution of  $\text{SO}_4^{2-}$  or  $\text{S}_n^{2-}$  in  
890 the reaction of  $\text{S}_{(s,l)}$  precipitation. In contrast,  $\text{S}^0_{\text{thios}}$  is strongly  $^{34}\text{S}$ -depleted compared to  $\text{H}_2\text{S}$  (by as much as  
891 -12 ‰). As a result, isotope analyses of  $\text{S}^0$  in natural hot spring discharges, which are commonly out of



892 equilibrium owing to fast temperature changes, may actually bear information about the evolution of  
893 hydrothermal fluids upon their cooling and rise to the surface.

894 *Third*, our study confirms the interpretations of small  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  variations ( $< \pm 0.1$  and  $< \pm 1$  ‰,  
895 respectively) in inorganic sulfur-bearing fluid - mineral (pyrite) systems as MDF in terms of reaction kinetics  
896 and mixing of S reservoirs (e.g., Ono et al., 2006; Stefansson et al., 2015; Syverson et al., 2015; McDermott  
897 et al., 2015; Gunnarsson-Robin et al., 2017). These variations are thus an efficient complement to the  
898 traditional  $\delta^{34}\text{S}$  tracer to monitor the approach to equilibrium and evolution of hydrothermal fluids and  
899 mineralization in a wide range of temperatures and S concentration and chemical speciation.

900 *Finally*, our data do not reveal any systematic mass-independent fractionation (MIF) of  $^{33}\text{S}$  in the  
901 experimental S-bearing fluid-pyrite systems over a wide range of S concentrations (0.1-1 m), pH (4-8) and  
902 temperatures (300-450°C), with  $\Delta^{33}\text{S}$  values of any S species being  $0.0 \pm 0.1$  ‰. Such values fall well within  
903 the traditionally accepted general MDF threshold of  $\pm 0.2$  ‰ (Farquhar and Wing, 2003) and the known  
904 variations of  $\lambda_{33}$  MDF slope values (e.g., Otake et al., 2008; Eldridge et al., 2016; LaFlamme et al., 2018a).  
905 Thus, our results do not confirm expectations raised in a number of recent studies (e.g., Truche et al., 2014;  
906 Pokrovski et Dubessy, 2015; Selvaraja et al., 2017; LaFlamme et al., 2018a,b) that  $\text{S}_3^{\cdot-}$ , being a radical, might  
907 generate a significant mass-independent fractionation, in addition to the widely recognized processes of  $\text{SO}_2$   
908 and other gaseous S species photolysis that shall still be considered as the primary cause of sulfur MIF  
909 signatures. Thus, at the current state of our knowledge,  $\Delta^{33}\text{S}$  rock record continues to serve as an efficient  
910 chemically conservative isotopic tracer of Archean sediment contributions as has been widely used in  
911 sedimentary and ore deposit geochemistry over the last 20 years.

912

## 913 **5.2. Can reactions involving sulfur radical ions generate MIF in fluid-mineral systems?**

914 The data obtained in this study account neither for findings of MIF  $^{33}\text{S}$  signatures in some post-  
915 Archean magmatic-metamorphic sulfides (e.g., Farquhar et al., 2002; Bekker et al., 2009; Cabral et al., 2013;  
916 Young et al., 2013; LaFlamme et al., 2018b) nor in experiments of sulfate reduction by amino-acids in  
917 hydrothermal solution (Watanabe et al., 2009; Oduro et al., 2011) or liquid-phase photolysis of particular  
918 organic thiol compounds (e.g., Kopf and Ono, 2012). Therefore, the question yet remains open as to whether  
919 or not reactions of sulfur radical ions may generate MIF signatures in fluid-mineral systems. Several specific  
920 environments in the Earth's crust may offer potential for MIF-generating reactions involving S radical  
921 species. The first is TSR processes in sedimentary/metamorphic settings in which  $\text{S}_3^{\cdot-}$  is expected to be  
922 abundant enough above 150°C (e.g., Truche et al., 2014; Pokrovski et Dubessy, 2015; Barré et al., 2017).  
923 Until now, however, no unambiguous evidence of anomalous S isotope signatures in TSR phenomena other  
924 than those in the presence of amino-acids (such as glycine, Watanabe et al., 2009; Oduro et al., 2011) is  
925 available so far. But experimental data at relevant *T-P* conditions are lacking in the presence of hydrocarbon  
926 compounds ( $\text{C}_x\text{H}_y$ ), a type of organic matter which is the most abundant in sedimentary basins. Such  
927 environments may offer a large range of chemical pathways and reaction rates involving, in addition to  $\text{S}_3^{\cdot-}$ ,

928 different organic S-bearing radical species (e.g., Lewan, 1998). The particularly rich chemistry of such  
929 settings enlarges the probability to find a subtle favorable interplay of kinetic factors and dynamic parameters  
930 of reactions (not too fast and not too slow; e.g., Buchachenko, 2001; 2013), and reaction mechanisms  
931 involving radical-radical pairs, molecular cages (e.g., Kopf and Ono, 2012; references therein) or specific  
932 mineral surfaces (e.g., Lasaga et al., 2008). All these factors are expected to favor magnetic isotope effects  
933 (MIE) on the nuclear-spin possessing  $^{33}\text{S}$ . Another natural environment that might meet some of the MIE  
934 requirements is ultramarine minerals of the zeolite group that host a plethora of S species, from  $\text{S}^{2-}$  to  $\text{SO}_4^{2-}$ ,  
935 including  $\text{S}^0$  and the radical ions, stabilized in Si/Al network structure cages (e.g., Reinen and Lindner, 1999;  
936 Tauson et al., 2011), as well as  $\text{S}_3^{\cdot-}$ -bearing blue fluorites (Müller, 2018). Such minerals form in a wide range  
937 on hydrothermal-metamorphic conditions and may provide an efficient structural trap for S aqueous species  
938 allowing preservation of their anomalous isotope signatures. A third possible environment for MIF-  
939 generating reactions might be in magmatic-hydrothermal settings due to the presence of another radical ion,  
940  $\text{S}_2^{\cdot-}$ , which forms at the expense of  $\text{S}_3^{\cdot-}$  in S-rich fluids containing sulfate and sulfate at temperatures from  
941  $450^\circ\text{C}$  to at least  $800^\circ\text{C}$  as demonstrated by in-situ Raman spectroscopy (Pokrovski and Dubessy, 2015;  
942 Colin et al., 2018, 2020; Pokrovski et al., 2019). Having a magnetic moment similarly to  $\text{S}_3^{\cdot-}$ ,  $\text{S}_2^{\cdot-}$  might  
943 potentially be capable of producing, in fluid-magma systems, MIF anomalies at least on  $^{33}\text{S}$ , provided other  
944 factors required for MIE have been met. In addition, an improved analytical resolution on the  $^{36}\text{S}$  non-  
945 magnetic isotope may also help discriminating the factors leading to MIF. For example, the  $\Delta^{33}\text{S}/\Delta^{36}\text{S}$  ratio  
946 has been used to differentiate the Archean MIF array from the kinetic MDF array (e.g., Johnston, 2011;  
947 LaFlamme et al., 2018a). Verifying the hypotheses evoked above, both in nature and laboratory, would  
948 require a judicious combination of in-situ time-resolved experiments with highly sensitive analytical methods  
949 for different sulfur species and the four S isotopes in the high  $T$ - $P$  fluid phase, thus posing a formidable  
950 challenge for future research in sulfur isotope geochemistry.

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1225**Table 1.** Summary of the experiments conducted in this study.

Run/step	Experimental system composition at each step (moles of substance/kg fluid)	pH <sub>T,P</sub> <sup>a</sup>	pH <sup>0</sup> <sub>T,P</sub> <sup>b</sup>	T, °C	P range, bar	Duration, of step, days	Injected aqueous solution	Predicted concentration of S <sub>3</sub> <sup>•-</sup> , mol S/kg fluid	Solid phases precipitated
m22/1	K <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (0.49), HCl(0.14), QMM <sup>c</sup>	4.5	5.7	350	335-370	10	-	0.067	native sulfur
m22/2	K <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (0.38), HCl(0.11), KCl(0.10), FeCl <sub>2</sub> (0.18), BaCl <sub>2</sub> (0.09)	3.8	5.7	350	360-380	14	KCl-FeCl <sub>2</sub> -BaCl <sub>2</sub>	0.0005	pyrite, barite, alunite
m29/1	K <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (0.19), KOH(0.091)	7.3	5.7	350	400-405	13	-	0.0004	-
m29/2	K <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (0.16), KOH(0.075), FeCl <sub>2</sub> (0.059)	5.3	5.7	350	380-410	6	FeCl <sub>2</sub>	0.0002	pyrite
m32/1 <sup>d</sup>	K <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (0.50), KOH(0.30)	6.9	5.5	300	430-480	13	-	0.004	-
m32/2	K <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (0.50), KOH(0.30)	7.9	6.0	450	690-725	14	-	0.007	-
m32/3	K <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (0.41), KOH(0.20), HCl (0.17)	6.8	6.0	450	705-710	8	HCl	0.037	-
m32/4	K <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (0.34), KOH(0.17), HCl (0.14), FeCl <sub>2</sub> (0.051)	5.9	6.0	450	695-720	8	FeCl <sub>2</sub>	0.020	pyrite
m33/1	K <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (0.48)	5.3	5.5	300	410-565	15	-	0.065	-
m33/2	K <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (0.32)	5.3	5.5	300	430-550	18	H <sub>2</sub> O	0.024	-
m33/3	K <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (0.21)	5.3	5.5	300	380-505	8	H <sub>2</sub> O	0.008	-

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1232<sup>a</sup> Calculated pH of the fluid at each injection step at indicated *T-P*.<sup>b</sup> Calculated pH of the neutrality point of water at indicated *T-P* as  $a[\text{H}^+] = a[\text{OH}^-] = 0.5 \times \log_{10} K_w$ , where  $K_w = 1/(a_{\text{H}^+} \times a_{\text{OH}^-})$  is the water dissociation constant, and  $a$  is H<sup>+</sup> or OH<sup>-</sup> activity.<sup>c</sup> Quartz-Muscovite-Microcline mineral assemblage.<sup>d</sup> The pH and S<sub>3</sub><sup>•-</sup> concentration values will be slightly refined in the course of this study for experiment m32/1-4 after correction for K<sub>2</sub>SO<sub>4</sub> precipitation (section 4.1.1, Fig. 4c, Appendix A3).



1234 **Table 2.** Fluid composition and sulfur speciation measured in sampled fluids from the experiments of this study.

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N	Duration, days	T, °C	P, bar	S <sub>tot</sub>	S <sub>red</sub>	S <sub>sulfide</sub>	S <sub>sulfate</sub>	S <sup>0</sup> <sub>hexane</sub>	S <sup>0</sup> <sub>balance</sub> <sup>a</sup>	K	Cl	Fe	K <sub>2</sub> SO <sub>4</sub> mol	Pyrite mol	m fluid g
<b>m22: K<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (0.49 m)-HCl (0.14 m), Quartz-Muscovite-Microcline mineral assemblage</b>															
1	1	350	370	1.01	-	0.31	0.41	-	0.29	1.00	0.13	10 <sup>4</sup>	-	-	150.00
2	3	350	335	1.09	-	0.31	0.43	-	0.35	1.02	0.13	2x10 <sup>-5</sup>	-	-	142.72
3	7	350	370	0.96	0.34	0.30	0.42	-	0.21	0.92	0.13	2x10 <sup>-5</sup>	-	-	136.87
4	10	350	370	0.98	0.33	0.30	0.40	-	0.26	0.97	0.13	10 <sup>-5</sup>	-	-	130.05
<i>Injection of KCl-BaCl<sub>2</sub>-FeCl<sub>2</sub></i>															
5	14	350	380	0.27	0.02	<0.01	0.23	-	<0.03	0.86	0.74	0.027	-	0.028	153.19
6	17	350	370	0.28	0.02	<0.01	0.22	-	<0.04	0.88	0.74	0.023	-	0.028	144.80
7	24	350	360	0.27	0.02	<0.01	0.21	-	<0.04	0.86	0.75	0.014	-	0.028	136.83
<b>m29: K<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (0.19 m) - KOH (0.091 m)</b>															
1	7	352	400	0.37	0.18	0.17	0.17	-	<0.02	0.48	0.02	4x10 <sup>-5</sup>	-	-	65.62
2	13	352	405	0.34	0.16	0.14	0.15	-	<0.03	0.48	<0.01	5x10 <sup>-5</sup>	-	-	57.57
<i>Injection of FeCl<sub>2</sub></i>															
3	16	352	410	0.13	<0.005	<0.01	0.14	-	<0.01	0.39	0.20	<0.002	-	0.0039	59.51
4	19	352	380	0.11	<0.005	<0.01	0.10	-	<0.01	0.39	0.19	<0.002	-	0.0039	51.73
<b>m32: K<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (0.50 m) - KOH (0.30 m)</b>															
1	3	302	480	0.94	0.28	0.20	0.18	-	0.48	1.15	-	-	0.0083	-	111.23
2	8	301	430	0.89	0.31	0.20	0.17	-	0.41	1.11	-	-	0.0095	-	101.69
3	13	299	440	0.86	0.28	0.25	0.24	-	0.34	1.06	-	-	0.011	-	96.16
<i>Temperature rise to 450°C</i>															
4	16	451	695	0.71	0.31	0.40	0.32	0.062	<0.01	0.79	-	-	0.023	-	90.72
5	20	451	685	0.69	0.28	0.35	0.24	0.005	0.10	0.78	-	-	0.022	-	84.36
6 <sup>d</sup>	23	453	725	0.75	0.53	-	-	-	-	0.93	-	-	0.014	-	78.02
7 <sup>d</sup>	27	452	690	0.59	0.33	0.37	0.28	0.006	<0.01	0.60	-	-	0.026	-	75.57
<i>Injection of HCl</i>															
8	29	452	710	0.62	0.20	0.20	0.35	0.008	0.07	0.74	0.20	-	0.012	-	84.82
9	32	451	710	0.57	0.19	0.19	0.31	0.060	0.07	0.68	0.18	-	0.014	-	79.26
10	35	452	700	0.54	0.19	0.25	0.32	0.117	<0.01	0.61	0.22	-	0.015	-	72.16
<i>Injection of FeCl<sub>2</sub></i>															
11	37	452	720	0.43	0.09	0.13	0.33	0.023	<0.01	0.68	0.27	-	0.0063	0.0041	79.48
12	41	452	710	0.47	0.10	0.11	0.28	0.032	0.08	0.76	0.29	-	0.0027	0.0041	70.14
13	44	451	695	0.48	0.03	0.084	0.30	-	0.10	0.75	0.28	-	0.0028	0.0041	63.31
<b>m33: K<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (0.48 m)</b>															
1	<1	300	570	0.96	0.20	0.28	0.40	0.87 <sup>b</sup>	0.28	0.99	-	-	-	-	83.65
2	2	300	470	0.98	0.30	0.25	0.44	0.60 <sup>b</sup>	0.24	1.02	-	-	-	-	70.28
<i>Injection of K<sub>2</sub>S<sub>2</sub>O<sub>3</sub></i>															

3	5	300	510	1.11	0.26	0.26	0.42	0.61	0.43	1.01	-	-	-	-	76.11
4	15	300	410	1.15	0.16	0.21	0.38	0.034 <sup>c</sup>	0.56	1.07	-	-	-	-	64.99
<i>Injection of H<sub>2</sub>O</i>															
5	21	300	545	0.62	0.20	0.21	0.28	0.39	0.13	0.60	-	-	-	-	84.60
6	26	300	490	0.64	0.21	0.22	0.27	0.31	0.15	0.64	-	-	-	-	77.73
7	33	300	425	0.60	0.16	0.21	0.26	0.15	0.13	0.63	-	-	-	-	69.42
<i>Injection of H<sub>2</sub>O</i>															
8	35	300	505	0.42	0.15	0.14	0.19	0.14	0.08	0.44	-	-	-	-	81.00
9	37	300	440	0.42	0.12	0.16	0.19	0.013	0.07	0.43	-	-	-	-	72.71
10	41	300	380	0.38	0.13	0.14	0.22	0.005	0.02	0.39	-	-	-	-	64.87
<i>error</i>		±2	±15	±10%	±10%	±20%	±15%	±50%	±30%	±5%	±10%	±10%			

1236 “-“ means not analyzed or not applicable.

1237 S<sub>red</sub> includes S species other than sulfate and molecular sulfur, which all react with iodine (sulfide, radical ions, polysulfide ions, sulfite, thiosulfate).

1238 <sup>a</sup> S<sup>0</sup><sub>balance</sub> = S<sub>tot</sub> - (S<sub>red</sub> + S<sub>sulfate</sub>); if S<sub>red</sub> < S<sub>sulfide</sub> or not available then S<sub>sulfide</sub> was used instead of S<sub>red</sub>.

1239 <sup>b</sup> Likely overestimated because of the S<sup>0</sup> UV signal contamination by organic impurities from the acetate decomposition.

1240 <sup>c</sup> Underestimated because of insufficient time of reaction with hexane.

1241 <sup>d</sup> Temperature instability due to heat regulation failure around samples #6 and #7 (see Appendix A3 for details).

1243 **Table 3.** Isotopic composition (in ‰) of sulfate (as BaSO<sub>4</sub>), sulfide (as ZnS) and molecular sulfur (S<sup>0</sup>, where available) analyzed in  
 1244 sampled fluids from the experiments of this study.  
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N	Duration, days	$\delta^{34}\text{S}_{\text{sulfide}}$	$\delta^{34}\text{S}_{\text{S}_0}$	$1000 \times \ln \alpha_{\text{S}_0}$	$\delta^{34}\text{S}_{\text{sulfate}}$	$1000 \times \ln \alpha_{\text{S}_{04}}$	$\Delta^{33}\text{S}_{\text{sulfide}}$	$\Delta^{33}\text{S}_{\text{S}_0}$	$\Delta^{33}\text{S}_{\text{sulfate}}$	$\Delta^{36}\text{S}_{\text{sulfide}}$	$\Delta^{36}\text{S}_{\text{S}_0}$	$\Delta^{36}\text{S}_{\text{sulfate}}$
<b>m22: K<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (0.49 m)-HCl (0.14 m), Quartz-Muscovite-Potassic feldspar mineral buffer</b>												
1	1	-13.84	-13.87	-0.03	-	-	0.017	0.011	-	-0.51	0.16	-
2	3	-14.13	-14.15	-0.02	-	-	0.015	0.022	-	-0.39	-0.31	-
3	7	-13.86	-13.75	-0.10	-	-	0.013	0.031	-	-0.23	-0.83	-
4	10	-14.71	-14.16	0.54	-0.60 <sup>a</sup>	14.10	0.023	0.052	0.042 <sup>a</sup>	0.71	-0.73	-0.05 <sup>a</sup>
<i>Injection of KCl-BaCl<sub>2</sub>-FeCl<sub>2</sub></i>												
5	14	-12.05	-11.80	0.24	-	-	0.036	0.054	-	0.17	-0.78	-
6	17	-11.89	-13.14	-1.26	-	-	0.020	0.035	-	-0.72	-0.67	-
7	24	-12.92	-12.68	0.25	7.75	20.68	0.024	0.046	-0.024	-	0.76 <sup>e</sup>	-
<b>m29: K<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (0.19 m) - KOH (0.091 m)</b>												
1	7	-14.58	-	-	3.95	18.53	0.028	-	-	-0.72	-	-0.41
2	13	-15.01	-	-	-	-	0.034	-	-	-0.79	-	-
<i>Injection of FeCl<sub>2</sub></i>												
3	16	-	-	-	6.85	-	-	-	0.029	-	-	0.13
4	19	-	-	-	2.17	-	-	-	0.052	-	-	-0.58
<b>m32: K<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (0.50 m) - KOH (0.30 m)</b>												
<i>300°C</i>												
0	0	7.18 <sup>b</sup>	-	-	-1.26 <sup>c</sup>	N/A	0.004 <sup>b</sup>	-	0.061 <sup>c</sup>	-0.09 <sup>b</sup>	-	-0.25 <sup>c</sup>
1	3	-3.45	2.00 <sup>f</sup>	5.45 <sup>f</sup>	4.56	8.01	-0.001	-	0.013	-0.44	-	-0.41
2	8	-3.25	-0.50 <sup>f</sup>	2.75 <sup>f</sup>	8.42	11.67	0.001	-	0.051	-0.48	-	-0.40
3	13	-2.40	-4.40 <sup>f</sup>	-2.00 <sup>f</sup>	9.68	12.08	-0.022	-	0.069	-0.29	-	0.15
<i>Temperature rise to 450°C</i>												
4	16	-2.36	-13.96	-11.61	10.41	12.76	0.020	0.065	0.035	-0.44	-0.80	-0.23
5	20	-2.34	-	-	10.75	13.09	0.018	-	0.033	-0.53	-	-0.27
6	23	-	-	-	-	-	-	-	-	-	-	-
7	27	-2.31	-	-	-	-	0.024	-	-	-0.46	-	-
<i>Injection of HCl</i>												
8	29	-2.11	-1.00	1.11	-	-	0.017	-0.016	-	-0.47	-0.02	-
9	32	-2.41	-2.40	0.01	11.30	13.71	0.013	-0.003	0.026	-0.52	-0.27	-0.19
10	35	-2.50	-	-	11.98	14.48	0.020	-	0.023	-0.48	-	-0.18
<i>Injection of FeCl<sub>2</sub></i>												
11	37	-1.26	-	-	11.24	12.50	0.011	-	0.042	-0.49	-	-0.30
12	41	-1.57	-	-	13.03	14.60	0.018	-	0.020	-0.43	-	-0.18

13	44	-1.27	-	-	13.85	15.13	0.021	-	0.022	-0.33	-	-0.16
<b>m33: K<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (0.48 m)</b>												
0	0	5.37 <sup>b</sup>	-	-	5.08 <sup>a,c</sup>	-	0.012 <sup>b</sup>	-	0.028 <sup>a,c</sup>	0.45 <sup>b</sup>	-	0.45 <sup>a,c</sup>
1	<1	-4.93	-	-	12.93	17.86	0.004	-	0.053	0.04	-	0.11
2	2	-6.61	-3.87	2.74	11.50	18.11	0.010	0.034	0.054	0.61 <sup>d</sup>	-0.47	-0.07
<i>Injection of K<sub>2</sub>S<sub>2</sub>O<sub>3</sub></i>												
3	5	-7.51	-4.78 <sup>e</sup>	2.73 <sup>e</sup>	16.61 <sup>e</sup>	24.13 <sup>a</sup>	0.022	0.080 <sup>e</sup>	0.047 <sup>e</sup>	0.28	3.51 <sup>e</sup>	0.24 <sup>e</sup>
4	15	-6.04	-	-	16.46 <sup>e</sup>	22.50	0.025	-	0.026 <sup>e</sup>	0.72 <sup>d</sup>	-	5.01 <sup>e</sup>
<i>Injection of water</i>												
5	21	-6.73	-7.27	-0.54	13.70	20.43	0.035	0.029	0.037	1.02 <sup>d</sup>	-0.51	0.17
6	26	-6.32	-3.35 <sup>e</sup>	2.97 <sup>e</sup>	12.35	18.67	0.013	0.023 <sup>e</sup>	0.045	-0.25	0.97 <sup>e</sup>	0.09
7	33	-7.10	-6.59	0.51	13.41	20.51	0.031	0.004	0.050	-0.38	-0.53	0.61
<i>Injection of water</i>												
8	35	-7.38	-	-	11.44 <sup>e</sup>	18.82	0.041	-	0.087 <sup>e</sup>	-0.26	-	3.76 <sup>d,e</sup>
9	37	-7.23	-2.41 <sup>e</sup>	4.82 <sup>e</sup>	14.29	21.52	0.025	0.011 <sup>e</sup>	0.055	0.28	-0.14 <sup>e</sup>	0.66
10	41	-8.04	-8.61	-0.57	12.37	20.40	0.024	0.010	0.027	0.13	-0.04	0.05
Error, ‰		±0.05	±0.05	±0.10	±0.05	±0.10	±0.010	±0.020	±0.02	±0.20	±0.20	±0.20

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Note that two different sources of thiosulfate have been used for experiments m22 plus m29 and m32 plus m33, resulting in different  $\delta^{34}\text{S}$  values relative to V-CDT.

“-“not available or analysis was judged to be unreliable.

<sup>a</sup> Chemical yield <10%.

<sup>b</sup> Ag<sub>2</sub>S fraction of the initial K<sub>2</sub>S<sub>2</sub>O<sub>3</sub> corresponding to the isotope composition of the sulfane group.

<sup>c</sup> BaSO<sub>4</sub> fraction of the initial K<sub>2</sub>S<sub>2</sub>O<sub>3</sub> corresponding to the isotope composition of the sulfonate group.

<sup>d</sup> Error (1 SD) >0.5‰.

<sup>e</sup> Micro-volume measurement (<30 μg of S).

<sup>f</sup> Calculated values using mass and isotope balance (see Appendix A5).

1258 **Table 4.** Sulfur isotope composition (in ‰) of precipitated pyrite, and pyrite-aqueous sulfide fractionation factors in the experiments of this study.  
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Run	$T$ , °C	$N_{\text{pyrite}}$ pts	$\delta^{34}\text{S}_{\text{pyrite}}^{\text{a}}$	$\Delta^{33}\text{S}_{\text{pyrite}}$	$\Delta^{36}\text{S}_{\text{pyrite}}$	$N_{\text{sulfide}}$ pts	$\delta^{34}\text{S}_{\text{sulfide}}^{\text{b}}$	$\Delta^{33}\text{S}_{\text{sulfide}}$	$\Delta^{36}\text{S}_{\text{sulfide}}$	$1000 \times \ln \alpha_{\text{py}}^{\text{c}}$	$\Delta^{33}\text{S}_{\text{pyrite}} - \Delta^{33}\text{S}_{\text{sulfide}}$	$\Delta^{36}\text{S}_{\text{pyrite}} - \Delta^{36}\text{S}_{\text{sulfide}}$
m22	350	2	-13.8±0.5	0.036±0.010	-0.22±0.25	6	-13.3±1.2	0.022±0.008	-0.1±0.6	-0.5±1.3	0.014±0.013	-0.13±0.60
m29	350	4	-13.3±0.5	0.046±0.007	-0.81±0.26	2	-14.8±0.8	0.031±0.004	-0.8±0.1	1.5±0.9	0.014±0.008	-0.05±0.30
m32 <sup>d</sup>	450	1	-1.5±0.5	0.010±0.010	-0.30±0.18	6	-1.9±0.6	0.017±0.004	-0.5±0.1	0.3±0.7	-0.006±0.011	0.15±0.30

1260

1261 <sup>a</sup>  $\delta^{34}\text{S}_{\text{pyrite}}$  is the average of  $N_{\text{pyrite}}$  independent IRMS measurements for the same sample (error is 1SD of the mean).

1262 <sup>b</sup>  $\delta^{34}\text{S}_{\text{sulfide}}$  corresponds to the  $\delta^{34}\text{S}$  value of the ZnS fraction in the sampled fluid, calculated as the average of the indicated  $N_{\text{sulfide}}$  number of samples taken before and after  $\text{FeCl}_2$  injection for  
 1263 experiments m32 and m22 (3 samples before and 3 after), and before  $\text{FeCl}_2$  injection for experiment m29 (2 samples).

1264 <sup>c</sup>  $\alpha_{\text{py}} = \delta^{34}\text{S}_{\text{pyrite}} - \delta^{34}\text{S}_{\text{sulfide}}$ .

1265 <sup>d</sup> A different source of thiosulfate has been used in m32 resulting in different  $\delta^{34}\text{S}$  values relative to V-CDT compared to m22 and m29.

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## Figure captions

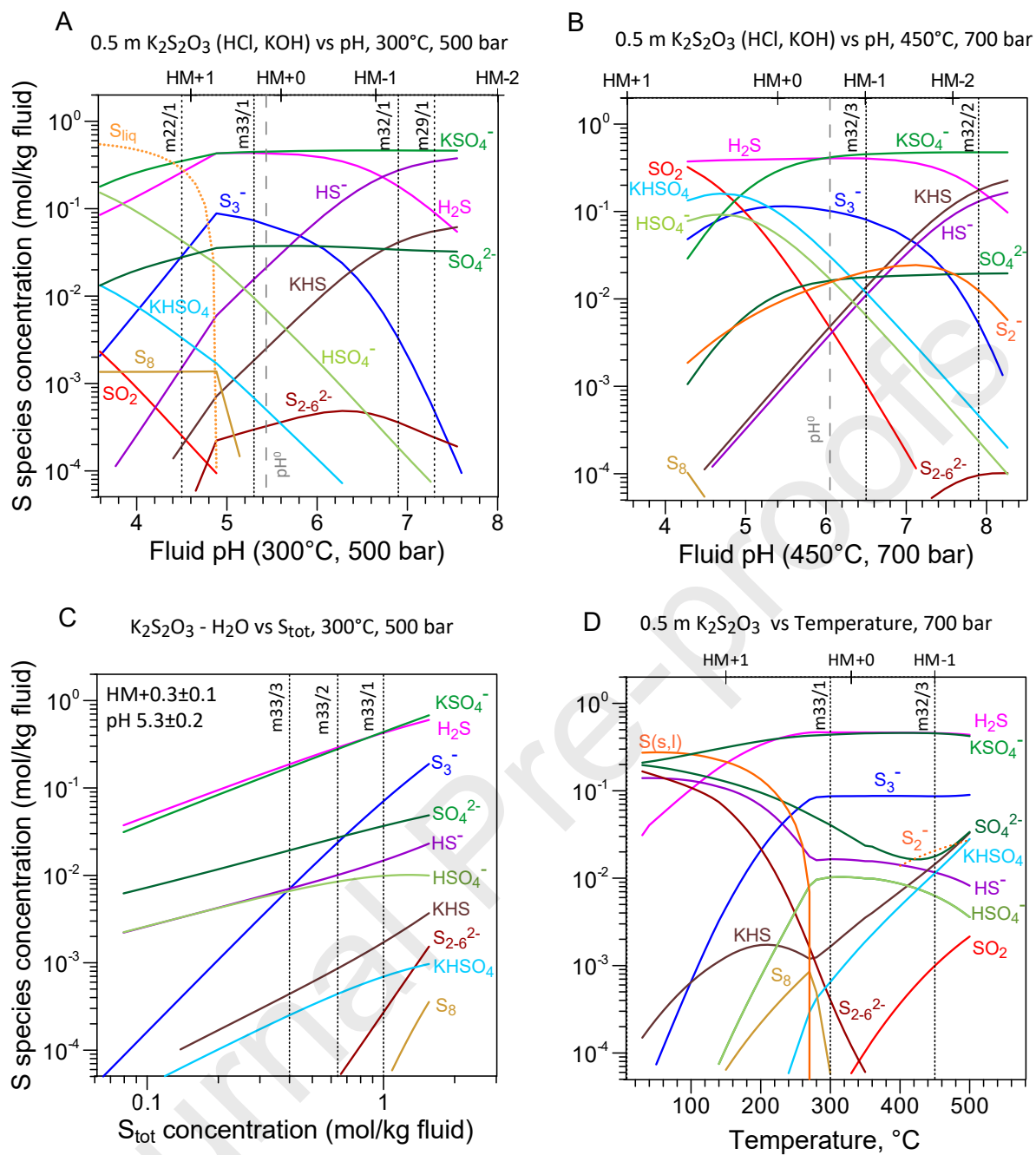
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1270 **Fig. 1.** Sulfur species concentrations in aqueous  $K_2S_2O_3$ -bearing fluids representative of this study, predicted  
1271 using thermodynamic modeling with available data sources (Table A2.1), at the indicated compositions as a  
1272 function of pH (adjusted by adding KOH or HCl) at 300°C, 500 bar (A) and 450°C, 700 bar (B), total sulfur  
1273 ( $S_{tot}$ ) concentration at 300°C, 500 bar (C), and temperature at 700 bar (D). Vertical dashed lines in (A) and (B)  
1274 indicate the pH of the neutrality point of water at the given  $T$  and  $P$ ; vertical dotted lines show approximate  
1275 compositions of our experiments (see Table 1 and Fig. 4 for calculations at specific compositions of each  
1276 experimental step; note that experiments m22 and m29 carried out at 350°C are indicated in (A) for the sake  
1277 of completeness). The oxygen fugacity is indicated relative to the hematite-magnetite buffer (HM, in log units).  
1278
- 1279 **Fig. 2.** Sequence of the experimental procedures of this study using the flexible-cell hydrothermal reactor.  
1280
- 1281 **Fig. 3.** Evolution of sulfur speciation in the fluid with time in experiments performed in this study (m22, m29,  
1282 m32, and m33).  $S_{total}$ ,  $S_{sulfide}$ ,  $S_{sulfate}$  and  $S^0_{hexane}$  denote analyzed concentrations whereas  $S^0_{balance}$  is the difference  
1283 in S concentration between measured  $S_{tot}$  and ( $S_{red} + S_{sulfate}$ ). Dashed vertical lines show the time of in-situ  
1284 injection into the reactor of the indicated aqueous solutions (see Table 1 and 2 for the exact fluid compositions).  
1285
- 1286 **Fig. 4.** Comparisons between experimentally measured aqueous sulfate and sulfide concentrations and the  
1287 corresponding thermodynamically predicted values, and between mass-balance derived molecular sulfur  
1288 ( $S^0_{balance}$ ) and thermodynamically predicted  $S_3^{2-}$  (plus  $S_2^{2-}$  at 450°C), at each sampling point of the four  
1289 conducted experiments. Calculations for m32 (C) take into account corrections for  $K_2SO_4$  precipitation and  
1290 stability constant of  $KSO_4^-$  (see Appendix A3).  
1291
- 1292 **Fig. 5.** Values of  $\delta^{34}S$  (‰) of the indicated aqueous S species and pyrite and the corresponding isotope  
1293 fractionation factor ( $\alpha$ , relative to sulfide) of sulfate,  $S^0$  and pyrite as a function of time in experiment m32 (A  
1294 and C) and m33 (B and D). The dotted curve and 4 cross symbols in (A) show the evolution of  $S^0$  isotope  
1295 composition calculated using sulfur mass and isotope balance (see Appendix A5). The dotted curves ( $\pm 1$  SD)  
1296 in (C and D) show a fit of experimental points at 300°C using the rate law from Ohmoto and Lasaga (1982):  
1297  $2.303 \times \log_{10}((\alpha_e - \alpha)/(\alpha_e - \alpha_0)) = -k_r \times t \times ([\Sigma SO_4^{2-}] + [\Sigma S^{2-}])$ , where  $t$  is the reaction time (in days);  $\alpha_0$ ,  $\alpha$  and  $\alpha_e$   
1298 are the fractionation factors of sulfate, respectively, at  $t=0$  (initial condition), during the course of reaction, and at  
1299 equilibrium; and  $[\Sigma SO_4^{2-}] + [\Sigma S^{2-}]$  is the sum of concentrations of sulfate and sulfide species. The equilibrium  
1300 fractionation factor ( $1000 \times \ln \alpha_e = 20.2$  ‰) was taken from Ohmoto and Lasaga (1982). The fractionation  
1301 factors  $1000 \times \ln \alpha_0$  at  $t=0$  for m32 and m33 are  $6.0 \pm 1.0$  and  $17.5 \pm 1.0$  ‰, respectively, as estimated from time-  
1302 series fractionation data points regressed to zero. Fitting the 3 data points (m32) and 9 data points (m33, by  
1303 excluding a single outlier from this trend,  $1000 \times \ln \alpha_{SO_4} \sim 24$  ‰, sample #3, which might be due to analytical  
1304 issues related to a low  $SF_6$  fluorination yield) at 300°C for  $\alpha$  yields a  $\log_{10} k_r$  value (in hour<sup>-1</sup>) of  $-2.4 \pm 0.2$  (pH  
1305 6.9, m32) and  $-1.9 \pm 0.3$  (pH 5.3, m33), respectively.  
1306
- 1307 **Fig. 6.** Isotope composition of the indicated sulfur species in samples from experiment m32 ( $K_2S_2O_3$ -KOH-  
1308 HCl; 300 and 450°C). Uncertainties of the coefficients of the linear regression equation in (A) are given for  
1309 95% confidence level (2 SD). The lower and upper limits of the reported  $\lambda_{33}$  (from 0.505 to 0.519) and  $\lambda_{36}$   
1310 (from 1.88 to 1.96) MDF slopes that encompass both equilibrium ab-initio calculated (Otake et al., 2008, for  
1311  $\lambda_{33}$  and  $\lambda_{36}$ ) and experimental and natural equilibrium and kinetic (LaFlamme et al., 2018a; references  
1312 therein, for  $\lambda_{33}$ ) variations are shown in (B) and (C) by the blue area within which most of datapoints fall  
1313 (except only few outliers for sulfate and sulfonate S that are very likely to be related to analytical difficulties  
1314 of  $BaSO_4$  conversion). The MDF  $\Delta^{36}S$  vs  $\Delta^{33}S$  array (MDF-S, slope of -9 to -7) and the Archean MIF array  
1315 (MIF-S, slope of -2 to -1) according to Johnston (2011) are shown in (D).  
1316
- 1317 **Fig. 7.** Sulfur isotope compositions of the indicated species in samples from experiment m33 ( $K_2S_2O_3$ ; 300°C).  
1318 See Fig. 6 caption for details about the plots.  
1319

1320 **Fig. 8.** The difference of  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  values for the sulfate-sulfide pair as a function of time in experiments  
1321 m32 and m33. Gray symbols at time 0 indicate the difference values for the sulfonate-sulfane pair in the initial  
1322 thiosulfate.

1323

1324 **Fig. 9.** Schematic summary of the formation mechanisms of molecular sulfur in hydrothermal fluids  
1325 and associated sulfur isotope fractionation between the resulting  $\text{S}^0$  and aqueous sulfide ( $1000 \times \ln \alpha_{\text{S}^0} \approx$   
1326  $\delta^{34}\text{S}_{\text{S}^0} - \delta^{34}\text{S}_{\text{sulfide}}$ ) identified in this study. Blue and red arrows indicate, respectively, fluid cooling and  
1327 heating.

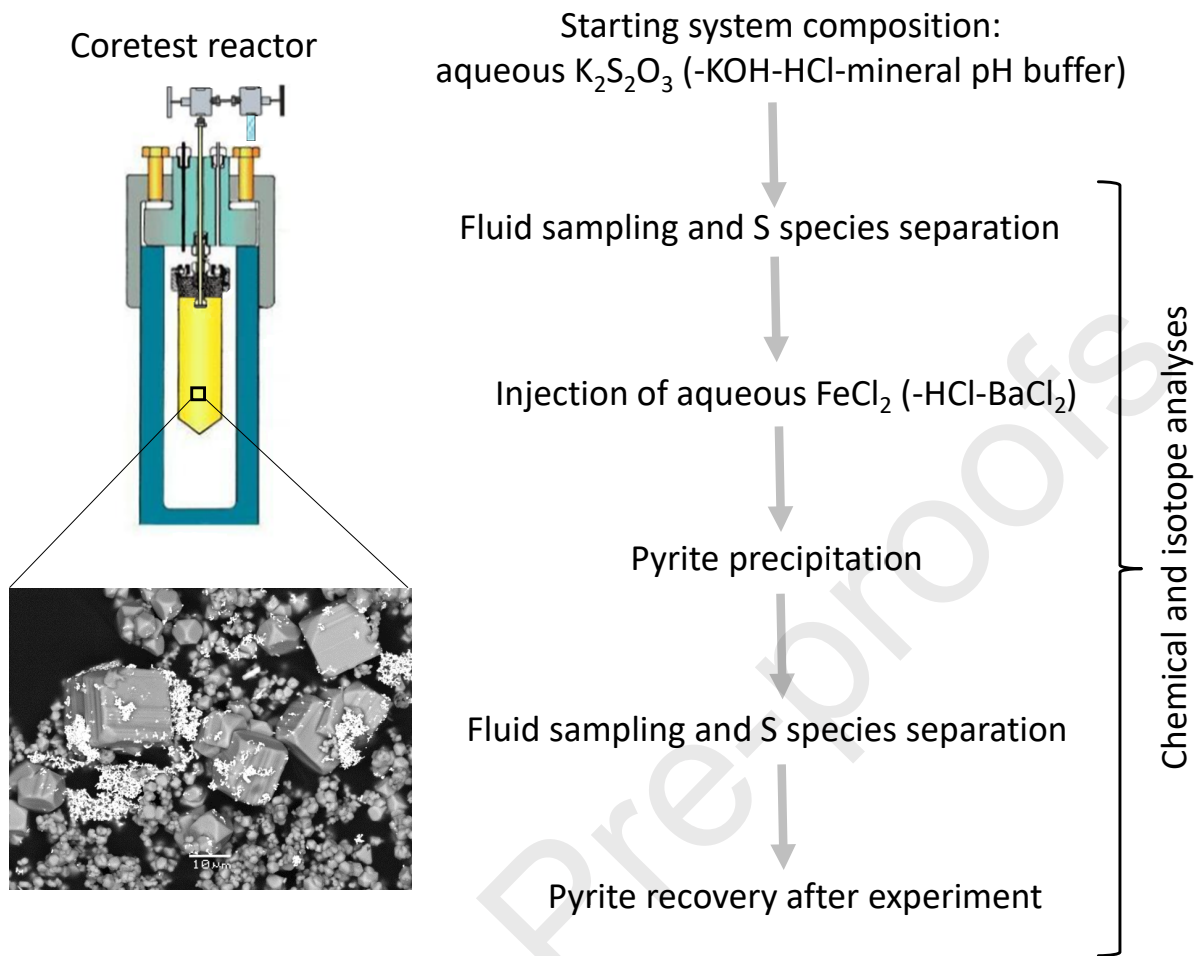
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**Fig. 1**

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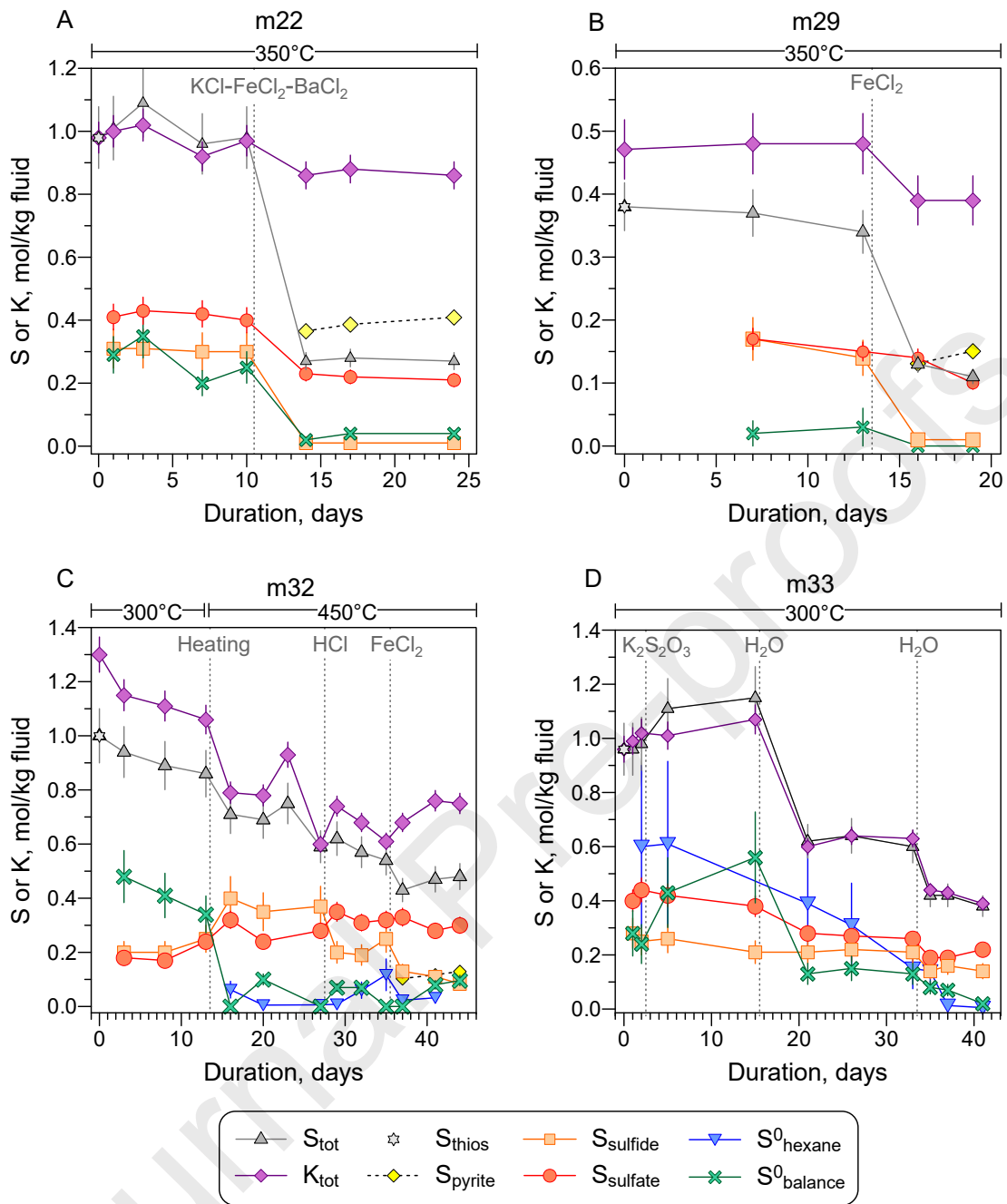
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**Fig. 2**



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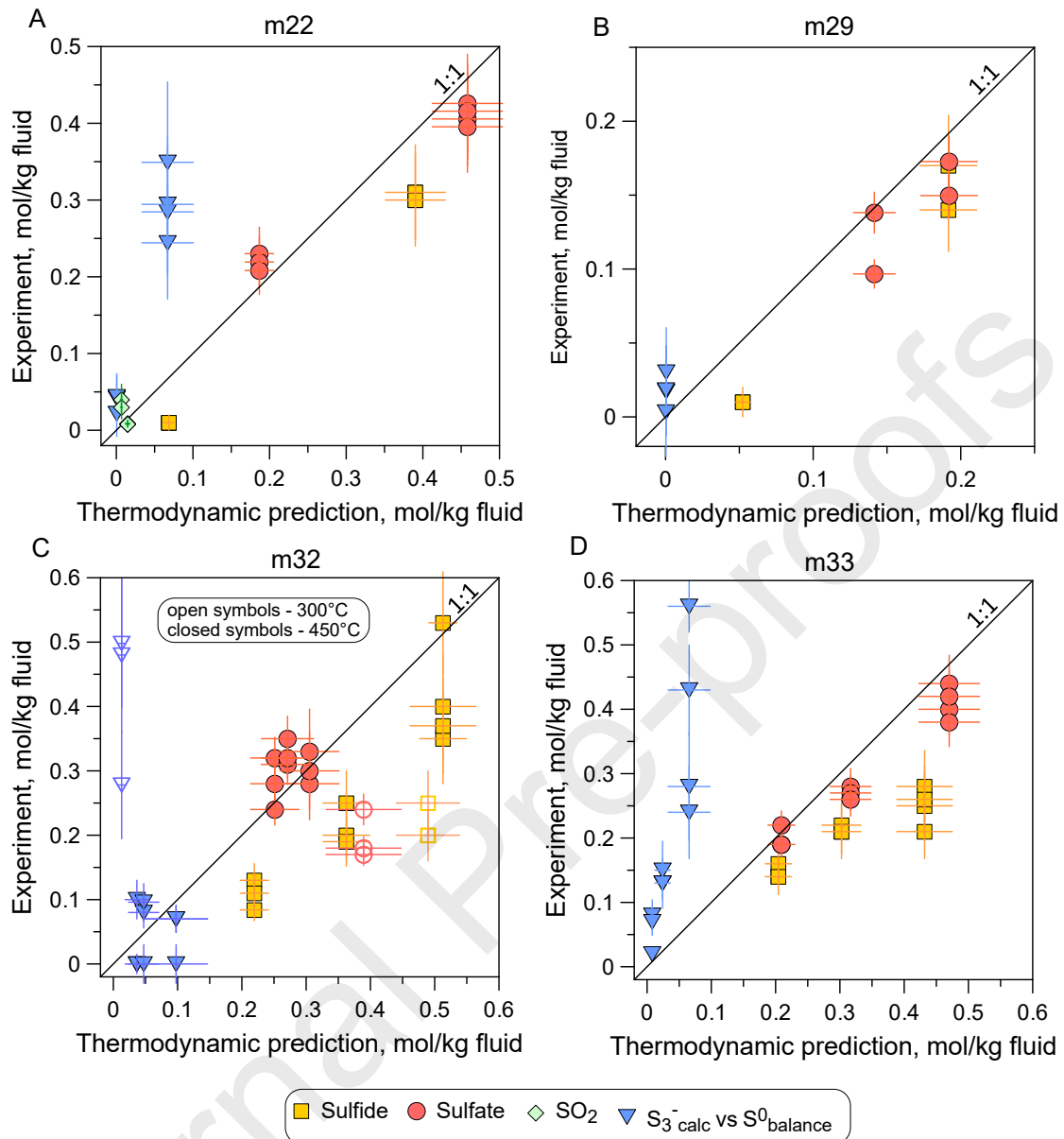
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**Fig. 3.**



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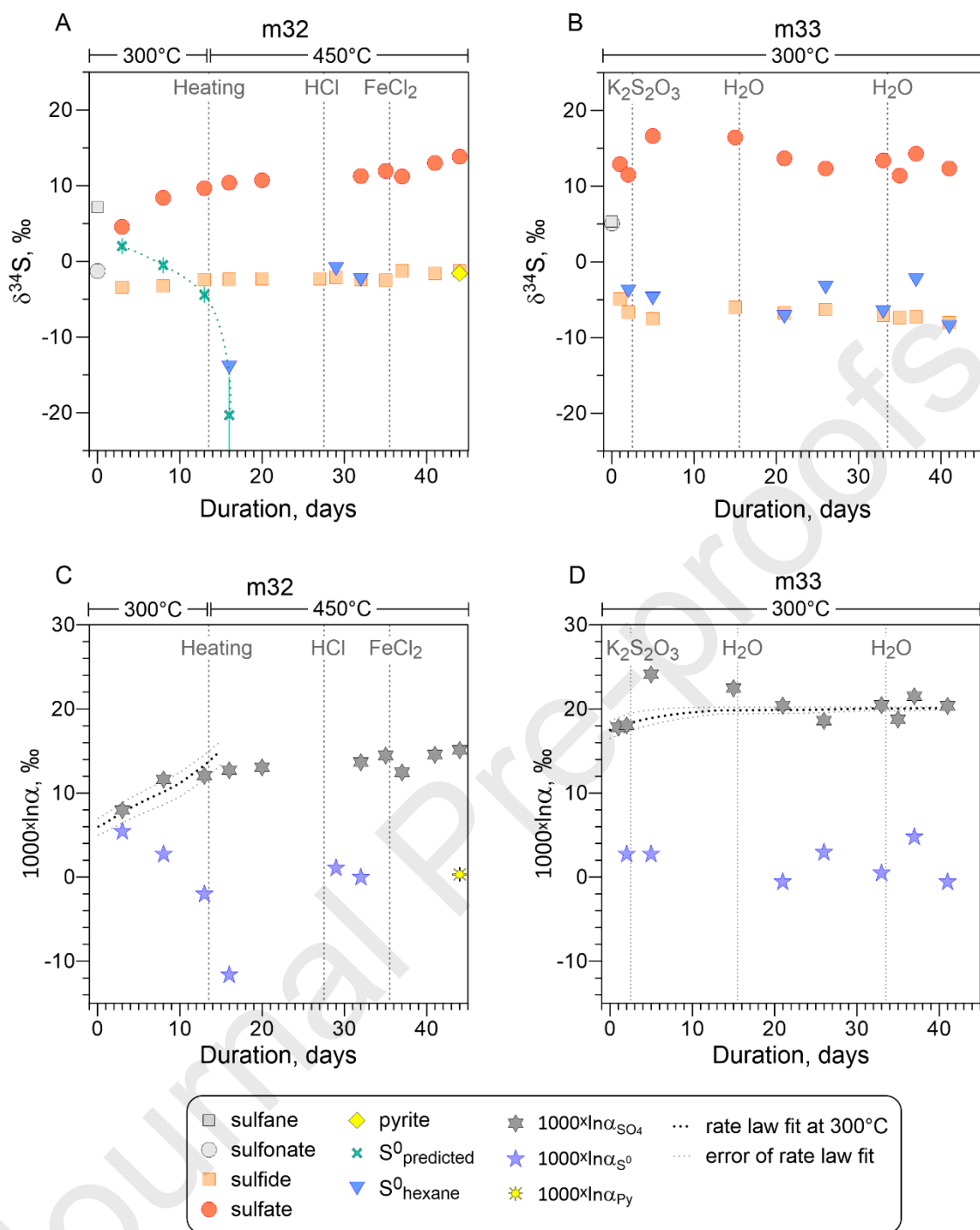
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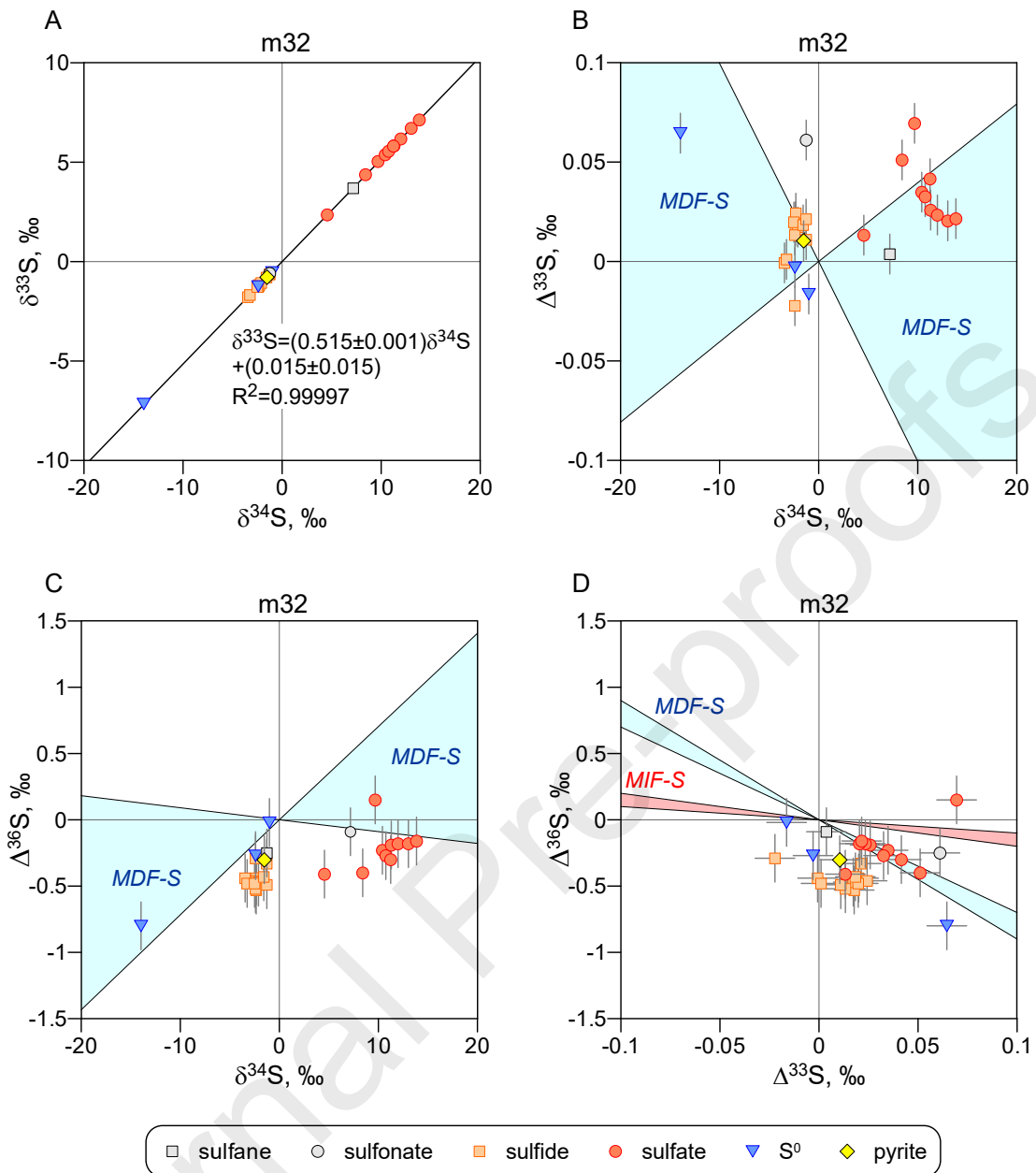
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**Fig. 4.**



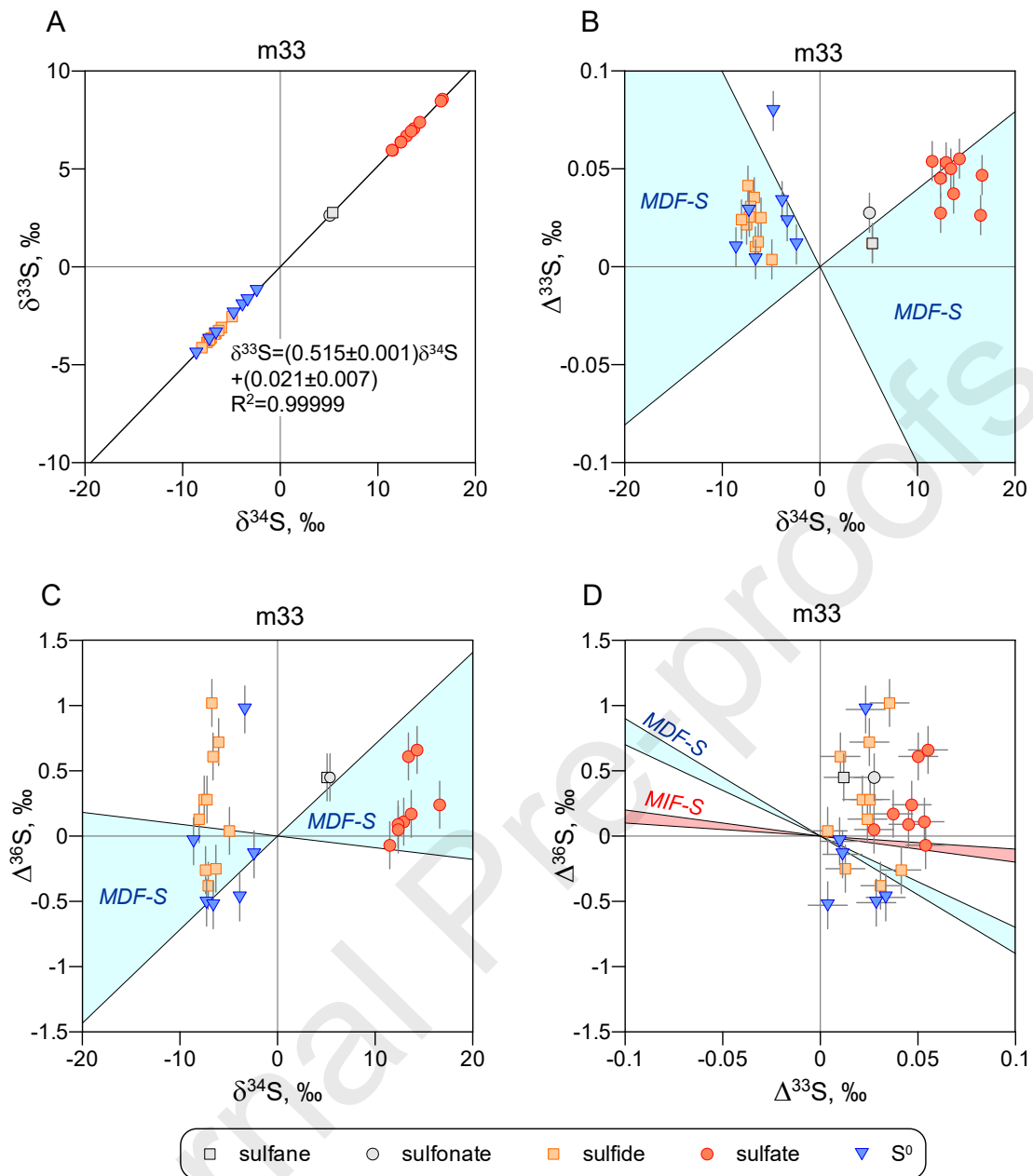
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**Fig. 5.**



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**Fig. 6.**



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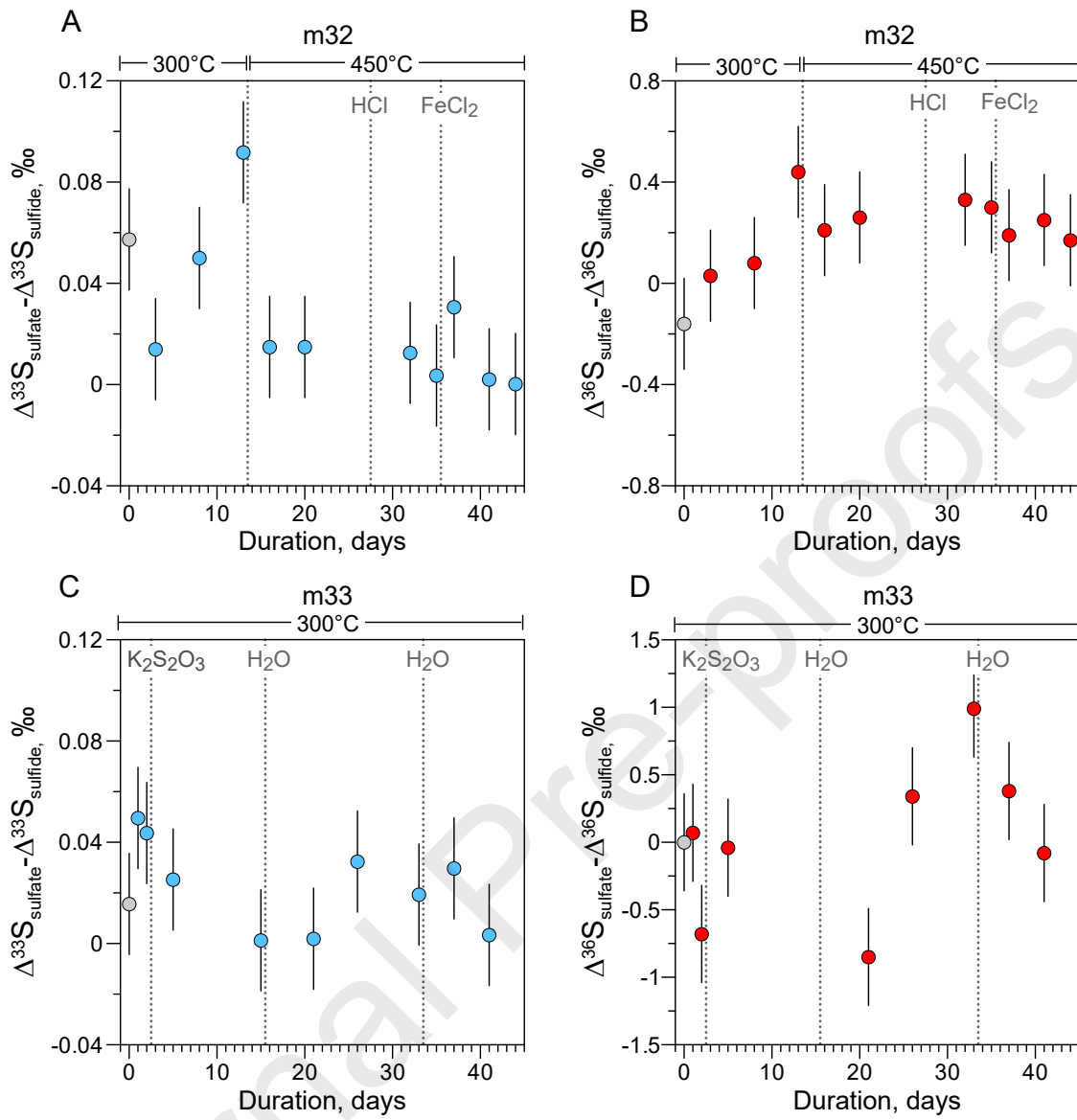
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**Fig. 7.**

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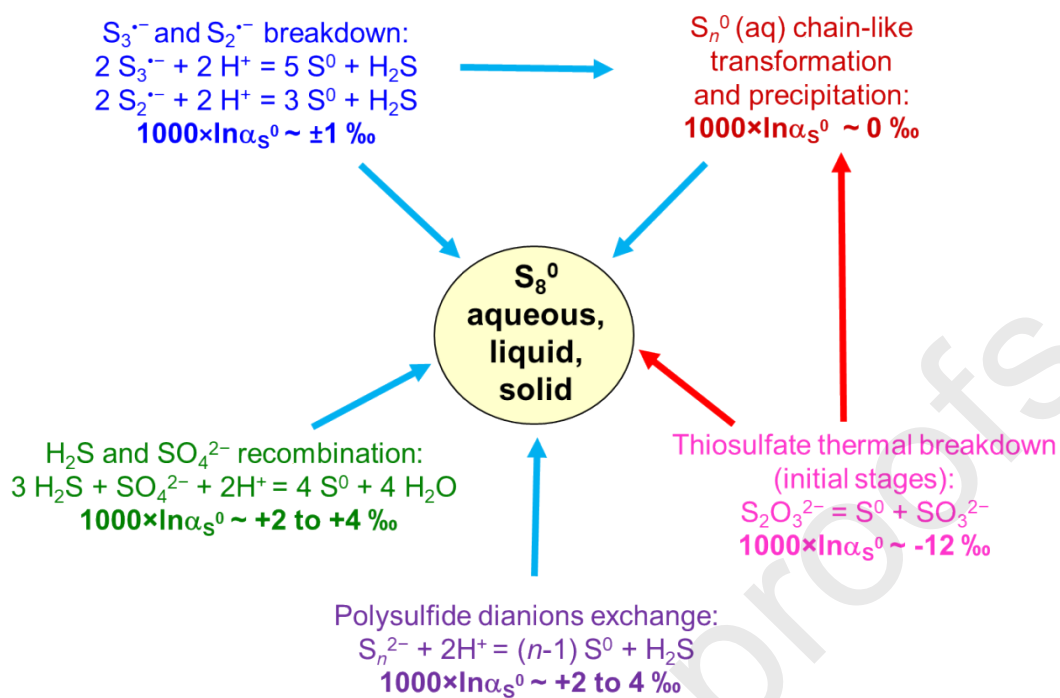
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**Fig. 8.**



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Fig. 9.