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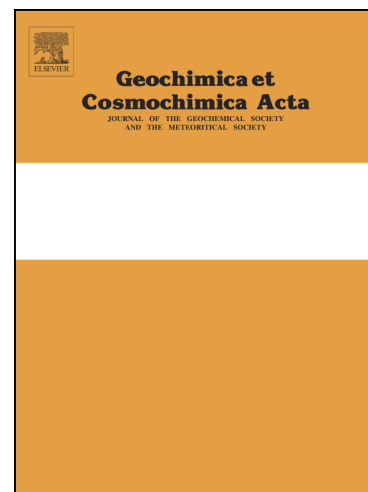
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2 **Multiple sulfur isotope fractionation in hydrothermal**
3 **systems in the presence of radical ions and molecular**
4 **sulfur**

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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 ± 0.1 ‰ and ± 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}S , ^{33}S , ^{34}S , and ^{36}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 ($\Delta^{33}\text{S} > 0.2\text{‰}$)¹ were identified in
 71 pyrite and barite from Archean sedimentary rocks likely caused by 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}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

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

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

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 ‘S⁰’.

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 S₃⁻(S₂⁻)-S⁰-sulfate-sulfide hydrothermal fluids, *ii*) precise analyses of the multiple sulfur
137 isotope ratios in the different sulfur aqueous forms (sulfate, sulfide and S⁰) 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.

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2. MATERIALS AND METHODS

2.1. Experimental strategy and conditions

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Alternatively, acidity buffering at slightly acidic pH values may also be achieved by using alkali
aluminosilicate mineral assemblages, such as quartz-muscovite-microcline, which was used in one of our
experiments (m22, see below). Furthermore, equilibria between sulfate and sulfide at elevated temperatures
impose oxygen fugacity (f_{O_2}), which typically ranges, depending on pH, from HM-2 to HM+2 (where HM
denotes the $\log f_{\text{O}_2}$ value of the conventional hematite-magnetite mineral buffer):

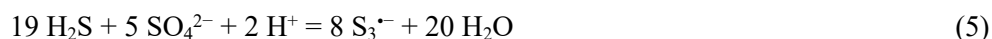
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The formation of S₃⁻ in such sulfate-sulfide solutions can be formally described by the reaction

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This reaction implies that the abundance of S₃⁻ is controlled by total S concentration (S_{tot}, which is
proportional to the sum of the dominant sulfate and sulfide), solution pH, and the H₂S/SO₄ ratio (and therefore

168 oxygen fugacity), with a maximum abundance at a given set of T , S_{tot} and 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 S_3^{*-} formation and breakdown, but only
170 illustrates the fundamental thermodynamic controls on the 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, pH
172 and T - P conditions, variable amounts of sulfate and sulfide ion pairs with K^+ , SO_2 , S_8^0 (both aqueous and
173 molten), disulfur ion S_2^{*-} , and polysulfide dianions 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_{tot} - pH -redox range of this study, and Table 1 overviews the
178 composition and different steps of the conducted experiments. In this manuscript, all pH values are
179 thermodynamically calculated at the corresponding T - P -composition. Two exploratory runs (m22 and m29)
180 at 350°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 S_3^{*-} -rich (~ 0.07 m S in the form of S_3^{*-}) and S_3^{*-} -poor (< 0.001 m S) fluids,
182 respectively. A more elaborated experiment (m32) consisted of two succeeding steps in slightly alkaline S_3^{*-}
183 - poor conditions (~ 0.005 m S) at two contrasting temperatures, 300 and 450°C , followed by an acidification
184 of the fluid at 450°C to increase S_3^{*-} concentration by a factor of 10 (~ 0.04 m S). In addition, the 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 FeCl_2 (plus 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°C at near-neutral pH (~ 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 S_3^{*-} concentration by a factor of 10 (from ~ 0.07 to 0.008 m S),
191 to examine the effect of changing of 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°C , pressures of 100 - 1000 bar, a wide 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 ~ 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- μm 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 cm^3 of initial volume) is inserted into a high-pressure vessel (~ 1000 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 (~ 2.5 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 HNO_3 and annealed at 380°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 cm^3). This
220 injection allows controlled changes of the fluid pH and S_{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 FeCl_2 (- 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.

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

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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 I_2 , $\text{Cd}(\text{CH}_3\text{COO})_2$, $\text{Zn}(\text{CH}_3\text{COO})_2$, 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_{tot}) was analyzed in samples taken into aqueous
238 ammonia (28 wt% 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 H_2O_2) of all S forms to sulfate. Total aqueous chloride was also analyzed by HPLC in the same NH_3

241 and H₂O₂-treated samples. Total reduced sulfur (S_{red}, comprising H₂S/HS⁻/KHS, S_n²⁻ and, eventually, SO₂
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 I₂ by a standard thiosulfate solution, since all these reduced
244 S species react with I₂ (e.g., Charlot, 1966; Dadze and Sorokin, 1993). Sulfide-type sulfur (S_{sulfide}, comprising
245 H₂S, HS⁻ 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 I₂-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., H₂S), so that oxidation by air is
250 negligible. Sulfate-type aqueous sulfur (S_{sulfate}, comprising SO₄²⁻, HSO₄⁻, and their K⁺ ion pairs, existing at
251 experimental *T-P* conditions, Fig. 1) was quantified by HPLC as the SO₄²⁻ 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 S⁰_{hexane}) collected
255 from samples trapped into Cd acetate solution followed by removal of CdS via centrifugation. The hexane
256 fraction was then analyzed for S⁰ 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 S⁰ 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 S⁰, which has always been found below the detection limit (<0.0001 m
262 S). An independent way for estimating S⁰ concentrations in the sampled fluid was using sulfur mass balance
263 between S_{tot} and the sum of sulfate and reduced sulfur (hereafter S⁰_{balance}), because S⁰ 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 NH₃ 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% HNO₃ 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**

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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 BaSO₄ in the sampling vial. However,
284 difficulties were encountered when converting ZnS to H₂S from the fine-grained ZnS-BaSO₄ mixture that
285 prevented ZnS, being armored by BaSO₄, 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 BaSO₄, which was then
291 centrifuged, washed, dried similarly to the ZnS precipitate, and reserved for isotope analyses.

292 Molecular sulfur S⁰ was separated by extraction into hexane after precipitating H₂S 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 S⁰ and H₂S/HS⁻ prone to rapid re-equilibration, and *ii*) possible recombination of sulfate
295 and sulfide to form additional S⁰. 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 S⁰ in the sampled fluid cannot be distinguished
299 by bulk S⁰ chemical analyses, their isotopic composition is expected to reflect those mechanisms. The
300 supernatant containing sulfate and S⁰ 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 S⁰ into the hexane phase, as checked by
305 time-dependent analyses. The S⁰-bearing hexane fraction was then recovered and analyzed for S⁰ 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 (S²⁻)
309 and sulfonate (S⁶⁺) parts according to the slightly modified protocols of Uyama et al. (1985) and Syverson et
310 al. (2015). An aqueous 0.1 m AgNO₃ solution was used to precipitate the sulfane sulfur as Ag₂S from an
311 aqueous 0.05 m K₂S₂O₃ 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 BaSO₄, 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, BaSO₄ and S⁰ were converted to solid silver sulfide (Ag₂S)
 320 using established techniques (Thode et al., 1961; Canfield et al., 1986; Labidi et al., 2012). The obtained
 321 Ag₂S was in turn quantitatively converted to sulfur hexafluoride gas (SF₆) 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 Ag₂S and subsequent Ag₂S fluorination
 324 and purification, are too low to be quantified (nano-molal levels). The S isotope composition of SF₆(g) was
 325 analyzed at mass-to-charge ratio values of 127, 128, 129, and 131 corresponding to the S³²F₅⁺, S³³F₅⁺, S³⁴F₅⁺,
 326 and S³⁶F₅⁺ ions, respectively (note that fluorine has a single stable isotope, ¹⁹F, 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 δ³⁴S, Δ³³S and Δ³⁶S, respectively. Typical external reproducibility on
 329 δ³⁴S, Δ³³S, and Δ³⁶S 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 δ³⁴S, Δ³³S and Δ³⁶S 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 (Ag₂S), with a δ³⁴S value of -0.30‰
 336 relative to V-CDT (Ding et al., 2001; references therein). Because there is presently no international standard
 337 for δ³³S and δ³⁶S, in this study we anchored our ³³S and ³⁶S data to the V-CDT reference scale, for consistency
 338 with the recent studies (Ono et al., 2007) assuming that δ³³S_{V-CDT} = -0.055±0.14 ‰, δ³⁶S_{V-CDT} = -1.37±0.5 ‰,
 339 Δ³³S_{V-CDT} = 0.100±0.003 ‰, and Δ³⁶S_{V-CDT} = -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 Δ³³S and Δ³⁶S were calculated according to Farquhar and
 342 Wing (2003):

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

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

345 where λ³³ and λ³⁶ 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 δ³⁴S) is expressed relative to aqueous sulfide analyzed as
 348 ZnS:

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

350 where i denotes sulfate sulfur (collectively termed as SO_4), molecular sulfur (S^0) or pyrite (Py), and α_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 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, H_2S , SO_2 , as well
369 as H_2 and 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 (S_n^{2-} , where n is between
373 2 and 6) and aqueous 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 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 S_3^- (Fig. 1b). However, the uncertainties
377 on such predictions are large (of an order of magnitude); furthermore, the 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 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 (HS_n^-), for which no thermodynamic data are currently available at elevated temperatures.
385 Estimations of Pokrovski and Dubessy (2015) suggest that 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_{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 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, 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 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 S_3^{2-} -rich (~ 0.07 m S) and S_3^{2-} -poor (~ 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 FeCl_2 injection, sulfate and sulfide
412 represent the major fraction of dissolved sulfur. Reduced sulfur (S_{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 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_{tot}) analyzed in the less concentrated alkaline-pH run (m29) match
418 the sum of S_{sulfate} and S_{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_{tot} and the sum of S_{red} and S_{sulfate} is apparent in the more concentrated acidic run (m22). This
421 imbalance (S^0_{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_{balance} may have multiple origins that will be

423 discussed in section 4. In the next step of both experiments, after the injection of FeCl₂ (m29) and KCl-FeCl₂-
424 BaCl₂ (in m22), S_{tot} becomes largely dominated by sulfate given that a major part of reduced sulfur
425 precipitated as pyrite. Concentrations of S_{tot} are similar within errors to S_{sulfate} in m29, and are slightly higher
426 than S_{sulfate} in m22, likely due to the presence of minor amounts of SO₂ 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 K₂S₂O₃-0.3 m KOH pH_{300°C} ~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_{450°C} ~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_{450°C} ~7), allowing a better identification of S₃⁻ 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 FeCl₂ solution was
436 injected, resulting in pyrite precipitation and further fluid acidification (pH_{450°C} ~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 K₂SO₄(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 K₂SO₄(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 K₂SO₄(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_{tot} by a factor of ~2 (Table 2, Fig. 3c), demonstrating the
448 presence of analytically unreactive molecular sulfur (S⁰_{balance}). Concentrations of S⁰_{balance} decreased by ~50%
449 accompanied by an increase in both sulfate and sulfide (in the 2nd week), reflecting a slow and complex
450 kinetics of thiosulfate transformation. A fourth species contributing to aqueous S is the thiosulfate ion, S₂O₃²⁻,
451 which was detected by HPLC analyses in sample #1 solution after separation of ZnS. The presence of
452 undecomposed S₂O₃²⁻ and/or its possible intermediate decomposition products (SO₃²⁻) at this stage is also
453 independently confirmed by the systematically higher measured concentrations of S_{red} compared to S_{sulfide},
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 S⁰_{balance} 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 S⁰ values exhibit a large
457 scatter due to both analytical difficulties for measuring S⁰ in hexane extracts (S⁰_{hexane}) and the use of mass-
458 balance relations (S⁰_{balance}) for deriving close-to-zero values (~0.01 m S). Yet, despite the scatter, the S⁰_{hexane}
459 concentrations appear, on average, quite similar to the S⁰_{balance} ones (Fig. A4.3), yielding a mean value of

460 0.04±0.02 m S (1 SD) for S⁰ concentration for the whole set of datapoints over the three steps at 450°C
 461 (m32/2, 3, 4). Both types of S⁰ 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 K₂S₂O₃ solution at near-
 465 neutral pH (pH_{300°C} ~5.3). This experiment was designed to better explore the effect of dilution resulting in
 466 large changes in S₃⁻ (and S⁰) concentrations without much changing the overall solution chemistry and
 467 acidity. At the initial stage (~0.5 m K₂S₂O₃, m33/1), sulfate and sulfide account for >60% of S_{tot} (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_{red} and S_{sulfide}
 470 concentrations, suggesting the absence of significant amounts (>0.02 m S) of reduced species other than
 471 H₂S/HS⁻ (e.g., polysulfide ions, SO₂, or undecomposed thiosulfate). In contrast, there is yet significant
 472 imbalance (up to 30% S_{tot}) between S_{tot} and the sum of S_{sulfide} and S_{sulfate}, due to the presence of molecular
 473 sulfur (S⁰_{balance}, Table 2), as was also confirmed by direct analyses of S⁰_{hexane}. After the first injection of water,
 474 this imbalance is significantly reduced as a result of dilution (to ~15% S_{tot}). After the second injection of
 475 water, the S⁰ fraction further decreased to become <5% S_{tot} after 1 week (Table 2, Fig. 3d). Like in experiment
 476 m32, both types of S⁰ datapoints (S_{hexane} and S_{balance}) 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_{sulfide}
 483 (trapped as ZnS) and S⁰ (analyzed by the CRS treatment of the ZnS-BaSO₄ mixture in m22; Appendix A1).
 484 Only few data points could be collected from S_{sulfate} (trapped as BaSO₄) due to imperfections in separating
 485 ZnS from BaSO₄. The δ³⁴S_{sulfide} and δ³⁴S_{S⁰} values are consistently more negative, by 14-21 ‰, than the
 486 δ³⁴S_{sulfate} values; however, the paucity of the BaSO₄ 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 (O₃-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 ³⁴S-enriched and ³⁴S-depleted, respectively. In other words, the
 492 difference in 1000×lnα_{SO₄} (δ³⁴S_{sulfate} - δ³⁴S_{sulfide}) 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 δ³⁴S_{sulfate},
 494 whereas δ³⁴S_{sulfide} 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, δ³⁴S_{sulfide} values stay constant while δ³⁴S_{sulfate} 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°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 S^0 isotope data points,
502 obtained in samples #8 and #9 taken respectively 2 and 5 days after the HCl injection at 450°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 (-S) sulfur
507 of the initial thiosulfate rapidly evolves upon heating to 300°C , with sulfate and sulfide becoming with time
508 ^{34}S -enriched and ^{34}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 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}S and ^{36}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 (SO_4^{2-} , HSO_4^- , KSO_4^- , and KHSO_4^0), sulfide
526 (H_2S , HS^- , and KHS^0), radical ions ($\text{S}_3^{\cdot-}$ at all T , and $\text{S}_2^{\cdot-}$ at 450°C), and pyrite (FeS_2). In addition, in m22
527 aqueous SO_2 and three other phases, $\text{S}_{(\text{s,l})}$, at step m22/1, and barite (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 S_8^0 , and traditional polysulfide ions, represent a negligibly small amount of S_{tot} at equilibrium ($<0.1\%$).

531 Comparisons between calculated and measured concentrations of sulfate, sulfide, 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 K_2SO_4 solid (in m32), sulfate-sulfide-pyrite equilibration, and the formation of 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 $\text{K}_2\text{SO}_4(\text{s})$, 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 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 KSO_4^- from K^+ and 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 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 K_2SO_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 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 S_2^{2-} forming at the
565 expense of H_2S . 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 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_{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_{sulfide} concentrations measured before and after the FeCl_2 injection. However, for all
 574 three experiments in the presence of pyrite, the measured aqueous S_{sulfide} concentrations are somewhat lower
 575 than those predicted using equilibrium thermodynamics (Fig. 4a-c). The difference between measured and
 576 predicted S_{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

580 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°C with the lowest S_{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 S_3^{2-}
 584 (<0.001 m S). The small imbalance between S_{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 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 S^0 (~ 0.3 m S) as clearly apparent from
 590 mass balance between measured S_{tot} and the sum of S_{sulfate} and S_{sulfide} (Table 2). Such elevated S^0
 591 concentrations are not accounted for by thermodynamics, which predicts <0.001 m of S_8^0 (aq) at equilibrium
 592 using the thermodynamic data sources from Table A2.1 (Fig. 1). The contribution from breakdown of S_3^{2-} to
 593 molecular sulfur on cooling during sampling can be estimated by the reaction:



595 Molecular sulfur and H_2S 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 S_6^{2-} that is known to form by recombination of two 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 S_3^{2-} breakdown in this experiment. Yet, the maximum
 601 produced amount of S^0 by 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 (~ 0.3 m S, Fig. 4a). It
 603 is thus very likely that the major part of 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°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°C during sampling, $>30\%$ of S_{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°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_{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_{red} and S_{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_{balance} concentration; and *iii*) increase of S_{sulfate} and S_{sulfide} with time at 300°C (Table 2, Fig. 3c) in line
 632 with reactions (11) and (12). With the T rise to 450°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°C) and near-neutral pH, S^0 concentration that could
 638 be produced by S_3^{2-} breakdown is ~ 5 times lower than the concentration obtained using mass balance between
 639 measured S_{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 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_{hexane}^0 and S_{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_{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_{tot} concentrations
 661 ($<0.4\text{ m}$) and/or higher temperatures (450°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}S compared to the coexisting sulfide, in
 673 agreement with general concepts of isotope fractionation that more oxidized S atoms such as in 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 H_2S (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°C), between 14 and 21 ‰ (m22 and m29,
 677 350°C), and $15.1 \pm 0.2\text{ ‰}$ (m32/2-4, 450°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 $\delta^{34}\text{S}_{\text{sulfate}}$ (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}S . Such a reservoir is consistent with the detection of significant amounts of 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 H_2S and the associated reduced S species (S^0 , 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 hour^{-1}) for an isotope exchange reaction
692 between sulfide and sulfate at 300°C in these experiments was estimated to be -2.4 ± 0.2 and -1.9 ± 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 H_2S - 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 S^0 and
698 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 S^0 and 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}S
704 and ^{34}S) and minor (^{33}S and ^{36}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 S^0 isotope data
706 in terms of S^0 - H_2S 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 S^0 , Table 3), yielding a mean isotope fractionation
712 factor $1000 \times \ln \alpha_{\text{S}^0}$ of 0 ± 1 ‰ for the most robust data points. The absence of significant fractionation between
713 S^0 and sulfide is confirmed by the few available literature data for both solid/liquid and aqueous 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 H_2S being only slightly enriched in ^{34}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 S^0 had values of $\delta^{34}\text{S}$ and $\delta^{33}\text{S}$ identical to or slightly heavier
718 than those of H_2S (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 S_n^{2-} with $n > 4$ were reported to be
722 ^{34}S -enriched compared to 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 S_3^{2-} fractionation
725 factor compared to H_2S ($\delta^{34}\text{S}_{\text{S}_3^{2-}} - \delta^{34}\text{S}_{\text{H}_2\text{S}}$), has been reported to be about -1.0% at 450°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 S_3^{2-} , S^0 and H_2S 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 S_3^{2-} (and S_2^{2-} and chain-like 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°C and early stages at 450°C in alkaline solution. This particular type of 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 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 S^0 - H_2S isotope equilibrium fractionation value supported so
738 far by the few available experimental and theoretical data. Thus, the anomalously light 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 S^0 produced by irreversible reaction
741 (10) in the lighter, i.e. generally more reactive, isotope ^{32}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 S^0 fraction is likely to originate from S_3^{2-} (and S_2^{2-}) breakdown to S^0 and H_2S upon fluid quench according
746 to reactions (9) and (13). Indeed, if no isotope exchange occurs during these fast reactions, the resulting
747 measured S^0 should carry a $\delta^{34}\text{S}$ value similar to that of the radical ions.

748 Finally, an additional contribution to S^0 might result from direct precipitation of solid/liquid sulfur
749 on cooling via recombination of H_2S and SO_4^{2-} according to the reverse of reaction (12) and/or via 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 ~ 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 ~ 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 ± 1.3 ‰ (m22, pH change upon pyrite precipitation from 4.5 to 3.7) to 1.5 ± 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 ± 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 H₂S
788 and HS⁻ in the fluid before pyrite precipitation, is in reasonable agreement with those predictions. In contrast,
789 for a more acidic (i.e. H₂S-dominated) and S⁰ and S₃⁻-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 H₂S 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 H₂S-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) H₂S-HSO₄⁻ solutions, in which both S⁰ and
798 S₃⁻ are negligible. Their experimental approach used 3-isotope systematics, convincingly demonstrating
799 attainment of isotope equilibrium between pyrite and H₂S, 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 β -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⁻ versus H₂S; Syverson et al., 2015) and, more generally, by
817 inaccuracies in assessing thermodynamic properties of aqueous non-electrolytes, such as H₂S, 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 ± 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 λ_{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 λ_{36} slopes for MDF fractionation among S aqueous species (Fig. 6c, 7c, A4.2c; $1.88 < \lambda_{36} < 1.96$; 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 S_3^{2-} and 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 S_3^{2-} (and 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 S_3^{2-} (and S_2^{2-}), but also from partial recombination of sulfate and
886 sulfide or isotope exchange between polysulfide dianions and H_2S 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 S^0 have isotopic signatures indistinguishable from aqueous H_2S . The $\text{S}_{(s,l)}$ phase may
889 be slightly ^{34}S -enriched (by 2-4 ‰) compared to H_2S thereby reflecting the contribution of SO_4^{2-} or S_n^{2-} in
890 the reaction of $\text{S}_{(s,l)}$ precipitation. In contrast, $\text{S}^0_{\text{thios}}$ is strongly ^{34}S -depleted compared to H_2S (by as much as
891 -12 ‰). As a result, isotope analyses of 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}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 ± 0.1 ‰. Such values fall well within
903 the traditionally accepted general MDF threshold of ± 0.2 ‰ (Farquhar and Wing, 2003) and the known
904 variations of λ_{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 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}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 (C_xH_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}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 S^{2-} to SO_4^{2-} ,
935 including 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°C to at least 800°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}S , provided other
944 factors required for MIE have been met. In addition, an improved analytical resolution on the ^{36}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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965

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1221 sulfate reduction. *Science* **324**, 370-373.
- 1222

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

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1232^a Calculated pH of the fluid at each injection step at indicated *T-P*.^b 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⁺ or OH⁻ activity.^c Quartz-Muscovite-Microcline mineral assemblage.^d The pH and S₃^{•-} concentration values will be slightly refined in the course of this study for experiment m32/1-4 after correction for K₂SO₄ 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 _{tot}	S _{red}	S _{sulfide}	S _{sulfate}	S ⁰ _{hexane}	S ⁰ _{balance} ^a	K	Cl	Fe	K ₂ SO ₄ mol	Pyrite mol	m fluid g
m22: K₂S₂O₃ (0.49 m)-HCl (0.14 m), Quartz-Muscovite-Microcline mineral assemblage															
1	1	350	370	1.01	-	0.31	0.41	-	0.29	1.00	0.13	10 ⁴	-	-	150.00
2	3	350	335	1.09	-	0.31	0.43	-	0.35	1.02	0.13	2x10 ⁻⁵	-	-	142.72
3	7	350	370	0.96	0.34	0.30	0.42	-	0.21	0.92	0.13	2x10 ⁻⁵	-	-	136.87
4	10	350	370	0.98	0.33	0.30	0.40	-	0.26	0.97	0.13	10 ⁻⁵	-	-	130.05
<i>Injection of KCl-BaCl₂-FeCl₂</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
m29: K₂S₂O₃ (0.19 m) - KOH (0.091 m)															
1	7	352	400	0.37	0.18	0.17	0.17	-	<0.02	0.48	0.02	4x10 ⁻⁵	-	-	65.62
2	13	352	405	0.34	0.16	0.14	0.15	-	<0.03	0.48	<0.01	5x10 ⁻⁵	-	-	57.57
<i>Injection of FeCl₂</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
m32: K₂S₂O₃ (0.50 m) - KOH (0.30 m)															
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 ^d	23	453	725	0.75	0.53	-	-	-	-	0.93	-	-	0.014	-	78.02
7 ^d	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 FeCl₂</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
m33: K₂S₂O₃ (0.48 m)															
1	<1	300	570	0.96	0.20	0.28	0.40	0.87 ^b	0.28	0.99	-	-	-	-	83.65
2	2	300	470	0.98	0.30	0.25	0.44	0.60 ^b	0.24	1.02	-	-	-	-	70.28
<i>Injection of K₂S₂O₃</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 ^c	0.56	1.07	-	-	-	-	64.99
<i>Injection of H₂O</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 H₂O</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_{red} includes S species other than sulfate and molecular sulfur, which all react with iodine (sulfide, radical ions, polysulfide ions, sulfite, thiosulfate).

1238 ^a S⁰_{balance} = S_{tot} - (S_{red} + S_{sulfate}); if S_{red} < S_{sulfide} or not available then S_{sulfide} was used instead of S_{red}.

1239 ^b Likely overestimated because of the S⁰ UV signal contamination by organic impurities from the acetate decomposition.

1240 ^c Underestimated because of insufficient time of reaction with hexane.

1241 ^d 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 BaSO₄), sulfide (as ZnS) and molecular sulfur (S⁰, where available) analyzed in
 1244 sampled fluids from the experiments of this study.
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N	Duration, days	$\delta^{34}\text{S}_{\text{sulfide}}$	$\delta^{34}\text{S}_{\text{S}_0}$	$1000 \times \ln \alpha_{\text{S}_0}$	$\delta^{34}\text{S}_{\text{sulfate}}$	$1000 \times \ln \alpha_{\text{S}_{04}}$	$\Delta^{33}\text{S}_{\text{sulfide}}$	$\Delta^{33}\text{S}_{\text{S}_0}$	$\Delta^{33}\text{S}_{\text{sulfate}}$	$\Delta^{36}\text{S}_{\text{sulfide}}$	$\Delta^{36}\text{S}_{\text{S}_0}$	$\Delta^{36}\text{S}_{\text{sulfate}}$
m22: K₂S₂O₃ (0.49 m)-HCl (0.14 m), Quartz-Muscovite-Potassic feldspar mineral buffer												
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 ^a	14.10	0.023	0.052	0.042 ^a	0.71	-0.73	-0.05 ^a
<i>Injection of KCl-BaCl₂-FeCl₂</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 ^e	-
m29: K₂S₂O₃ (0.19 m) - KOH (0.091 m)												
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 FeCl₂</i>												
3	16	-	-	-	6.85	-	-	-	0.029	-	-	0.13
4	19	-	-	-	2.17	-	-	-	0.052	-	-	-0.58
m32: K₂S₂O₃ (0.50 m) - KOH (0.30 m)												
<i>300°C</i>												
0	0	7.18 ^b	-	-	-1.26 ^c	N/A	0.004 ^b	-	0.061 ^c	-0.09 ^b	-	-0.25 ^c
1	3	-3.45	2.00 ^f	5.45 ^f	4.56	8.01	-0.001	-	0.013	-0.44	-	-0.41
2	8	-3.25	-0.50 ^f	2.75 ^f	8.42	11.67	0.001	-	0.051	-0.48	-	-0.40
3	13	-2.40	-4.40 ^f	-2.00 ^f	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 FeCl₂</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
m33: K₂S₂O₃ (0.48 m)												
0	0	5.37 ^b	-	-	5.08 ^{a,c}	-	0.012 ^b	-	0.028 ^{a,c}	0.45 ^b	-	0.45 ^{a,c}
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 ^d	-0.47	-0.07
<i>Injection of K₂S₂O₃</i>												
3	5	-7.51	-4.78 ^e	2.73 ^e	16.61 ^e	24.13 ^a	0.022	0.080 ^e	0.047 ^e	0.28	3.51 ^e	0.24 ^e
4	15	-6.04	-	-	16.46 ^e	22.50	0.025	-	0.026 ^e	0.72 ^d	-	5.01 ^e
<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 ^d	-0.51	0.17
6	26	-6.32	-3.35 ^e	2.97 ^e	12.35	18.67	0.013	0.023 ^e	0.045	-0.25	0.97 ^e	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 ^e	18.82	0.041	-	0.087 ^e	-0.26	-	3.76 ^{d,e}
9	37	-7.23	-2.41 ^e	4.82 ^e	14.29	21.52	0.025	0.011 ^e	0.055	0.28	-0.14 ^e	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.

^a Chemical yield <10%.

^b Ag₂S fraction of the initial K₂S₂O₃ corresponding to the isotope composition of the sulfane group.

^c BaSO₄ fraction of the initial K₂S₂O₃ corresponding to the isotope composition of the sulfonate group.

^d Error (1 SD) >0.5‰.

^e Micro-volume measurement (<30 μg of S).

^f 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_{pyrite} pts	$\delta^{34}\text{S}_{\text{pyrite}}^{\text{a}}$	$\Delta^{33}\text{S}_{\text{pyrite}}$	$\Delta^{36}\text{S}_{\text{pyrite}}$	N_{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 ^d	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

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

1262 ^b $\delta^{34}\text{S}_{\text{sulfide}}$ corresponds to the $\delta^{34}\text{S}$ value of the ZnS fraction in the sampled fluid, calculated as the average of the indicated N_{sulfide} number of samples taken before and after FeCl_2 injection for
 1263 experiments m32 and m22 (3 samples before and 3 after), and before FeCl_2 injection for experiment m29 (2 samples).

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

1265 ^d 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

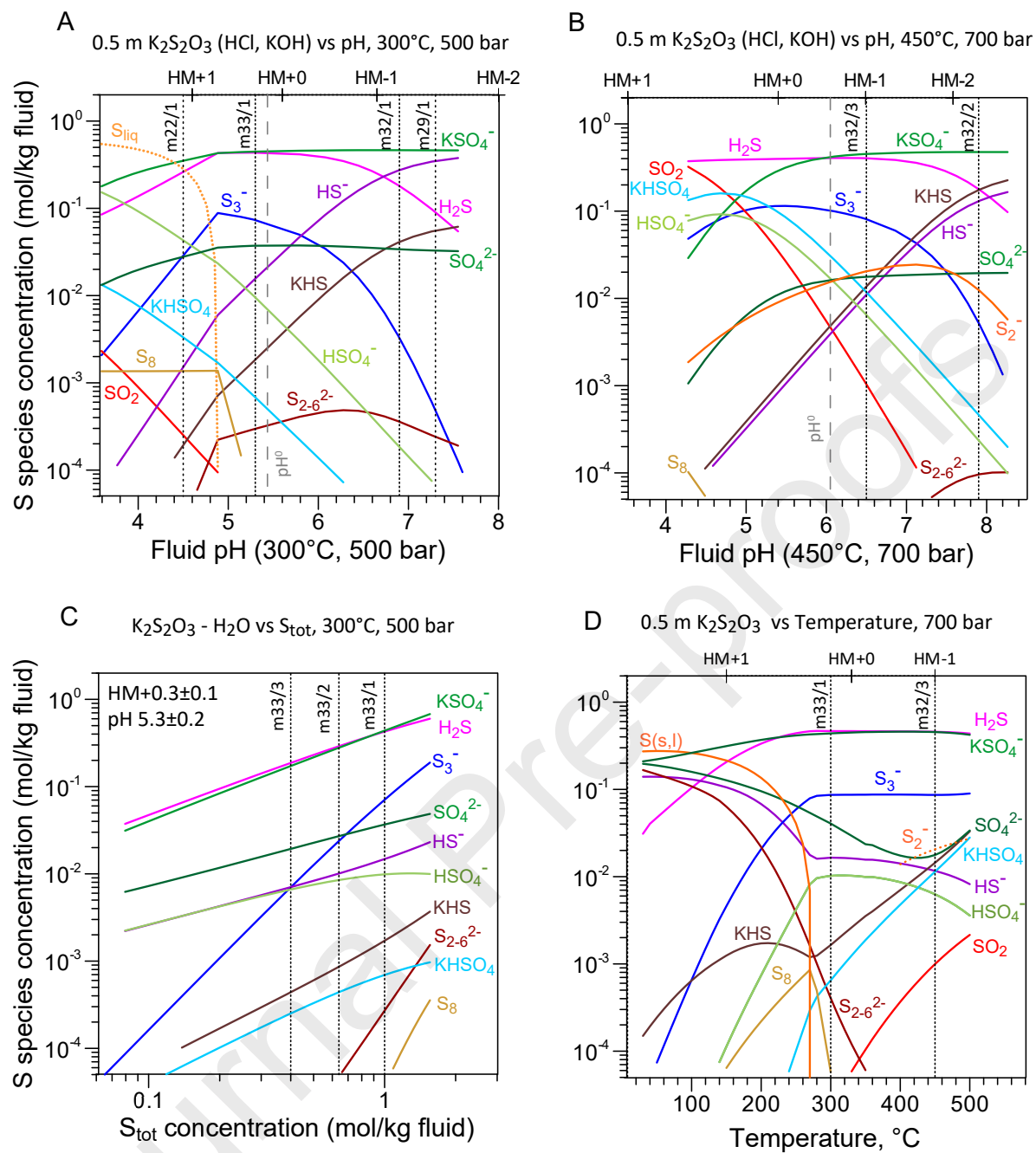
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1270 **Fig. 1.** Sulfur species concentrations in aqueous $K_2S_2O_3$ -bearing fluids representative of this study, predicted
1271 using thermodynamic modeling with available data sources (Table A2.1), at the indicated compositions as a
1272 function 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 (α , 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 (± 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); α_0 , α and α_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 ± 1.0 and 17.5 ± 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 α yields a $\log_{10} k_r$ value (in hour⁻¹) of -2.4 ± 0.2 (pH
1305 6.9, m32) and -1.9 ± 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 λ_{33} (from 0.505 to 0.519) and λ_{36}
1310 (from 1.88 to 1.96) MDF slopes that encompass both equilibrium ab-initio calculated (Otake et al., 2008, for
1311 λ_{33} and λ_{36}) and experimental and natural equilibrium and kinetic (LaFlamme et al., 2018a; references
1312 therein, for λ_{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 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.

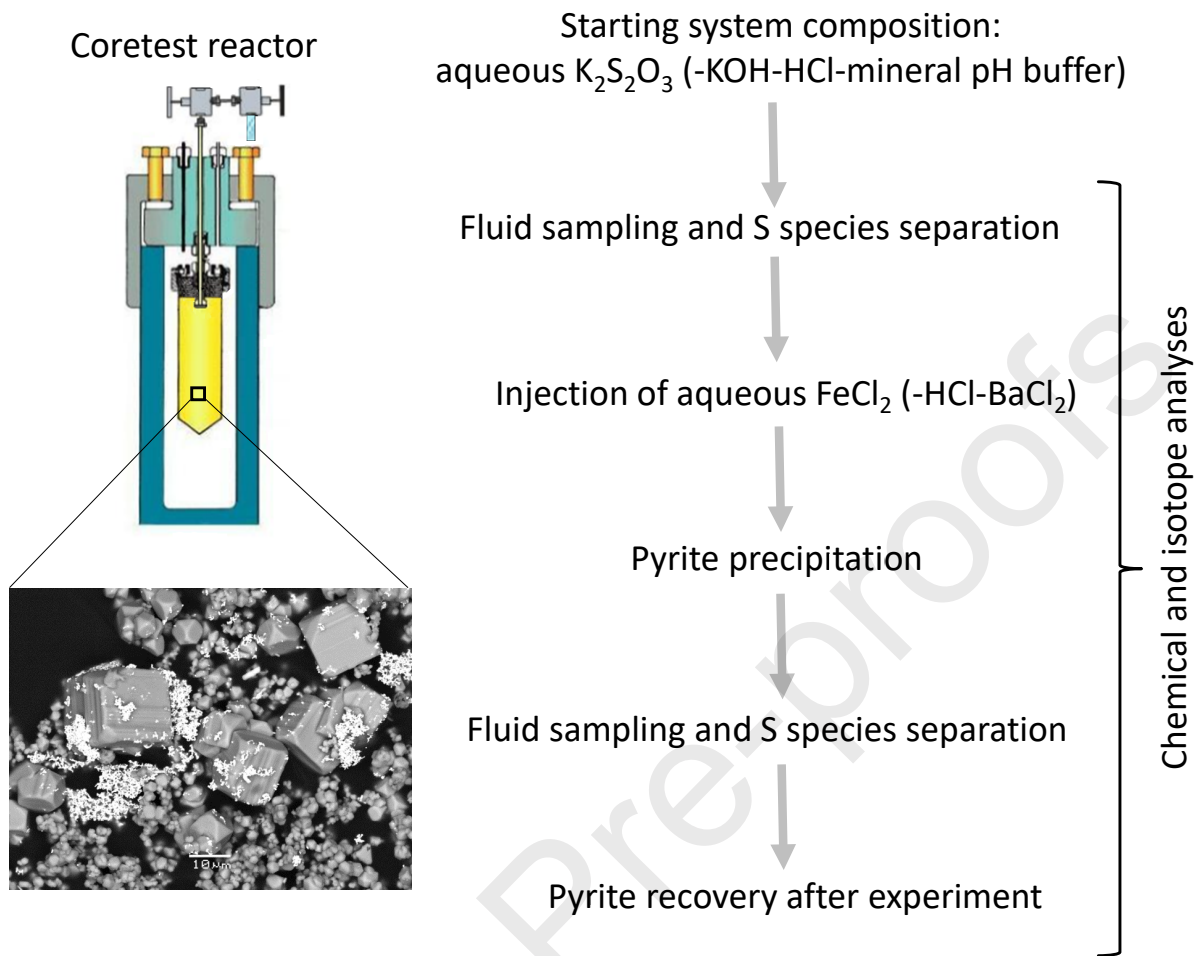
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Fig. 1

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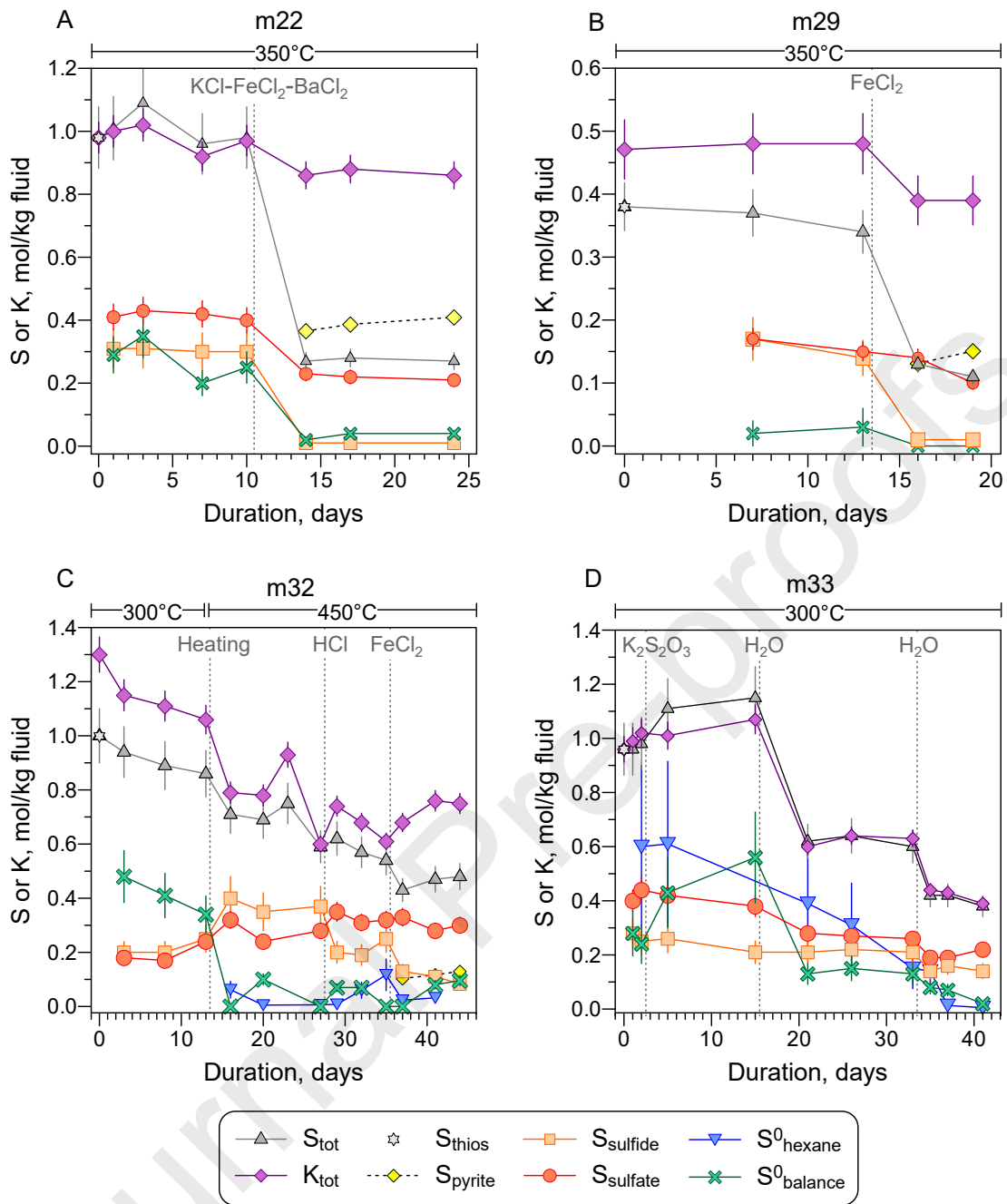
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Fig. 2



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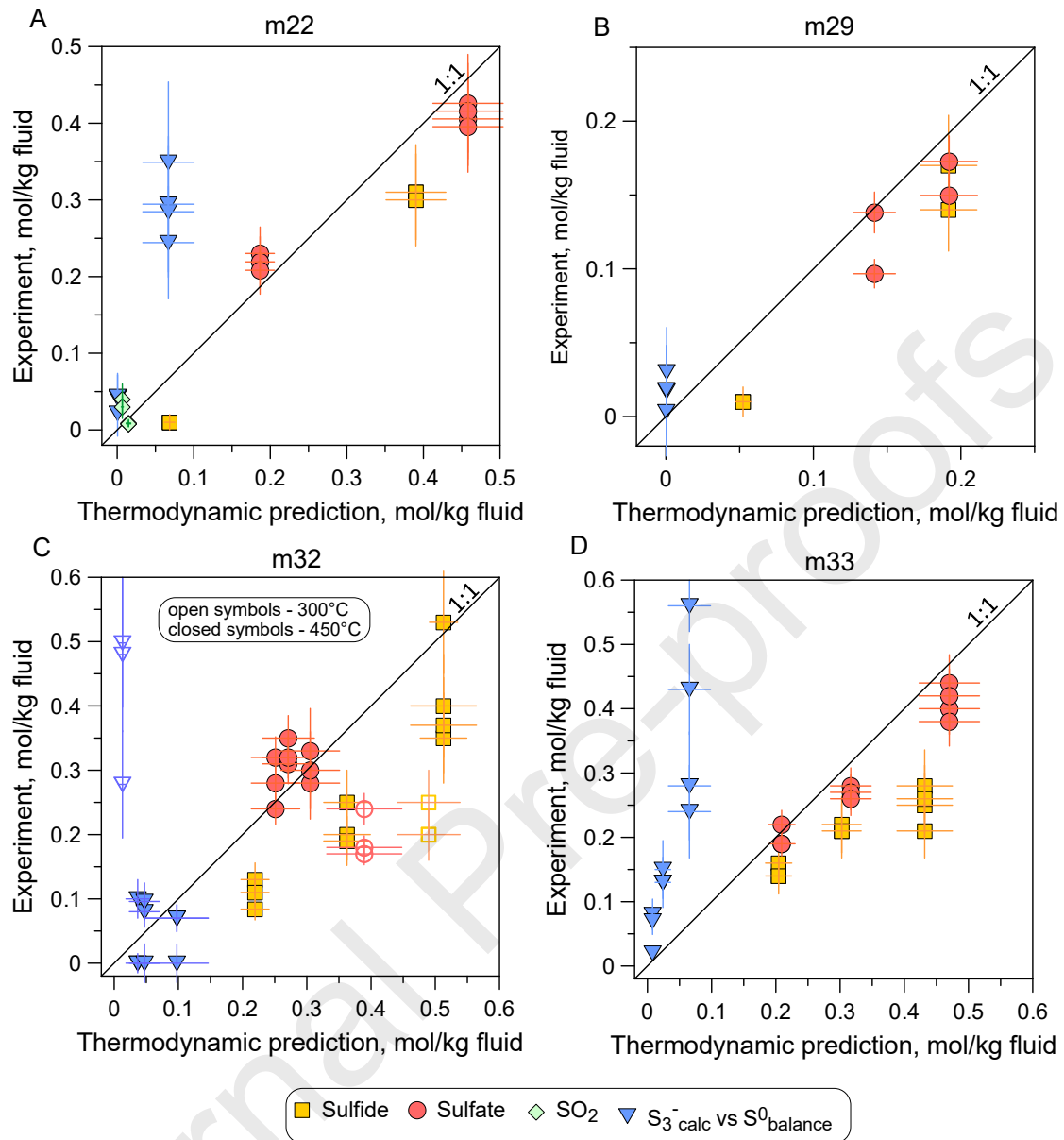
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Fig. 3.

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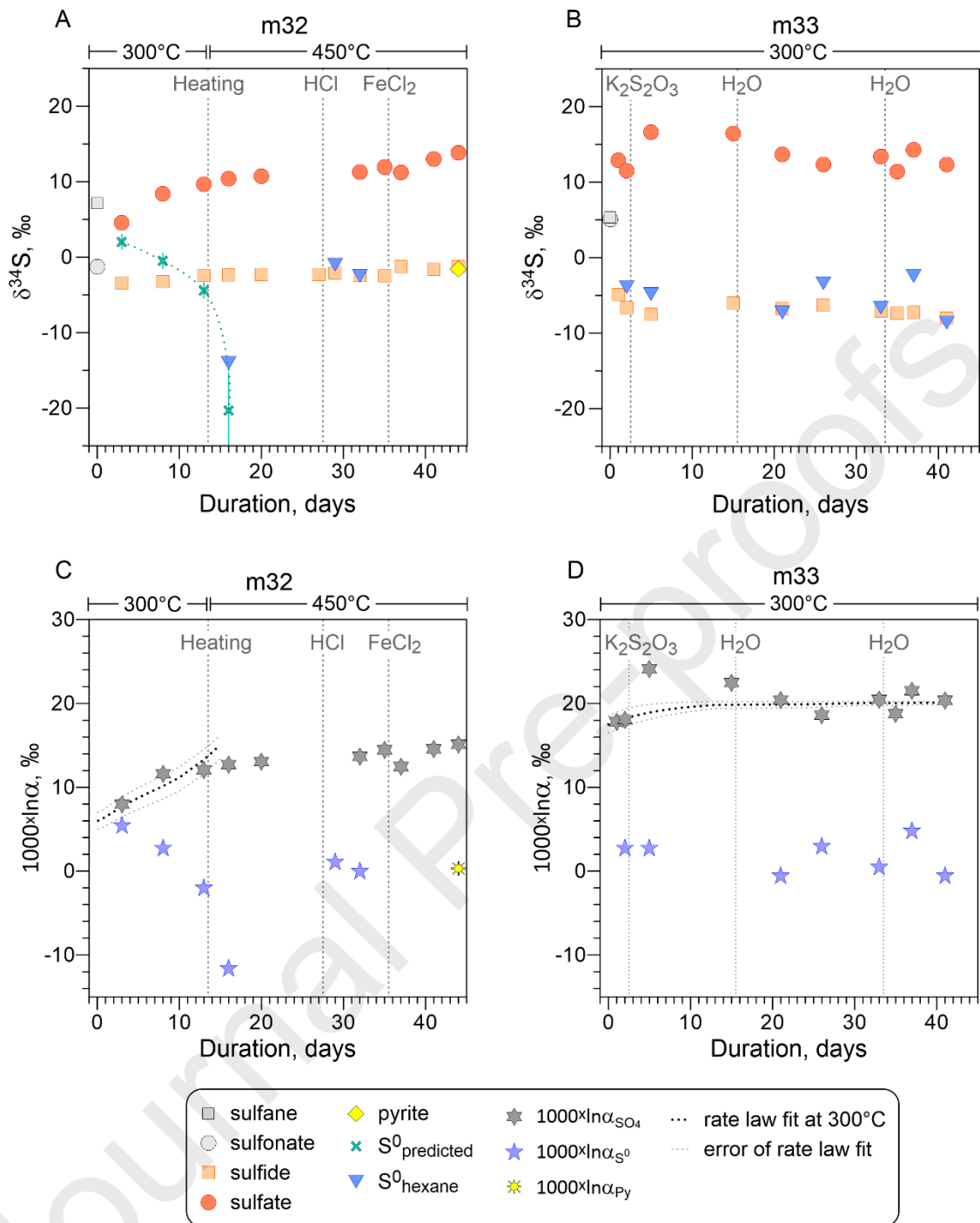
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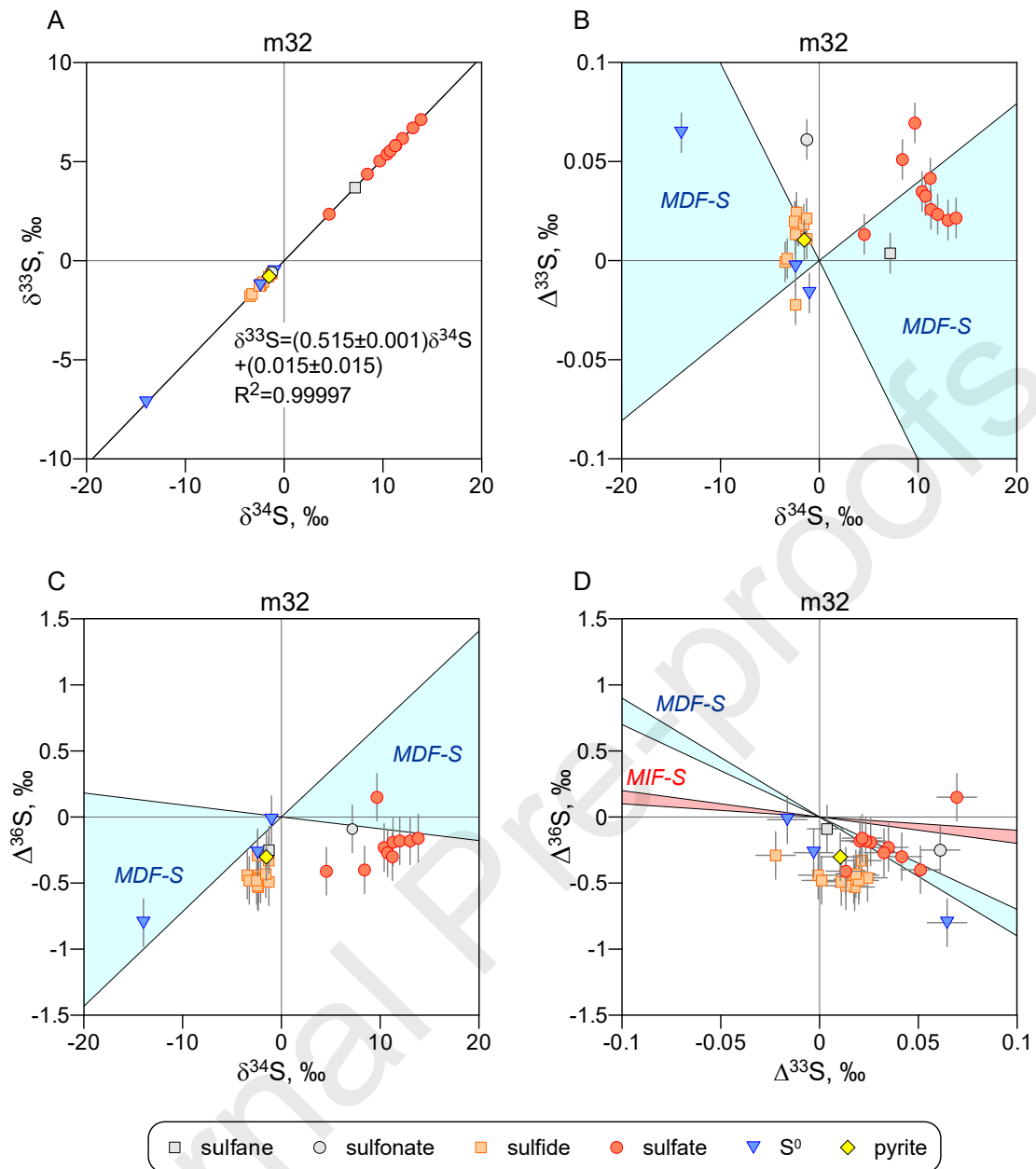
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Fig. 4.



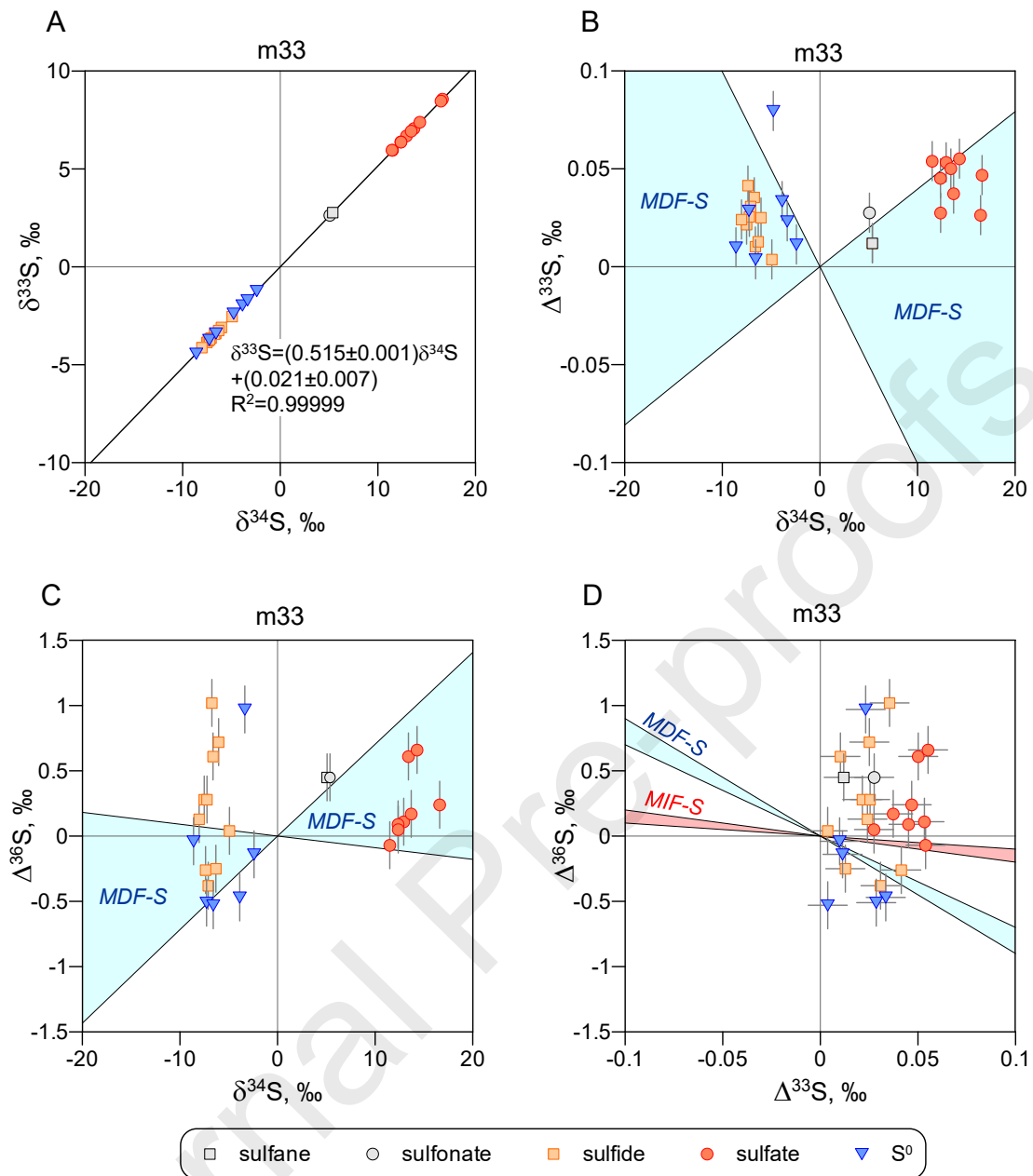
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Fig. 5.



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Fig. 6.



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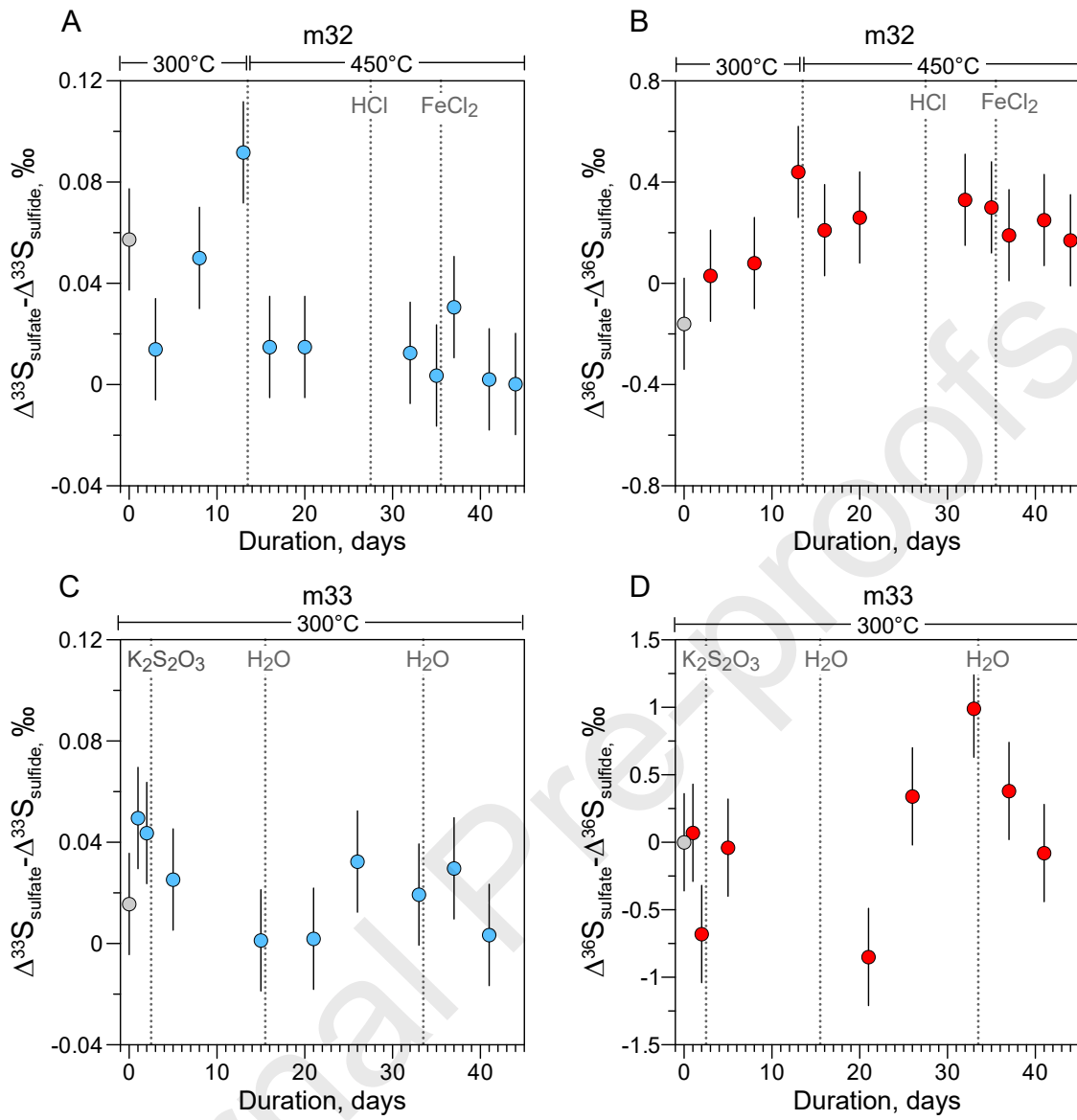
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Fig. 7.

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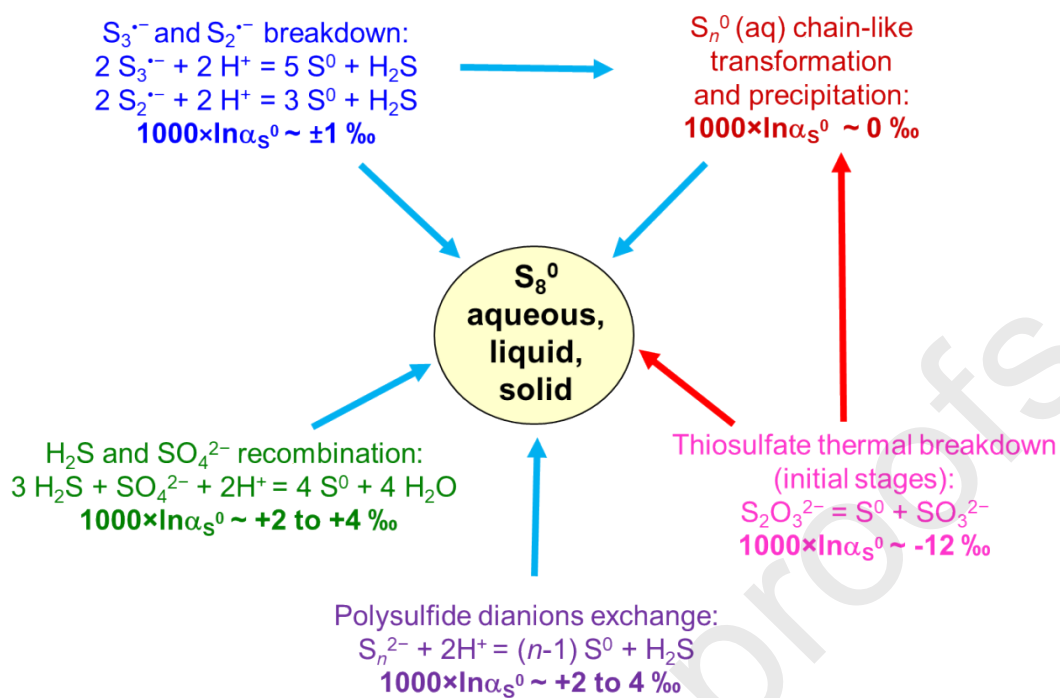
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Fig. 8.

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Fig. 9.