



**HAL**  
open science

## Multiple sulfur isotopes signature of Thermochemical Sulfate Reduction (TSR): Insights from Alpine Triassic evaporites

Guillaume Barré, Émilie Thomassot, Raymond Michels, Pierre Cartigny,  
Pierre Strzeczynski, Laurent Truche

### ► To cite this version:

Guillaume Barré, Émilie Thomassot, Raymond Michels, Pierre Cartigny, Pierre Strzeczynski, et al.. Multiple sulfur isotopes signature of Thermochemical Sulfate Reduction (TSR): Insights from Alpine Triassic evaporites. *Earth and Planetary Science Letters*, 2021, 576, pp.117231. 10.1016/j.epsl.2021.117231 . hal-03396230

**HAL Id: hal-03396230**

**<https://hal.science/hal-03396230v1>**

Submitted on 26 Oct 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# 1 Multiple sulfur isotopes signature of Thermochemical Sulfate

## 2 Reduction (TSR): insights from Alpine Triassic evaporites

3 **Guillaume Barré<sup>1\*</sup>, Émilie Thomassot<sup>2</sup>, Raymond Michels<sup>1</sup>, Pierre Cartigny<sup>3</sup>, Pierre**  
4 **Strzeczynski<sup>4</sup>, Laurent Truche<sup>1,5</sup>**

5 *<sup>1</sup>Université de Lorraine, CNRS, GeoRessources, UMR 7359, BP 70239, F-54506 Vandœuvre-*  
6 *lès-Nancy, France*

7 *<sup>2</sup>Université de Lorraine, CNRS, UMR 7358, CRPG, Vandœuvre-lès-Nancy, France*

8 *<sup>3</sup>Université de Paris, Institut de physique du globe de Paris, CNRS, F-75005 Paris, France*

9 *<sup>4</sup>Laboratoire de Géologie UFR Sciences et Technique, Université du Mans, Avenue O.*  
10 *Messiaen, 72000 Le Mans, France*

11 *<sup>5</sup>Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, IRD, IFSTTAR, ISTERre, 38000*  
12 *Grenoble, France.*

13 *\*e-mail: [guillaume.barre.2@ulaval.ca](mailto:guillaume.barre.2@ulaval.ca)*

14 *\*Present address: Département de géologie et génie géologique, centre E4M, Université Laval,*  
15 *Québec, Canada*

### 16 **Abstract**

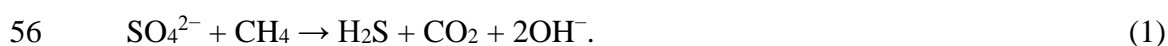
17 The sulfur cycle is driven by redox processes, among which sulfate reduction is of primary  
18 importance. Sulfate is reduced to sulfide either abiotically by Thermochemical Sulfate  
19 Reduction (TSR) or biotically by Microbial Sulfate Reduction (MSR). Although these two  
20 processes occur at different temperature regimes (>100°C and <80°C, respectively), they  
21 generate similar by-products (e.g., sulfides, elemental sulfur). The <sup>34</sup>S/<sup>32</sup>S ratio is often used as  
22 the sole criterion to identify the origin of reduced sulfur compounds, but overlaps prevent  
23 unambiguous conclusions. Contrary to MSR, the multiple sulfur isotopic signatures ( $\delta^{33}\text{S}$ ,  $\delta^{34}\text{S}$ ,  
24  $\delta^{36}\text{S}$ ) of natural TSR remains uncharacterized. Here, we performed multiple sulfur isotopes

25 analyses of sulfates, sulfides, and elemental sulfur from six sites in the Alpine Triassic  
26 evaporites formation to better constrain the isotopic signatures of TSR. Unlike MSR, TSR can  
27 induce slight negative deviations ( $\Delta^{33}\text{S}$  down to  $-0.08\text{‰}$ ) relative to the initial sulfate  $\Delta^{33}\text{S}$   
28 value, which significantly discriminates between these two processes. Isotopic equilibria  
29 between anhydrite and either elemental sulfur or sulfides (pyrite or chalcopyrite) were verified  
30 according to their mass-fractionation exponents ( $^{33/34}\theta = 0.5140$  and  $0.5170$ , respectively).  
31 Using sulfate-elemental sulfur ( $\Delta^{34}\text{S}_{\text{SO}_4^{2-}\text{-s}_8}$ ) or sulfate-sulfide ( $\Delta^{34}\text{S}_{\text{SO}_4^{2-}\text{-s}^{2-}}$ ) fractionation pairs  
32 and respective fractionation factors ( $^{34}\alpha$ ) for samples that fulfilled the criteria of isotopic  
33 equilibrium, we determined the precipitation temperatures of elemental sulfur and sulfides  
34 (pyrite or chalcopyrite) to be  $194 \pm 14$  °C and  $293\text{--}488$  °C, respectively. Interestingly, the  
35 obtained temperature of elemental sulfur precipitation corresponds exactly to the solid-liquid  
36 phase transition of native sulfur. Using  $\Delta^{33}\text{S}$  vs.  $\delta^{34}\text{S}$  and  $\Delta^{33}\text{S}$  vs.  $\Delta^{36}\text{S}$  diagrams, we are able  
37 to fully explain the isotopic signatures of disequilibrium sulfides by the mixing of sulfate with  
38 either elemental or organic sulfur in the aqueous fluid. Mixing curves allow the determination  
39 of the relative proportions of sulfate and organic and elemental sulfur, the latter being formed  
40 by the recombination of polysulfides during cooling. It appears that the sulfides' signatures are  
41 best explained by a 33% contribution of polysulfides (i.e., elemental sulfur signatures),  
42 consistent with the relative proportion of dissolved polysulfides previously measured in fluid  
43 inclusions from this formation at  $>200$  °C. Finally, no sulfur mass independent fractionation  
44 (S-MIF) is observed in this evaporitic formation, consistent with the TSR signature generated  
45 both at equilibrium and by mixing. This implies that TSR does not generate S-MIFs. Our results  
46 thus provide multiple sulfur isotopes signatures of TSR, which may be used to reliably identify  
47 this process in variable geological settings.

48 **Keywords:** Quadrupole sulfur isotopes, TSR, Sulfur cycle, Isotopic equilibrium, Two-  
49 components mixing curves, Alps

## 50 1. INTRODUCTION

51 Sulfate reduction is one of the most important processes controlling the sulfur cycle; it can  
52 occur abiotically (by Thermochemical Sulfate Reduction, TSR), or be driven by biological  
53 activity (Microbial Sulfate Reduction, MSR; Machel, 2001). Although MSR generates lesser  
54 amounts of the reaction products than TSR, the overall mass balance of the reaction is identical  
55 for the two processes and can be approximated as (here, using methane as a reducing agent):



57 Apart from methane, the involvement of other reducing agents (e.g., hydrocarbons,  $\text{Fe}^{2+}$ ,  $\text{H}_2$ )  
58 leads to different MSR and TSR reactions. In detail, the reaction is much more complex because  
59 numerous sulfur species of intermediate valence are involved throughout the transfer of eight  
60 electrons from sulfate to sulfide (Goldstein and Aizenshtat, 1994; Farquhar et al., 2007;  
61 Johnston et al., 2007; Sim et al., 2011; Truche et al., 2014, 2009; Barré et al., 2017). The two  
62 processes can occur sequentially during the diagenetic/tectonic history of a sedimentary basin,  
63 or separately accordingly to geological context. Indeed, MSR generally occurs during the early  
64 stages of diagenesis at  $T < 80^\circ\text{C}$  (see review by Machel, 2001). As temperature increases during  
65 burial, sulfate-reducing bacteria cease to metabolize (Roussel et al., 2015) and TSR takes over  
66 at  $T > 100\text{--}120^\circ\text{C}$  (Machel et al., 1995). The sulfur isotopic compositions ( $\delta^{34}\text{S}$ ) of sulfate and  
67 reduced sulfur compounds (elemental sulfur and sulfides) have been used to distinguish TSR  
68 from MSR because each process induces specific sulfate-sulfide fractionations ( $\Delta^{34}\text{S}_{\text{SO}_4^{2-}\text{-S}^{2-}} =$   
69  $\delta^{34}\text{S}_{\text{SO}_4^{2-}} - \delta^{34}\text{S}_{\text{S}^{2-}}$ ). In the case of MSR, such fractionations range from 15 to 72‰; this large  
70 range results from the heterogeneous isotopic fractionations associated with distinct sulfato-  
71 reducing bacteria that employ different metabolic pathways with various intermediate-valence  
72 sulfur species (Machel et al., 1995; Farquhar et al., 2007; Johnston et al., 2007; Sim et al., 2011;  
73 Labrado et al., 2019).

74 For TSR, the observed isotopic fractionation depends on temperature and it can be kinetically  
75 controlled or occur at isotopic equilibrium (e.g., Ohmoto and Lasaga, 1982). Kinetic isotopic  
76 fractionations are attributed to the initial rupture of the S-O bond in sulfate, resulting in the  
77 relative enrichment of  $^{32}\text{S}$  (depletion of  $^{34}\text{S}$ ) in the reduced product and the depletion of  $^{32}\text{S}$   
78 (enrichment of  $^{34}\text{S}$ ) in the residual sulfate (e.g., Cross, 1999). Experimental studies have shown  
79 that kinetic effects lead to a maximum  $\Delta^{34}\text{S}_{\text{SO}_4^{2-}\text{-S}^{2-}}$  value of 12.4‰ (e.g., Goldstein and  
80 Aizenshtat, 1994; Meshoulam et al., 2016, and references therein). In contrast, at isotopic  
81 equilibrium, theoretical calculations using the fractionation factor between  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{S}_{\text{aq}}$  at  
82 various temperatures (Eldridge et al., 2016) indicate that  $\Delta^{34}\text{S}_{\text{SO}_4^{2-}\text{-S}^{2-}}$  ranges from 11‰ at 500  
83 °C to 43‰ at 100 °C. Because this range overlaps that observed for MSR,  $\Delta^{34}\text{S}_{\text{SO}_4^{2-}\text{-S}^{2-}}$  values  
84 alone cannot indisputably discriminate TSR from MSR, whatever the origin of the fractionation  
85 (abiotic or biotic, equilibrium or kinetic). At present, additional petrographic and geochemical  
86 information is required to reliably identify TSR. Multiple sulfur isotopes analyses ( $\delta^{33}\text{S}$ ,  $\delta^{34}\text{S}$ ,  
87  $\delta^{36}\text{S}$ ) have been successfully used to better understand both the isotopic fractionation and the  
88 reaction pathways involved during the metabolism of sulfate-reducing bacteria (e.g., Farquhar  
89 et al., 2007; Johnston et al., 2007; Zerkle et al., 2009; Sim et al., 2011). However, this technique  
90 has not yet been used to characterize the multiple sulfur isotopes signature of the TSR reaction  
91 pathway, nor to attempt to discriminate it from that of MSR.

92 Here, we used multiple sulfur isotopes analysis ( $\delta^{33}\text{S}$ ,  $\delta^{34}\text{S}$ ,  $\delta^{36}\text{S}$ ) as a promising geochemical  
93 tool to characterize the isotopic signature of TSR. This methodology allows both the robust  
94 determination of isotopic equilibrium and the calculation of mixing curves between different  
95 sulfur reservoirs. Finally, we explore the potential of TSR to generate sulfur mass independent  
96 fractionations (S-MIF) signatures. We focus on the “Nappe des Gypses”, a meta-evaporitic  
97 formation in the western French Alps. Our approach gives access to the temperatures at which

98 reduced phases precipitated and allows us to explain the S isotopic signatures of all the S-rich  
99 minerals observed.

## 100 **2. THE NAPPE DES GYPSES FORMATION**

101 The studied area encompasses seven evaporite outcrops in the western French Alps near  
102 the villages of Modane, Bramans, and Sollières-l'Envers (Arc Valley), the Ambin stream, the  
103 Mont-Cenis Lake, the Roubion stream (near Névache village), and Tignes Lake (Fig. 1). The  
104 Nappe des Gypses outcrops comprise 100–400 m of massive anhydrite deposits interbedded  
105 with dolomitic boudins, micaschists and black shales centimeter to meters in thickness. During  
106 the subduction-collision path of the Alps, the Nappe des Gypses formation acted as a major  
107 decollement that was crucial to the structuring of the Alps. The formation underwent three  
108 metamorphic and deformational events typical of the Alps (namely D1, D2, and D3), which  
109 favored fluid-rock interactions (see Barré et al., 2020, for a complete description of the tectonic  
110 evolution of the Nappe des Gypses). Sulfides (pyrite and minor chalcopyrite) and elemental  
111 sulfur (Fig. 2; Barré et al., 2017) are observed in direct association with anhydrite and  
112 recrystallized carbonates (Barré et al., 2020), corresponding to a typical TSR paragenesis (e.g.,  
113 Machel et al., 1995). In addition, the characteristic intermediate-valence sulfur species required  
114 for TSR to occur,  $S_3^-$  and  $S_n^{2-}$  (polysulfides), have been identified by *in-situ* Raman analyses  
115 of heated fluid inclusions (Barré et al., 2017). Thus, all physico-chemical conditions necessary  
116 for TSR to occur were present in the Nappe des Gypses.

## 117 **3. MATERIALS AND METHODS**

### 118 **3.1 Multiple sulfur isotopes notation**

119 We performed multiple sulfur isotopes analyses by measuring  $\delta^{33}\text{S}$ ,  $\delta^{34}\text{S}$ , and  $\delta^{36}\text{S}$ . All  
120 results are reported in the conventional  $\delta^x\text{S}$  notation with respect to Vienna Cañon Diablo  
121 Troilite (V-CDT) as:

$$122 \quad \delta^x\text{S} = \left( \frac{{}^x\text{R}_{\text{sample}}}{{}^x\text{R}_{\text{reference}}} - 1 \right) \times 1000 \quad (\text{‰}) \quad (2)$$

123 where  $x$  is the mass number of the sulfur isotope (33, 34, or 36) and  $R$  is the isotopic ratio  $^x\text{S}/^{32}\text{S}$ .

124 The sulfur isotope fractionation factor between two compounds A and B (Hulston and Thode,

125 1965; Ono et al., 2006; Farquhar et al., 2007) is defined as:

$$126 \quad {}^x\alpha_{\text{A-B}} = (\delta^x\text{S}_{\text{A}} + 1000) / (\delta^x\text{S}_{\text{B}} + 1000) \quad (3).$$

127 Isotopic fractionation between two minerals, here between the oxidized mineral (sulfate)

128 and its reduced counterparts (sulfide or elemental sulfur), are calculated as:

$$129 \quad \Delta^{34}\text{S}_{\text{S-SO}_4} \approx \delta^{34}\text{S}_{\text{reduced S}} - \delta^{34}\text{S}_{\text{sulfate}} \quad (4)$$

130 Mass fractionation exponents are defined as:

$$131 \quad {}^x\lambda_{\text{A-B}} = \ln({}^x\alpha_{\text{A-B}}) / \ln({}^{34}\alpha_{\text{A-B}}), \quad (5)$$

132 where  $x = 33$  or  $36$ .

133 These were calculated to determine potential sub-percent deviations from the conventional

134 reference equilibrium values of 0.515 and 1.90 for  $^{33}\lambda$  and  $^{36}\lambda$ , respectively (Hulston and

135 Thodes, 1965; Ono et al., 2006; Farquhar et al., 2007; Eldridge et al., 2016). For most species,

136 exponent values approaching 0.515 and 1.90 indicate an equilibrium process, whereas kinetic

137 processes deviate from equilibrium values (Ono et al., 2006). These deviations can vary

138 depending on the species present (Farquhar and Wing, 2003) and temperature (Otake et al.,

139 2008). Note that, at isotopic equilibrium,  $^{33}\lambda_{\text{A-B}}$  and  $^{36}\lambda_{\text{A-B}}$  are conventionally written as  $^{33}\theta_{\text{A-B}}$

140 and  $^{36}\theta_{\text{A-B}}$ , respectively, although the calculation does not differ from that in Eq. (5).

141 We used capital delta values defined as:

$$142 \quad \Delta^{33}\text{S} = \delta^{33}\text{S} - [(\delta^{34}\text{S} / 1000 + 1)^{0.515} - 1] \times 1000 \quad (6)$$

143 and

$$144 \quad \Delta^{36}\text{S} = \delta^{36}\text{S} - [(\delta^{34}\text{S} / 1000 + 1)^{1.90} - 1] \times 1000 \quad (7)$$

145 for a more convenient graphical representation and to facilitate discussion of subtle

146 isotopic variations. Note that  $^{36}\text{S}$  is a minor isotope (abundance 0.02%); consequently, the

147 statistical error related to its measurement is greater than those for  $^{33}\text{S}$  and  $^{34}\text{S}$ .

### 148 3.2 Analytical procedure

149 Multiple sulfur isotopic analyses were performed separately on anhydrite, sulfides (pyrite  
150 or chalcopyrite), and elemental sulfur samples. Between 2 and 1,000 mg of powder of each  
151 mineral phase was collected using a Dremel tool to bore holes 1 or 2 mm in diameter. This  
152 allowed us to precisely target the desired mineral phases within <1 mm, regardless of the host  
153 environment. Sulfur was extracted from each phase by wet chemistry at the Centre de  
154 Recherches Pétrographiques et Géochimiques (CRPG, Vandœuvre-Lès-Nancy, France),  
155 following previously established species-specific protocols: (i) sulfides were extracted using 5  
156 N HCl and a chromium-reduced sulfides (CRS) solution (Canfield et al., 1986); (ii) elemental  
157 sulfur was extracted using 5 N HCl and a CRS solution with added ethanol to optimize  
158 extraction yields (Gröger et al., 2009); and (iii) sulfates were extracted by adding a strongly  
159 reducing hydriodic hypophosphorous acid solution (Kitayama et al., 2017). In all cases, H<sub>2</sub>S  
160 was liberated from the rock powder, converted into Ag<sub>2</sub>S by reaction with an AgNO<sub>3</sub> solution,  
161 and cleaned with milli-Q water and dissolved ammonia. To determine the efficiency and  
162 repeatability of our sulfur extraction procedure, we performed preliminary extractions on pure  
163 phases (pyrite, elemental sulfur, anhydrite), which resulted in systematic conversion yields of  
164 87–100%. Such high yields do not impact the measured isotopic compositions (Kitayama et al.,  
165 2017). We therefore assume that all our extractions from natural samples (i.e., non-pure phases)  
166 resulted in similar extraction yields that did not impact the isotopic compositions. This is  
167 confirmed by the good reproducibility of extractions and associated isotopic compositions for  
168 replicate analyses of a given same sample.

169 High-precision isotopic measurements by gas-source mass spectrometry require that the  
170 sample be analyzed as SF<sub>6</sub> to prevent any isobaric interference classically associated with SO<sub>2</sub>  
171 analyses (i.e., due to multiple O isotopes). The recovered Ag<sub>2</sub>S was fluorinated in nickel  
172 reaction bombs by reaction with excess F<sub>2</sub> overnight at 250 °C to produce SF<sub>6</sub>. After purification



173 using cryogenic traps and gas chromatography, the recovered SF<sub>6</sub> was introduced into a  
174 ThermoFinnigan MAT 253 dual-inlet gas-source mass spectrometer at the Institut de Physique  
175 du Globe de Paris (IPGP, France).

176 Standard deviations on isotopic analyses were estimated as the sum of the internal  
177 (corresponding to standard deviation during sample measurement by mass spectrometry) and  
178 external errors (corresponding to sulfur extraction and purification steps) after the complete  
179 extraction, fluorination, and measurement procedure, and after comparison with International  
180 Atomic Energy Agency (IAEA) Ag<sub>2</sub>S standards S1 and S2. Standard deviations are better than  
181 0.1‰, 0.01‰, and 0.1‰ for δ<sup>34</sup>S, Δ<sup>33</sup>S, and Δ<sup>36</sup>S, respectively.

## 182 **4. RESULTS**

### 183 **4.1 Petrographic analysis**

184 Sulfides (mostly pyrite and scarce texturally syngenetic chalcopyrite) are always observed  
185 in association with micaschist layers, occurring either as isolated grains/grain clusters in  
186 anhydrite facies (Fig. 2A–H–I) or as carbonate-quartz-sulfide veins in micaschists (Fig. 2D).  
187 When micaschists are absent, only elemental sulfur is observed, either well crystallized within  
188 fractures in gray dolomite sedimentary layers (often deformed as boudins; Fig. 2B) or in  
189 anhydrite deformation structures (Fig. 2C–E–F–G). Sulfides are only observed in centimeter-  
190 scale association with elemental sulfur in the presence of micaschist at the Sollières l'Envers  
191 outcrop (Fig. 2E).

### 192 **4.2 S isotopic compositions of sulfate, sulfide, and elemental sulfur**

193 We performed multiple sulfur isotopes analyses on 44 samples, comprising three mineral  
194 types collected across the six sampling sites: sulfates (anhydrite or gypsum), sulfides (pyrite or  
195 chalcopyrite), and elemental sulfur (Table 1). The sulfur isotopic compositions of sulfates and  
196 elemental sulfur are rather homogeneous across all six sites (Fig. 3). Anhydrite is enriched in  
197 <sup>34</sup>S (δ<sup>34</sup>S<sub>anhydrite</sub> = 12.74–18.39‰, mean 15.44 ± 1.53‰, all standard deviations reported as 1σ)

198 compared to elemental sulfur ( $\delta^{34}\text{S}_{\text{S}_8} = -18.82$  to  $-13.17\%$ , mean  $-15.40 \pm 1.91\%$ ), and both  
199 phases have small non-zero  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  values: for anhydrite,  $\Delta^{33}\text{S}_{\text{anhydrite}} = 0.00$ – $0.09\%$   
200 (mean  $0.03 \pm 0.03\%$ ) and  $\Delta^{36}\text{S}_{\text{anhydrite}} = -1.11$  to  $+1.26\%$  (mean  $-0.30 \pm 0.69\%$ ); for elemental  
201 sulfur,  $\Delta^{33}\text{S}_{\text{S}_8} = 0.00$ – $0.06\%$  (mean  $0.02 \pm 0.02\%$ ) and  $\Delta^{36}\text{S}_{\text{S}_8} = -0.95$  to  $+1.06\%$  (mean  $0.42$   
202  $\pm 0.68\%$ ). Sulfides (without distinction between pyrite and chalcopyrite) display more variable  
203 compositions with  $\delta^{34}\text{S}_{\text{sulfide}} = -5.44$  to  $+11.60\%$  (mean  $3.14 \pm 4.01\%$ ) and near-zero values  
204 for both  $\Delta^{33}\text{S}$  ( $0.00 \pm 0.03\%$ ) and  $\Delta^{36}\text{S}$  ( $0.09 \pm 0.54\%$ ). No relationship was observed between  
205 sulfur isotopic composition and petrographic context (i.e., native sulfur in fractures or within  
206 the schistosity of anhydrite; sulfides disseminated in anhydrite or present in carbonate-quartz-  
207 sulfide veins associated with micaschist layers).

## 208 5. DISCUSSION

### 209 5.1 Triassic sulfate signatures

210 The  $\delta^{34}\text{S}$  values of sulfates from the Nappe des Gypses range from  $12.74$  to  $18.39\%$ , similar  
211 to ranges reported in evaporites of the Khuff Formation (Abu Dhabi; Worden et al., 1997) and  
212 in gas fields of Alberta (Yang et al., 2001). In both cases, the isotopic compositions were  
213 interpreted as being inherited from dissolved sulfate during seawater evaporation. The Upper  
214 Triassic age of the Nappe de Gypses evaporites was previously estimated by paleontological  
215 studies (Debelmas et al., 1989) and the mean isotopic composition of sulfates reported here  
216 ( $\delta^{34}\text{S} = 15.44 \pm 1.53\%$ ) is consistent with the sulfate signature of Carnian seawater ( $16.15 \pm$   
217  $1.03\%$ ) recorded in anhydrite and gypsum from Israel and the Italian Alps (Fig. 3; Claypool et  
218 al., 1980; Crockford et al., 2019; and references therein). To our knowledge, the only coupled  
219  $\delta^{34}\text{S}$  and  $\Delta^{33}\text{S}$  values reported for Carnian seawater are for samples of carbonate associated  
220 sulfate (CAS; i.e., traces of seawater sulfate incorporated during carbonate precipitation), with  
221  $\delta^{34}\text{S} = 20.84 \pm 6.18\%$  and  $\Delta^{33}\text{S} = -0.01 \pm 0.03\%$  (Wu et al., 2014). These values agree well

222 with our data ( $\delta^{34}\text{S} = 15.44 \pm 1.53\text{‰}$ ,  $\Delta^{33}\text{S} = 0.03 \pm 0.03\text{‰}$ ) to which we add the first  $\Delta^{36}\text{S}$   
223 values for Carnian seawater:  $-0.30 \pm 0.69\text{‰}$ .

## 224 **5.2 Abiotic formation mechanism of sulfide and elemental sulfur**

225 Previous studies of natural samples indicate that reduced sulfur minerals (subscript 'S'; i.e.,  
226 sulfides or elemental sulfur) produced by TSR record isotopic fractionations of no more than  
227 20‰ relative to their reactant sulfate (i.e.,  $\Delta^{34}\text{S}_{\text{SO}_4\text{-S}} \geq 20\text{‰}$ ; e.g., Machel et al., 1995; Cross,  
228 1999). Meshoulam et al. (2016, and references therein) experimentally determined that a  
229 maximum fractionation of 12.4‰ between sulfates and sulfides ( $\Delta^{34}\text{S}_{\text{SO}_4^{2-}\text{-S}^{2-}}$ ) should be  
230 produced by kinetic effects during TSR alone. To our knowledge, only one study has reported  
231 a  $\Delta^{34}\text{S}_{\text{SO}_4\text{-S}}$  fractionation produced by TSR as high as 35‰ in natural samples (Alonso-Azcárate  
232 et al., 2001); they attributed such a high  $\Delta^{34}\text{S}_{\text{SO}_4\text{-S}}$  value to limited organic matter availability  
233 and high rates of isotopic equilibration. Higher  $\Delta^{34}\text{S}_{\text{SO}_4\text{-S}}$  values (up to 75‰) cannot be  
234 explained by abiotic geological processes because of the low inferred temperature and would  
235 thus generally result from MSR (e.g., Machel et al., 1995; Labrado et al., 2019).

236 Our results indicate that  $\Delta^{34}\text{S}_{\text{SO}_4^{2-}\text{-S}^{2-}}$  values between anhydrite and associated sulfides range  
237 from 4.2 to 20.4‰, consistent with TSR. In contrast,  $\Delta^{34}\text{S}_{\text{SO}_4^{2-}\text{-S}_8}$  values between anhydrite and  
238 associated elemental sulfur range from 28.1 to 33.3‰; a fractionation of such magnitude is  
239 more ambiguous and could potentially record a biological input via MSR. Indeed, the presence  
240 of elemental sulfur in salt dome caprocks and other evaporite settings is commonly explained  
241 by the late oxidation of  $\text{H}_2\text{S}$ , which is generated either microbiologically (see review by  
242 Labrado et al., 2019) or abiotically (e.g., Machel et al., 1995). The  $\delta^{33}\text{S}$  value of elemental sulfur  
243 can be used to differentiate between the two pathways. Indeed, equilibrium should lead to  $\Delta^{33}\text{S}$   
244 values near zero, whereas previous studies have reported systematic excesses of  $^{33}\text{S}$  in reduced  
245 MSR by-products, with  $\Delta^{33}\text{S}$  values up to  $0.2 \pm 0.05\text{‰}$  (and associated  $\Delta^{34}\text{S}_{\text{SO}_4\text{-S}}$  values of 10–

246 75‰) relative to the initial sulfates (e.g., Farquhar et al., 2007; Zerkle et al., 2009; Johnston,  
247 2011; Sim et al., 2011). In the present study, the  $\Delta^{33}\text{S}$  values of elemental sulfur from all studies  
248 sites are 0.00–0.06‰, comparable to those of sulfates (0.00–0.09‰; Table 1, Fig. 4). Such  
249 similar values are not consistent with the production of elemental sulfur by a bacterial-mediated  
250 reaction mechanism; if that were the case, one would expect the  $\Delta^{33}\text{S}$  values of elemental sulfur  
251 to be 0.05–0.2‰ greater than those of sulfates. Hence, our data are generally consistent with an  
252 equilibrium TSR process. Sulfides show  $\Delta^{33}\text{S}$  values between –0.06 and +0.06‰ (Table 1, Fig.  
253 4), slightly lower than those of sulfates. Moreover, the metamorphic path of the Nappe des  
254 Gypses formation was characterized by high temperatures of 137–431 °C throughout its history  
255 (Barré et al., 2020), and the occurrence of elemental sulfur in fractures and deformed anhydrite  
256 bedding (Fig. 2B, C, E) implies that it formed during the tectonic evolution of the Nappe des  
257 Gypses. Thus,  $\text{H}_2\text{S}$  cannot have been generated later by oxidation at the surface, again  
258 inconsistent with bacterial activity. This confirms that multiple sulfur isotopes can easily  
259 distinguish TSR from MSR, especially based on the  $\Delta^{33}\text{S}$  signatures of the reduced by-products:  
260 TSR results in  $\Delta^{33}\text{S}$  values equal or below those of the initial sulfate, whereas MSR leads to  
261 higher values.

### 262 **5.3 No S-MIF generated during TSR**

263 Multiple sulfur isotopes analyses are generally used to track photochemical reactions  
264 producing sulfur mass independent fractionations (S-MIFs; e.g., Farquhar et al., 2000;  
265 Johnston, 2011; Thomassot et al., 2015). Compared with common mass-dependent  
266 fractionations that produce zero to near-zero  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  values, S-MIFs correspond to  
267 anomalous  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  values that greatly depart from zero. Two studies have reported TSR  
268 experiments using concentrated amino acids as a reducing agent to produce significant S-MIFs.  
269 Watanabe et al. (2009) showed  $\Delta^{33}\text{S}$  fractionations up to +2.1‰ with associated  $\Delta^{36}\text{S}$  values  
270 between –1.1 and +1.1‰ in the amino acid residue; they attributed these fractionations to the

271 adsorption of S species on solid mineral surfaces and to a magnetic isotopic effect. Oduro et al.  
272 (2011) also attributed the large  $\Delta^{33}\text{S}$  fractionation (up to +13.1‰) observed in the residue of  
273 their experiments to an ion-radical pair mechanism that would generate a magnetic isotopic  
274 effect on odd isotopes (i.e.,  $^{33}\text{S}$ ), producing anomalous  $\Delta^{33}\text{S}$  values whereas  $\Delta^{36}\text{S}$  remains mass-  
275 dependent. They also concluded that TSR is not directly responsible for such fractionations  
276 because, so far, no study on natural samples has revealed a S-MIF specifically of odd isotopes.

277 Several studies have also speculated that the involvement of the radical ion  $\text{S}_3^-$  in the TSR  
278 process may contribute to anomalous sulfur isotopic compositions (Truche et al., 2014;  
279 Pokrovski and Dubessy, 2015; Barré et al., 2017) due to its interesting symmetry properties that  
280 are comparable to those of ozone which induces mass-independent oxygen isotopic  
281 fractionations (Michalski and Bhattacharya, 2009). However, recent experiments producing  
282 radical sulfur ions did not show any significant anomalies under the investigated conditions  
283 (Kokh et al., 2020), although their experiments did not directly correspond to TSR because their  
284 experimental setup did not involve a reducing agent. These experimental studies demonstrate  
285 that the different mechanisms associated with TSR process may or may not generate S-MIFs.  
286 Nonetheless, none of these experiments are representative of natural TSR conditions. It is  
287 therefore essential to identify the signature of TSR under natural conditions.

288 Only one study has documented S-MIF in natural sulfide samples for which TSR is  
289 suspected, showing  $\Delta^{33}\text{S}$  values up to +1.25‰ in Paleoproterozoic shales (Young et al., 2013).  
290 However, Hu et al. (2020) showed that the reduction of sulfates with initial non-zero  $\Delta^{33}\text{S}$   
291 values will produce sulfides along a classical mass-dependent line, which will thus preserve the  
292 initial anomalous signature of the sulfates. Thus, the S-MIF observed by Young et al. (2013) in  
293 Paleoproterozoic black shales may result from the reduction of sulfates or the leaching of  
294 Archean sulfides that already exhibited non-zero  $\Delta^{33}\text{S}$  values. Therefore, without direct

295 evidence of the occurrence of TSR in those rocks, it is impossible to prove that the observed S-  
296 MIF truly results from TSR.

297 In our study of the Nappe des Gypses formation, despite the clear occurrence of TSR and the  
298 presence of dissolved  $S_3^-$  as well as polysulfides ( $S_n^{2-}$ ) in fluid inclusions heated above 200 °C  
299 (Barré et al., 2017), we do not observe any significant S-MIF:  $\Delta^{33}S_{\text{anhydrite}} = 0.03 \pm 0.03\text{‰}$ ,  
300  $\Delta^{33}S_{\text{sulfide}} = 0.00 \pm 0.03\text{‰}$ , and  $\Delta^{33}S_{S_8} = 0.02 \pm 0.02\text{‰}$ , and  $\Delta^{36}S_{\text{anhydrite}} = -0.30 \pm 0.69\text{‰}$ ,  
301  $\Delta^{36}S_{\text{sulfide}} = 0.09 \pm 0.54\text{‰}$ , and  $\Delta^{36}S_{S_8} = 0.42 \pm 0.68\text{‰}$  (Table 2). In conclusion, our results do  
302 not evidence any TSR-driven mass-independent fractionation.

#### 303 **5.4 Equilibrium vs. disequilibrium as reflected by isotopic composition**

304 The use of isotopic geothermometers based on the fractionation factor between two  
305 syngenetic chemical species requires that they be in isotopic equilibrium. In most cases, this  
306 requirement is inferred based on petrographic observations. When two mineral species appear  
307 to be syngenetic, it is considered that they are at isotopic equilibrium. Jamieson et al. (2006)  
308 used multiple sulfur isotopes analyses to investigate the isotopic equilibrium between sulfide  
309 pairs (i.e., two sulfide species considered to be syngenetic) based on their respective  $\delta^{34}S$  and  
310  $\Delta^{33}S$  values. They showed that, given geological context and depending on the phases involved,  
311 two minerals with different  $\delta^{34}S$  values but similar  $\Delta^{33}S$  values are considered to be at isotopic  
312 equilibrium. By following a similar approach in our case study, it is possible to demonstrate if  
313 the reduced sulfur minerals and sulfates are truly at isotopic equilibrium.

314 Here, we used  $^{34}S/^{32}S$  fractionation factors at relevant temperatures between aqueous sulfates  
315 and aqueous  $H_2S$  from Eldridge et al. (2016) and between aqueous sulfates and aqueous  
316 elemental sulfur ( $S_8$ ) from Eldridge et al. (2021) to determine the equilibrium temperatures of  
317 the different reduced sulfur compounds (Table 2). Using this method, the apparent precipitation  
318 temperatures of some sulfides are higher (up to 980 °C; Table 2) than the metamorphic peak  
319 temperature of the Nappe des Gypses formation ( $431 \pm 28$  °C; Barré et al., 2020) despite

320 petrographic criteria indicating the phases to be syngenetic (Fig. 2). This implies that  
321 petrographic observations are not always a robust diagnostic tool for evaluating isotopic  
322 equilibrium.

323 Fortunately, the relationships between the  $^{33/32}\text{S}$ ,  $^{34/32}\text{S}$  and  $^{36/32}\text{S}$  fractionations (i.e., the mass  
324 fractionation exponents  $\lambda$ ) can be used as an independent test of whether two species are in  
325 isotopic equilibrium. We determined the mass-fractionation exponents  $^{33}\lambda$  and  $^{36}\lambda$   
326 (corresponding to the slopes of mass-dependent signatures in the  $\delta^{33}\text{S}$  vs.  $\delta^{34}\text{S}$  and  $\delta^{36}\text{S}$  vs.  $\delta^{34}\text{S}$   
327 diagrams, respectively) between sulfates and the associated reduced forms (elemental sulfur or  
328 sulfides) observed at each studied site (Table 2). We then further compared these mass-  
329 fractionation exponents, associated with their previously determined equilibrium temperatures,  
330 to those derived from theoretical calculations (Otake et al., 2008; Eldridge et al., 2016; Eldridge  
331 et al., 2021). Considering the different sulfur species observed ( $\text{H}_2\text{S}_{\text{aq}}$ ,  $\text{SO}_3^{2-}$ ,  $\text{S}_8$ ,  $\text{S}_3^-$ ,  $\text{S}_n^{2-}$  and  
332  $\text{CS}_{2\text{aq}}$ ), theoretical calculations give  $^{33}\theta$  values (i.e.,  $^{33}\lambda$  at isotopic equilibrium) between 0.5143  
333 and 0.5158 and  $^{36}\theta$  values (i.e.,  $^{36}\lambda$  at isotopic equilibrium) between 1.8783 and 1.9223 for  
334 temperatures of 25–1000 °C (Fig. 5). We note that, when plotting  $\delta^{33}\text{S}$  vs.  $\delta^{34}\text{S}$  and  $\delta^{36}\text{S}$  vs.  
335  $\delta^{34}\text{S}$ , larger  $\Delta^{34}\text{S}$  values (i.e., lower temperatures), provide more precise values of  $^{33}\lambda$  and  $^{36}\lambda$ ;  
336 this is why the errors on  $\lambda$  values are larger at higher temperatures than at lower temperatures.  
337 For that reason,  $\lambda$  values associated with high uncertainties cannot be used to demonstrate or  
338 infer isotopic equilibrium. This implies that the determination of the mass fractionation  
339 exponents mainly depends on the analytical precision and associated error on  $\delta^{33}\text{S}$ ,  $\delta^{34}\text{S}$  and  
340  $\delta^{36}\text{S}$ . Here, we use only the  $^{33}\lambda$  values to determine if a mineral pair is consistent with isotopic  
341 equilibrium because the precision on  $^{36}\text{S}$  measurements is lower than that for  $^{33}\text{S}$ ; the  $^{36}\lambda$  values  
342 presented in Table 2 are included only to broaden the published dataset. We consider a mineral  
343 pair to be at isotopic equilibrium only if the associated  $^{33}\lambda$  value is between 0.5140 and 0.5170;  
344 only in that case do we consider the associated equilibrium temperature (Fig. 5).

345 *Elemental sulfur at isotopic equilibrium.* The mass-fractionation exponents between sulfates  
346 and elemental sulfur ( $^{33}\lambda_{\text{SO}_4\text{-S}_8}$ ) at all analyzed sites are between 0.51467 and 0.51632 (Table 2,  
347 Fig. 5), implying that sulfates and all elemental sulfur samples are consistent with isotopic  
348 equilibrium. Their corresponding equilibrium temperatures are in the range 172–217 °C (Table  
349 2, Fig. 5). These temperatures correspond to the liquid-solid phase transition of elemental sulfur  
350 at the lowest P-T conditions recorded by the Nappe des Gypses formation (Fig. 6; Barré et al.,  
351 2020). This result implies with a unique P-T condition at which all elemental sulfur throughout  
352 the formation precipitated at the same time, which accounts for the similar isotopic signatures  
353 of all the analyzed samples. Interestingly, fluid inclusions from this evaporitic formation  
354 contain tiny crystals of elemental sulfur, in addition to sulfates and sulfides that are dissolved  
355 in the brines at room temperature. This elemental sulfur disproportionates when heating the  
356 fluid inclusions to >200 °C and significant concentrations (milli-molar range) of polysulfides  
357 (including the  $\text{S}_3^-$  radical ion) were measured by *in-situ* Raman spectroscopy (Barré et al.,  
358 2017). This indicates that elemental sulfur precipitates directly from the recombination of  
359 dissolved polysulfides (Steudel and Chivers, 2019) involved in TSR (Barré et al., 2017).  
360 Consequently, the elemental sulfur, as collected herein from the Nappe des Gypses formation,  
361 records the TSR-driven isotopic signatures of the polysulfides from which it formed.

362 *Sulfides at isotopic equilibrium.* Based on the mass-fractionation exponents calculated  
363 between sulfates and sulfides ( $^{33}\lambda_{\text{SO}_4\text{-H}_2\text{S}}$ ), only three of eleven samples are consistent with  
364 equilibrium isotopic exchange reactions: two pyrites from the Sollières and Ambin outcrops  
365 and one chalcopyrite from the Mont-Cenis Lake outcrop (Fig. 4C–E). Their equilibrium  
366 temperatures are  $293 \pm 20$  °C,  $344 \pm 20$  °C, and  $488 \pm 55$  °C, respectively (Table 2, Fig. 5),  
367 consistent with the kinetics of the isotopic equilibrium between  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{S}$ , which is  
368 attained within a few days at >350 °C (Ohmoto and Lasaga, 1982). These temperatures match  
369 well with the D2-D3 transition phase ( $259 \pm 24$  °C), the D1-D2 transition ( $350 \pm 20$  °C), and



370 the peak metamorphic temperature ( $431 \pm 28$  °C) of the Nappe des Gypses formation,  
371 respectively (Barré et al., 2020). This result suggests that TSR occurred at least from the  
372 metamorphic peak to the D2-D3 transition phase during the exhumation of the host formation.

373 All other samples present  $^{33}\lambda_{\text{SO}_4\text{-H}_2\text{S}}$  values between 0.517 and 0.523, i.e., significantly  
374 deviating from the estimated isotopic equilibrium range (Fig. 5). They cannot be at isotopic  
375 equilibrium, and therefore their derived “equilibrium temperatures” are not considered further.  
376 This means that another process was involved in their precipitation, as discussed in the  
377 following subsection.

### 378 **5.5 Evidence of mixing between sulfates and elemental sulfur**

379 In this subsection, we focus on the eight sulfide samples with  $^{33}\lambda_{\text{SO}_4\text{-H}_2\text{S}}$  values of 0.517–  
380 0.523 that deviate significantly from the theoretical equilibrium value of 0.515 (Table 2, Fig.  
381 5). Such deviations could reflect kinetically controlled S fractionation during sulfide  
382 precipitation. However, kinetic mechanisms generally involve percent-level deviations towards  
383 values below that of isotopic equilibrium (Ono et al., 2006); for oxygen isotopes, for example,  
384 the  $\lambda$  value can be lowered from the equilibrium value by 0.027 in an abiotic reaction (Clayton  
385 and Mayeda, 2009). Here, the  $^{33}\lambda$  values deviate from the previously determined isotopic  
386 equilibrium range (0.5148–0.5163) by +0.0021 to +0.0080. Because these values are higher  
387 than those at equilibrium, it is unlikely that they result from simple, unidirectional mechanisms.  
388 Alternatively, mixing between two reservoirs might explain such observations. To test this  
389 hypothesis, we performed two-component mixing calculations on  $\delta^{34}\text{S}$ ,  $\Delta^{33}\text{S}$ , and  $\Delta^{36}\text{S}$ . In our  
390 calculation, mixing between two pools occurs in the aqueous phase and the resulting isotopic  
391 composition derives from the proportion of each species in the fluid. Because TSR occurs in  
392 solution, mixing is possible between any two of the various sulfur species involved in the  
393 reaction (i.e., sulfates, sulfides, elemental sulfur, polysulfides, organic sulfur species, and other

394 minor intermediate-valence species; Goldstein and Aizenshtat, 1994; Meshoulam et al., 2016;  
395 Barré et al., 2017).

396 The sulfur reservoirs considered here are (1) dissolved Triassic sulfates, (2) elemental sulfur  
397 (corresponding to polysulfides dissolved in the hot fluid formed at isotopic equilibrium; see  
398 section 5.4), and (3) dissolved organic sulfur. Regarding the latter, evaporites of Upper Triassic  
399 (Carnian) age are known to present sedimentation conditions with high potential for sulfur-rich  
400 kerogen deposition (Cota and Baric, 1998). During the burial and exhumation history of the  
401 formation, these sulfur-rich kerogens can experience thermal cracking, releasing organic sulfur  
402 species into the fluid. Here, stromatolitic dolomites and black shales are observed in the Nappe  
403 des Gypses formation (Barré et al., 2020), which are good candidates for sedimentary facies  
404 containing S-rich kerogen. However, the kerogen in these rocks is too thermally mature to  
405 expect any preservation of organic sulfur, precluding the direct determination of its isotopic  
406 composition. Therefore, we used a theoretical organic S reservoir with a  $\delta^{34}\text{S}$  signature of  
407  $-30\%$ , consistent with values reported for the organic sources of  $\text{H}_2\text{S}$  in several sour gas fields  
408 (Werne et al., 2004, and references therein). We note that, because anhydrite is present in large  
409 excess compared to the other sulfur species, we consider sulfates as an infinite reservoir. The  
410 sulfate isotopic signature therefore remains constant throughout our calculation of the  
411 geological history of the Nappe des Gypses.

412 Mixing curves between sulfates and elemental sulfur (or organic sulfur) are calculated as:

$$413 \left( \frac{\delta^x S_{\text{mix}}}{1000} + 1 \right) = \left( \frac{\delta^x S_{\text{S}_8}}{1000} + 1 \right) \times \chi_{\text{S}_8} + \left( \frac{\delta^x S_{\text{SO}_4}}{1000} + 1 \right) \times \chi_{\text{SO}_4} \quad (8)$$

414 where  $x = 33, 34, \text{ or } 36$ ,  $\chi_{\text{S}_8}$  and  $\chi_{\text{SO}_4}$  are the proportions (between 0 and 1) of elemental sulfur  
415 ( $\text{S}_8$ ; or organic sulfur) and sulfate ( $\text{SO}_4$ ), respectively, and  $\delta^x S_{\text{mix}}$  is the isotopic value obtained  
416 by mixing of the measured sulfate and elemental sulfur compositions. The associated  $\Delta^{33}\text{S}$  and  
417  $\Delta^{36}\text{S}$  values are then deduced from  $\delta^x S_{\text{mix}}$  using Eqs. (6) and (7). We note that in the  $\Delta^{33}\text{S}$  vs.  
418  $\delta^{34}\text{S}$  and  $\Delta^{36}\text{S}$  vs.  $\Delta^{33}\text{S}$  diagrams (Figs. 4 and 7, respectively), a mixture between two reservoirs

419 corresponds to a curve, instead of a line as in a  $\delta$  vs.  $\delta$  diagram. For mixing to be a viable  
420 hypothesis, both the  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  values of the sulfides must be satisfactorily explained.

421 *Mixing between sulfate and elemental sulfur.* In this study, sulfides have  $\Delta^{33}\text{S}$  values that are  
422 equal or lower than those of associated sulfate and elemental sulfur, and  $\delta^{34}\text{S}$  values between  
423 +11.60 and -0.30‰. The obtained mixing curves are illustrated in the  $\Delta^{33}\text{S}$  vs.  $\delta^{34}\text{S}$  and  $\Delta^{33}\text{S}$   
424 vs.  $\Delta^{36}\text{S}$  diagrams (Figs. 4 and 7, respectively), showing that most of the sulfides (five of eight  
425 samples) are consistent with mixing between sulfate and elemental sulfur (representing  
426 dissolved polysulfides) to produce  $\text{H}_2\text{S}$ , the latter two species being generated during TSR. The  
427 mixing curves allow us to determine the relative proportions of each isotopic reservoir recorded  
428 by a single sulfide. Here, the proportion of elemental sulfur (i.e., dissolved polysulfides at  
429 higher temperature) ranges between 18 and 50% (mean  $33 \pm 10\%$ ), in good agreement with the  
430 proportion of dissolved polysulfides measured in fluid inclusions from the Nappe des Gypses  
431 formation, which can represent up to 25% of the total dissolved sulfur concentration in the fluid  
432 at 300 °C (Barré et al., 2017), and probably more at higher temperature (Pokrovski and  
433 Dubessy, 2015). Given a mixture of 33% elemental sulfur ( $\delta^{34}\text{S} = -15.40 \pm 1.91\text{‰}$ ,  $\Delta^{33}\text{S} =$   
434  $0.016 \pm 0.018\text{‰}$ ,  $\Delta^{36}\text{S} = 0.421 \pm 0.680\text{‰}$ ) with 67% sulfate ( $\delta^{34}\text{S} = 15.44 \pm 1.53\text{‰}$ ,  $\Delta^{33}\text{S} =$   
435  $0.033 \pm 0.027\text{‰}$ ,  $\Delta^{36}\text{S} = -0.297 \pm 0.690\text{‰}$ ), our calculation predicts the resulting sulfide  
436 isotopic composition to be  $\delta^{34}\text{S} = -2.33 \pm 2.35\text{‰}$ ,  $\Delta^{33}\text{S} = -0.0030 \pm 0.0011\text{‰}$ , and  $\Delta^{36}\text{S} =$   
437  $0.1826 \pm 0.0685\text{‰}$ . These values are very similar to the mean values measured in the observed  
438 sulfides ( $\delta^{34}\text{S} = 3.14 \pm 4.01\text{‰}$ ,  $\Delta^{33}\text{S} = -0.0025 \pm 0.0316\text{‰}$ ,  $\Delta^{36}\text{S} = 0.0873 \pm 0.5423\text{‰}$ ; Fig. 8).  
439 This result is consistent with previous reports that isotopic exchanges between polysulfides and  
440  $\text{H}_2\text{S}$  are extremely fast, even at room temperature, and that solid sulfides record up to 31% of  
441 the isotopic signature of the polysulfides from which they formed (Fossing and Jørgensen,  
442 1990; Fossing et al., 1992). Therefore, we conclude that the isotopic compositions of the  
443 observed sulfides represent the mixture of ~67% sulfate signature with ~33% elemental sulfur

444 signature (i.e., dissolved polysulfides at temperature) at conditions corresponding to isotopic  
445 equilibrium.

446 *Mixing between sulfate and organic sulfur.* At Névache and Bramans, three sulfides present  
447  $\Delta^{33}\text{S}$  values slightly lower than those at the other localities (Fig. 4A, B) but consistent with  
448 mixing between sulfate and elemental sulfur, considering the  $1\sigma$  error. However, taken together,  
449 their  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  values are not consistent with mixing between sulfates and elemental sulfur  
450 (Fig. 7A, B), implicating another sulfur reservoir. For these three samples, we assumed mixing  
451 between sulfate and a theoretical organic sulfur reservoir (again with  $\delta^{34}\text{S} = -30\text{‰}$ , see above).  
452 We estimated the  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  values of organic sulfur (using  $^{33}\lambda = 0.5152$  and  $^{36}\lambda = 1.89$ )  
453 that reproduce the three samples in both the  $\Delta^{33}\text{S}$  vs.  $\delta^{34}\text{S}$  and  $\Delta^{33}\text{S}$  vs.  $\Delta^{36}\text{S}$  diagrams. We  
454 obtained relative mixing proportions of organic sulfur of 28% at Névache and 22% at Bramans.

455 The good correlation between the mixing curves in both the  $\Delta^{33}\text{S}$  vs.  $\delta^{34}\text{S}$  and  $\Delta^{33}\text{S}$  vs.  $\Delta^{36}\text{S}$   
456 diagrams is consistent with the sulfur sources belonging to the Nappe des Gypses formation,  
457 and no other process than TSR is required. Because the observed compositions do not require  
458 an exogenous sulfur-rich fluid, the sulfides must have formed in a closed system. As mixing  
459 occurs in the aqueous phase, this implies that all sulfides precipitated before elemental sulfur  
460 crystallized, and that TSR probably ceased after the D2-D3 transition during cooling  
461 (corresponding to a change in tectonic regime that led the last exhumation step of the Nappe  
462 des Gypses formation; Barré et al., 2020).

## 463 **5.6 Implications for the TSR mechanism**

464 Our multiple sulfur isotopes results complement studies on MSR (e.g., Farquhar et al., 2007;  
465 Johnston et al., 2007; Zerkle et al., 2009; Sim et al., 2011) and show that TSR and MSR can be  
466 unambiguously discriminated based on the near zero to slightly negative (TSR) and positive  
467 (MSR)  $\Delta^{33}\text{S}$  values of all participating reduced sulfur-bearing phases. This geochemical tool  
468 can therefore prove extremely useful for better deciphering the sulfur cycle in contexts where

469 the occurrence of the two processes is debated (e.g., petroleum systems, ore deposits,  
470 hydrothermal settings).

471 These results also provide a new understanding of the TSR reaction pathway and associated  
472 isotopic exchanges. The fluids of the Nappe des Gypses formation are considered to have been  
473 in a closed system because they mainly correspond to gypsum dehydration and connate  
474 seawater without the involvement of external fluid (Grappin et al., 1979). This implies that TSR  
475 products in a closed system may or may not be at isotopic equilibrium with a single fluid under  
476 similar conditions, which can be explained by the variable availability of dissolved metals.  
477 Here, iron was released at different stages of the Nappe des Gypses metamorphic path (Barré  
478 et al., 2020), implying a variable metal concentration in the fluid through time. When the metal  
479 concentration is sufficiently high, all the H<sub>2</sub>S precipitates and no intermediate-valence sulfur  
480 species (i.e., polysulfides, S<sub>3</sub><sup>-</sup>) remain in the fluid because they are only stable when both  
481 sulfates and sulfides are in solution (Truche et al., 2014; Pokrovski and Dubessy, 2015; Barré  
482 et al., 2017). In this case, the fractionation between sulfate and precipitating sulfide is  
483 temperature dependent and occurs at isotopic equilibrium. In contrast, if H<sub>2</sub>S is in excess with  
484 respect to dissolved metals, only some H<sub>2</sub>S would precipitate. The resulting sulfide mineral  
485 would thus have an isotopic composition corresponding to mixing between the dissolved sulfur  
486 species (sulfates and polysulfides; Fig. 8), facilitated by the rapid isotopic exchange between  
487 polysulfides and H<sub>2</sub>S (Fossing and Jørgensen, 1990). The variable availability of metal in the  
488 system thus offers a plausible explanation for the distinct isotopic compositions of sulfides from  
489 the same geological context and involving only one fluid during TSR.

## 490 **6. CONCLUSIONS**

491 We presented a multiple sulfur isotopes analysis of coexisting sulfates, elemental sulfur, and  
492 sulfides in the Nappe des Gypses formation to characterize the reaction pathway of TSR and  
493 distinguish TSR from MSR. Our main conclusions are:

- 494 1. Multiple sulfur isotopes analysis can unambiguously differentiate TSR from MSR.  
495 Whereas MSR produces sulfide by-products with  $\Delta^{33}\text{S}$  values above those of reacted  
496 sulfates, TSR produces sulfides with similar or lower  $\Delta^{33}\text{S}$  values (down to  $-0.08\text{‰}$ ).
- 497 2. We used mass-fractionation exponents ( $^{33}\lambda$  and  $^{36}\lambda$ ) to determine if S-bearing mineral  
498 pairs (sulfate-elemental sulfur or sulfate-sulfide) were at isotopic equilibrium. We  
499 demonstrate that this technique is far more robust than petrographic observations of  
500 syngenetic relationships to resolve this crucial point for isotopic geothermometry. We  
501 also determined and validated the precipitation temperatures of TSR by-products (i.e.,  
502 pyrite, chalcopyrite, or elemental sulfur) based on the  $^{34}\text{S}$  fractionation factors between  
503 aqueous sulfates and reduced S species (sulfides or polysulfides). Interestingly,  
504 elemental sulfur precipitated between 172 and 217 °C, temperatures that correspond to  
505 the elemental sulfur liquid-solid phase transition at the lowest  $P$ - $T$  conditions recorded  
506 in the Nappe des Gypses formation.
- 507 3. Multiple sulfur isotopes analysis also allows interpretation of the isotopic compositions  
508 of all sulfides that are not at isotopic equilibrium. Whereas kinetic effects cannot explain  
509 these signatures, the two-component mixing calculations show that sulfides precipitated  
510 from a mixture between either sulfates and elemental sulfur (i.e., polysulfides at  $>200^\circ\text{C}$ )  
511 or sulfates and organic sulfur. The obtained mixing curves show that the sulfide  
512 compositions are best reproduced by the mixing of 67% sulfates and 33% elemental  
513 sulfur, consistent with the proportion of dissolved polysulfides measured at  $>200^\circ\text{C}$  in  
514 fluid inclusions from the Nappe des Gypses formation (Barré et al., 2017).
- 515 4. We observed no evidence of S-MIF, even though we demonstrated the occurrence of  
516 TSR and investigated three S-bearing phases (sulfate, sulfide, and elemental sulfur) at  
517 isotopic equilibrium.

518 This study opens new perspectives for improving our understanding of the sulfur cycle,  
519 especially TSR-related hydrothermal-metamorphic ores or sour gas fields. The multiple sulfur  
520 isotopic approach can be used to discriminate MSR from TSR; its systematic application and  
521 careful interpretation of the obtained results will improve our understanding of both the isotopic  
522 fractionations and the reaction pathways involved in TSR.

### 523 **Acknowledgements**

524 This work was funded by LABEX ANR-10-LABX-21-01 Ressources21 (Strategic metal  
525 resources of the 21st Century), the French Ministry of Higher Education and Research, and the  
526 project Dear\_Sir (ANR-15-CE31-0005). The authors would like to thank Robert Dennen who  
527 improved the fluidity and grammar of the paper. The paper was greatly improved thanks to  
528 relevant and detailed reviews by Simon Bottrell, two anonymous reviewers, and editorial  
529 support by Timothy Lyons.

### 530 **References**

- 531 Alonso-Azcárate, J., Bottrell, S.H., Tritlla, J., 2001. Sulfur redox reactions and formation of  
532 native sulfur veins during low grade metamorphism of gypsum evaporites, Cameros Basin  
533 (NE Spain). *Chem. Geol.* 174(4), 389-402.
- 534 Barré, G., Strzeczynski, P., Michels, R., Guillot, S., Cartigny, P., Thomassot, E., Lorgeoux, C.,  
535 Assayag, N., Truche, L., 2020. Tectono-metamorphic evolution of an evaporitic  
536 décollement as recorded by mineral and fluid geochemistry: The “Nappe des Gypses”  
537 (Western Alps) case study. *Lithos*, 358, 105419.
- 538 Barré, G., Truche, L., Bazarkina, E.F., Michels, R., Dubessy, J., 2017. First evidence of the  
539 trisulfur radical ion  $S_3^-$  and other sulfur polymers in natural fluid inclusions. *Chem. Geol.*  
540 462, 1-14.

541 Canfield, D.E., Raiswell, R., Westrich, J.T., Reaves, C.M., Berner, R.A., 1986. The use of  
542 chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales.  
543 Chem. Geol. 54(1-2), 149-155.

544 Claypool, G.E., Holser, W.T., Kaplan, I.R., Sakai, H., Zak, I., 1980. The age curves of sulfur  
545 and oxygen isotopes in marine sulfate and their mutual interpretation. Chem. Geol. 28, 199-  
546 260.

547 Clayton, R.N., Mayeda, T.K., 2009. Kinetic isotope effects in oxygen in the laboratory  
548 dehydration of magnesian minerals. J. Phys. Chem. A, 113(10), 2212-2217.

549 Cota, L., Baric, G., 1998. Petroleum potential of the Adriatic offshore, Croatia. Org. Geochem.  
550 29(1-3), 559-570.

551 Crapanzano, L. (2005). Polymorphism of sulfur: structural and dynamical aspects (Doctoral  
552 dissertation, Université Joseph-Fourier-Grenoble I).

553 Crockford, P.W., Kunzmann, M., Bekker, A., Hayles, J., Bao, H., Halverson, G.P., Peng, Y.,  
554 Bui, T.H., Cox, G.M., Gibson, T.M., Wörndle, S., Rainbird, R., Lepland, A., Swanson-  
555 Hysell, N.L., Master, S., Sreenivas, B., Kuznetsov, A., Krupenik, V., Wing, B.A., 2019.  
556 Claypool continued: Extending the isotopic record of sedimentary sulfate. Chem. Geol.,  
557 513, 200-225.

558 Cross, M.M., 1999. Rates and mechanisms of thermochemical sulphate reduction (Doctoral  
559 dissertation, Manchester University).

560 Debelmas, J., Desmons, J., Ellenberger, F., Goffé, B., Fabre, J., Jaillard, E., and Pachoud, A.,  
561 1989. Notice explicative de la feuille Modane. B.R.G.M., scale 1/50 000, 1 sheet, 53 p. text  
562 (in french).

563 Eldridge, D.L., Guo, W., Farquhar, J., 2016. Theoretical estimates of equilibrium sulfur isotope  
564 effects in aqueous sulfur systems: Highlighting the role of isomers in the sulfite and  
565 sulfoxylate systems. Geochim. Cosmochim. Acta 195, 171-200.



566 Eldridge, D.L., Kamyshny Jr, A., Farquhar, J., 2021. Theoretical estimates of equilibrium sulfur  
567 isotope effects among aqueous polysulfur and associated compounds with applications to  
568 authigenic pyrite formation and hydrothermal disproportionation reactions. *Geochim.*  
569 *Cosmochim. Acta* 310, 281-319.

570 Farquhar, J., Bao, H., Thiemens, M., 2000. Atmospheric influence of Earth's earliest sulfur  
571 cycle. *Science* 289(5480), 756-758.

572 Farquhar, J., Johnston, D.T., Wing, B.A., 2007. Implications of conservation of mass effects on  
573 mass-dependent isotope fractionations: influence of network structure on sulfur isotope  
574 phase space of dissimilatory sulfate reduction. *Geochim. Cosmochim. Acta* 71(24), 5862-  
575 5875.

576 Farquhar, J., Wing, B.A., 2003. Multiple sulfur isotopes and the evolution of the atmosphere.  
577 *Earth Planet. Sci. Lett.* 213(1), 1-13.

578 Fossing, H., Jørgensen, B.B., 1990. Isotope exchange reactions with radiolabeled sulfur  
579 compounds in anoxic seawater. *Biogeochemistry* 9(3), 223-245.

580 Fossing, H., Thode-Andersen, S., Jørgensen, B.B., 1992. Sulfur isotope exchange between <sup>35</sup>S-  
581 labeled inorganic sulfur compounds in anoxic marine sediments. *Marine Chemistry* 38(1-  
582 2), 117-132.

583 Goldstein, T.P., Aizenshtat, Z., 1994. Thermochemical sulfate reduction: A review. *J. Therm.*  
584 *Anal.* 42, 241-290.

585 Grappin, C., Saliot, P., Sabouraud, C., Touray, J.C., 1979. Les variations des rapports Cl/Br,  
586 Na/Br et K/Br dans les inclusions fluides des quartz de la cicatrice évaporitique de  
587 Bramans-Termignon (Vanoise, Alpes françaises). *Chem. Geol.* 25(1-2), 41-52.

588 Gröger, J., Franke, J., Hamer, K., Schulz, H.D., 2009. Quantitative recovery of elemental sulfur  
589 and improved selectivity in a chromium-reducible sulfur distillation. *Geostand. Geoanal.*  
590 *Res.* 33(1), 17-27.

591 Hu, D., Li, M., Zhang, X., Turchyn, A.V., Gong, Y., Shen, Y., 2020. Large mass-independent  
592 sulphur isotope anomalies link stratospheric volcanism to the Late Ordovician mass  
593 extinction. *Nature communications*, 11(1), 1-8.

594 Hulston, J.R., Thode, H.G., 1965. Variations in the S33, S34, and S36 contents of meteorites  
595 and their relation to chemical and nuclear effects. *J. Geophys. Res.* 70(14), 3475-3484.

596 Jamieson, J.W., Wing, B.A., Hannington, M.D., Farquhar, J., 2006. Evaluating isotopic  
597 equilibrium among sulfide mineral pairs in Archean ore deposits: case study from the Kidd  
598 Creek VMS deposit, Ontario, Canada. *Econ. Geol.* 101(5), 1055-1061.

599 Johnston, D.T., 2011. Multiple sulfur isotopes and the evolution of Earth's surface sulfur cycle.  
600 *Earth-Sci. Rev.* 106(1), 161-183.

601 Johnston, D.T., Farquhar, J., Canfield, D.E., 2007. Sulfur isotope insights into microbial sulfate  
602 reduction: when microbes meet models. *Geochim. Cosmochim. Acta* 71(16), 3929-3947.

603 Kitayama, Y., Thomassot, E., Galy, A., Golovin, A., Korsakov, A., d'Eyrames, E., Assayag, N.,  
604 Bouden, N. Ionov, D., 2017. Co-magmatic sulfides and sulfates in the Udachnaya-East pipe  
605 (Siberia): A record of the redox state and isotopic composition of sulfur in kimberlites and  
606 their mantle sources. *Chem. Geol.* 455, 315-330.

607 Kokh, M.A., Assayag, N., Mounic, S., Cartigny, P., Gurenko, A., Pokrovski, G.S., 2020.  
608 Multiple sulfur isotope fractionation in hydrothermal systems in the presence of radical  
609 ions and molecular sulfur. *Geochim. Cosmochim. Acta* 285, 100-128.

610 Labrado, A.L., Brunner, B., Bernasconi, S.M., Peckmann, J., 2019. Formation of large native  
611 sulfur deposits does not require molecular oxygen. *Front. Microbiol.* 10, 24.

612 Machel, H.G., 2001. Bacterial and thermochemical sulfate reduction in diagenetic settings –  
613 old and new insights. *Sediment. Geol.* 140, 143-175.

614 Machel, H.G., Krouse, H.R., Sassen, R., 1995. Products and distinguishing criteria of bacterial  
615 and thermochemical sulfate reduction. *Appl. Geochem.* 10(4), 373-389.

616 Meshoulam, A., Ellis, G.S., Ahmad, W.S., Deev, A., Sessions, A.L., Tang, Y., Adkins, J.F.,  
617 Jinzhong, L., Gilhooly, W.P., Aizenshtat, Z., Amrani, A., 2016. Study of thermochemical  
618 sulfate reduction mechanism using compound specific sulfur isotope analysis. *Geochim.*  
619 *Cosmochim. Acta* 188, 73-92.

620 Michalski, G., Bhattacharya, S.K., 2009. The role of symmetry in the mass independent isotope  
621 effect in ozone. *Proc. Natl. Acad. Sci. U.S.A.* 106(14), 5493-5496.

622 Oduro, H., Harms, B., Sintim, H.O., Kaufman, A.J., Cody, G., Farquhar, J., 2011. Evidence of  
623 magnetic isotope effects during thermochemical sulfate reduction. *Proc. Natl. Acad. Sci.*  
624 *U.S.A.* 108, 17635-17638.

625 Ohmoto, H., Lasaga, A.C., 1982. Kinetics of reactions between aqueous sulfates and sulfides  
626 in hydrothermal systems. *Geochim. Cosmochim. Acta*, 46(10), 1727-1745.

627 Ono, S., Wing, B., Johnston, D., Farquhar, J., Rumble, D., 2006. Mass-dependent fractionation  
628 of quadruple stable sulfur isotope system as a new tracer of sulfur biogeochemical cycles.  
629 *Geochim. Cosmochim. Acta* 70(9), 2238-2252.

630 Otake, T., Lasaga, A.C., Ohmoto, H., 2008. Ab initio calculations for equilibrium fractionations  
631 in multiple sulfur isotope systems. *Chem. Geol.* 249(3), 357-376.

632 Pokrovski, G.S., Dubessy, J., 2015. Stability and abundance of the trisulfur radical ion  $S_3^-$  in  
633 hydrothermal fluids. *Earth Planet. Sci. Lett.* 411, 298-309.

634 Roussel, E.G., Cragg, B.A., Webster, G., Sass, H., Tang, X., Williams, A.S., Gorra, R.,  
635 Weightman, A.J., Parkes, R.J., 2015. Complex coupled metabolic and prokaryotic  
636 community responses to increasing temperatures in anaerobic marine sediments: critical  
637 temperatures and substrate changes. *FEMS microbiology ecology*, 91(8), fiv084.

638 Sim, M.S., Bosak, T., Ono, S., 2011. Large sulfur isotope fractionation does not require  
639 disproportionation. *Science*, 333(6038), 74-77.

640 Steudel, R., Chivers, T., 2019. The role of polysulfide dianions and radical anions in the  
641 chemical, physical and biological sciences, including sulfur-based batteries. *Chem. Soc.*  
642 *Rev.* 48(12), 3279-3319.

643 Thomassot, E., O'Neil, J., Francis, D., Cartigny, P., Wing, B.A., 2015. Atmospheric record in  
644 the Hadean Eon from multiple sulfur isotope measurements in Nuvvuagittuq Greenstone  
645 Belt (Nunavik, Quebec). *Proc. Natl. Acad. Sci. U.S.A.* 112(3), 707-712.

646 Truche, L., Bazarkina, E.F., Barré, G., Thomassot, E., Berger, G., Dubessy, J., Robert, P., 2014.  
647 The role of  $S_3^-$  ion in thermochemical sulphate reduction: Geological and geochemical  
648 implications. *Earth Planet. Sci. Lett.* 396, 190-200.

649 Truche, L., Berger, G., Destrigneville, C., Pages, A., Guillaume, D., Giffaut, E. Jacquot, E.,  
650 2009. Experimental reduction of aqueous sulphate by hydrogen under hydrothermal  
651 conditions: implication for the nuclear waste storage. *Geochim. Cosmochim. Acta*,  
652 73(16), 4824-4835.

653 Watanabe, Y., Farquhar, J., Ohmoto, H., 2009. Anomalous fractionations of sulfur isotopes  
654 during thermochemical sulfate reduction. *Science* 324, 370-373.

655 Werne, J.P., Hollander, D.J., Lyons, T.W., Damsté, J.S.S., 2004. Organic sulfur  
656 biogeochemistry: recent advances and future research directions. *Geol. S. Am. S.* 379, 135-  
657 150.

658 Worden, R.H., Smalley, P.C., Fallick, A.E., 1997. Sulfur cycle in buried evaporites. *Geology*,  
659 25, 643-646.

660 Wu, N., Farquhar, J., Strauss, H., 2014.  $\delta^{34}S$  and  $\Delta^{33}S$  records of Paleozoic seawater sulfate  
661 based on the analysis of carbonate associated sulfate. *Earth Planet. Sci. Lett.* 399, 44-51.

662 Yang, C., Hutcheon, I., Krouse, H.R., 2001. Fluid inclusion and stable isotopic studies of  
663 thermochemical sulphate reduction from Burnt Timber and Crossfield East gas fields in  
664 Alberta, Canada. *Bull. Can. Petrol. Geol.* 49(1), 149-164.

665 Young, S.A., Loukola-Ruskeeniemi, K., Pratt, L.M., 2013. Reactions of hydrothermal solutions  
666 with organic matter in Paleoproterozoic black shales at Talvivaara, Finland: Evidence from  
667 multiple sulfur isotopes. *Earth Planet. Sci. Lett.* 367, 1-14.

668 Zerkle, A.L., Farquhar, J., Johnston, D.T., Cox, R.P., Canfield, D.E., 2009. Fractionation of  
669 multiple sulfur isotopes during phototrophic oxidation of sulfide and elemental sulfur by a  
670 green sulfur bacterium. *Geochim. Cosmochim. Acta* 73(2), 291-306.

## 671 **TABLE CAPTIONS**

672 **Table 1.** Multiple sulfur isotopes compositions of sulfur-bearing minerals from each studied  
673 site. Here,  $\sigma$  corresponds to analytical uncertainty.

674 **Table 2.**  $^{33}\lambda$  and  $^{36}\lambda$  values calculated between sulfates and either associated elemental sulfur  
675 ( $S_8$ ), pyrite, or chalcopyrite. When the  $^{33}\lambda$  value is between 0.5140 and 0.5170, we assume that  
676 isotopic equilibrium was attained and therefore that the associated apparent equilibrium  
677 temperature, determined using the respective  $\Delta^{34}S$  values and  $SO_4$ - $S_8$  (Eldridge et al., 2021)  
678 and  $SO_4$ - $H_2S$  (Eldridge et al., 2016) fractionation equations for each minerals pair, is valid.  
679 Note that isotopic composition of the sulfates is assumed to be constant because anhydrite is  
680 considered as an infinite reservoir.

## 681 **FIGURE CAPTIONS**

682 **Fig. 1.** Sampling locations on the simplified geological map of the Nappe des Gypses  
683 formation (Western French Alps; modified after Barré et al., 2020).

684 **Figure 2:** Typical sulfur-rich minerals observed in the Nappe des Gypses formation. (A)  
685 Pyrites in close association with anhydrite and white dolomite. (B, C) Crystals of elemental  
686 sulfur incorporated in gray dolomite “boudins” and diffuse elemental sulfur in the anhydrite  
687 facies. (D) Associated white dolomite, quartz, and pyrite association observed in carbonates-  
688 quartz-sulfides veins in micaschist layers. (E) Associated sulfides and elemental sulfur  
689 observed at the centimeter scale in the presence of micaschist at the Sollières l'Envers outcrop.

690 (F, G) Respective plane and cross-polarized light images depicting the typical occurrence of  
691 elemental sulfur in anhydrite. (H, I) Respective plane and cross-polarized light images depicting  
692 direct association of pyrites with white micas. Abbreviations: Anh = anhydrite; Py = pyrite; S  
693 = native sulfur; G-Dol = gray dolomite; W-Dol = white dolomite; Qtz = quartz; W-Mca = white  
694 micas; Fl = fluorite.

695 **Fig. 3.**  $\delta^{34}\text{S}$  values of sulfates, sulfides, and elemental sulfur at each studied site. The gray  
696 shaded band shows  $\delta^{34}\text{S}$  values typical of Carnian seawater (Claypool et al., 1980; Crockford  
697 et al., 2019). Error bars are smaller than the symbol sizes.

698 **Fig. 4.**  $\Delta^{33}\text{S}$  vs.  $\delta^{34}\text{S}$  diagrams for sulfates, sulfides, and elemental sulfur from each studied  
699 site. Outcrops are plotted from south to north: (A) Névache, (B) Bramans, (C) Ambin stream,  
700 (D) Sollières l'Envers, (E) Mont-Cenis Lake, and (F) Tignes. For each site, the mass  
701 fractionation exponent near 0.515 (i.e., for samples at isotopic equilibrium) between sulfates  
702 and elemental sulfur ( $^{33}\theta_{\text{SO}_4\text{-S}_8}$ ) and between sulfates and sulfides ( $^{33}\theta_{\text{SO}_4\text{-H}_2\text{S}}$ ) are calculated as  
703 well as the associated vector between sulfate and elemental sulfur (green arrow) and between  
704 sulfate and sulfide (red arrow). In these cases, isotopic equilibrium is confirmed (see section  
705 5.4) and the associated equilibrium temperature is determined using the respective  $\Delta^{34}\text{S}$  values  
706 and  $\text{SO}_4\text{-S}_{8(\text{aq})}$  (green; Eldridge et al., 2021) or  $\text{SO}_4\text{-H}_2\text{S}_{(\text{aq})}$  (red; Eldridge et al., 2016)  
707 fractionation equations. Two-component mixing curves (yellow dashed curves) are calculated  
708 between the most extreme sulfate and elemental sulfur compositions. In (A) and (B), the gray  
709 dashed curve is the mixing curve between sulfates and a theoretical organic sulfur reservoir  
710 (estimated at  $\delta^{34}\text{S} = -30\text{‰}$  and the  $\Delta^{33}\text{S}$  value determined using  $^{33}\lambda = 0.5152$ ). Errors bars  
711 represent  $1\sigma$  for dual-inlet mass-spectrometry measurements. Measurement errors on  $\delta^{34}\text{S}$  are  
712 smaller than the symbol sizes.

713 **Fig. 5.** Plots of  $^{33}\lambda$  vs. temperature between sulfates and either elemental sulfur (diamonds),  
714 pyrite (squares), or chalcopyrite (triangles). For each mineral pair, temperatures are estimated

715 from the respective  $\Delta^{34}\text{S}$  values and  $\text{SO}_4\text{-S}_{8(\text{aq})}$  (Eldridge et al., 2021) or  $\text{SO}_4\text{-H}_2\text{S}_{(\text{aq})}$  (Eldridge  
716 et al., 2016) fractionation equations. Curves indicate the evolution of  $^{33}\lambda$  as a function of  
717 temperature for different sulfur species relative to sulfates from theoretical calculations ( $\text{CS}_{2(\text{aq})}$   
718 is from Otake et al., 2008;  $\text{H}_2\text{S}_{\text{aq}}$  and  $\text{SO}_3^{2-}$  from Eldridge et al., 2016;  $\text{S}_8$ ,  $\text{S}_3^-$  and  $\text{S}_n^{2-}$  from  
719 Eldridge et al., 2021). Errors represent  $1\sigma$  for dual-inlet mass-spectrometry measurements.

720 **Fig. 6.** Elemental sulfur melting curve (black curve, shaded area indicates experimental  
721 errors; from Crapanzano, 2005). For comparison, the  $P$ - $T$  path of the Nappe des Gypses  
722 formation (blue arrow and squares; Barré et al., 2020) and the elemental sulfur precipitation  
723 temperature determined herein (yellow shaded area; see section 5.4 for details) are shown. The  
724 Nappe des Gypses  $P$ - $T$  path crosses the elemental sulfur melting curve at conditions consistent  
725 with the temperature range calculated from the isotopic compositions of our samples, indicating  
726 that all the elemental sulfur precipitated just after the D2-D3 tectonic transition during the  
727 exhumation of the Nappe des Gypses.

728 **Fig. 7.**  $\Delta^{33}\text{S}$  vs.  $\Delta^{36}\text{S}$  diagrams for sulfates, sulfides, and elemental sulfur from each studied  
729 site. Outcrops are plotted from south to north: (A) Névache, (B) Bramans, (C) Ambin stream,  
730 (D) Sollières l'Envers, (E) Mont-Cenis Lake, and (F) Tignes. Two-component mixing curves  
731 (yellow dashed curves) are calculated between the most extreme sulfate and elemental sulfur  
732 compositions. In (A) and (B), the gray dashed curve is the mixing curve between sulfates and  
733 a theoretical organic sulfur reservoir with estimated  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  values determined using  $^{33}\lambda$   
734  $= 0.5152$  and  $^{36}\lambda = 1.89$ , respectively. The mass-dependent fractionation line (dashed black line  
735 of slope  $-6.9$ ; Ono et al., 2006) is also shown for comparison. Errors bars represent  $1\sigma$  for dual-  
736 inlet mass-spectrometry measurements.

737 **Fig. 8.** Schematic summary of the TSR reaction pathway and associated isotopic  
738 fractionations. (Left) The initial thermodynamic state (Truche et al., 2014), isotopic signatures  
739 (this study), and relative proportions (Barré et al., 2017) of sulfates and elemental sulfur

740 reservoirs in the fluid during TSR. (Right) Three possibilities for generating the observed  
741 elemental sulfur and sulfide compositions. (1) When no metal is present in the system, the  
742 combination of polysulfides leads to elemental sulfur precipitation at isotopic equilibrium with  
743 the sulfate; the resulting isotopic signature is temperature dependent. (2) When a large amount  
744 of metal is released into the system, all reduced sulfur species ( $\text{H}_2\text{S}$  and  $\text{S}_n^{2-}$ ) precipitate as  
745 sulfide at isotopic equilibrium with sulfate and experience a temperature-dependent isotopic  
746 fractionation. (3) When only a small amount of metal (i.e., less than the reduced sulfur species)  
747 is released into the system, only some of the  $\text{H}_2\text{S}$  precipitates as sulfide. The resulting  
748 disequilibrium isotopic composition of the sulfides corresponds to the mixing between 33%  
749 elemental sulfur (i.e., polysulfides) with 67% sulfate. The similarity of the calculated and  
750 measured sulfide isotopic compositions (bottom right) confirms that the disequilibrium sulfides  
751 precipitated from the mixing of sulfates and polysulfides.

752

753



Figure 1

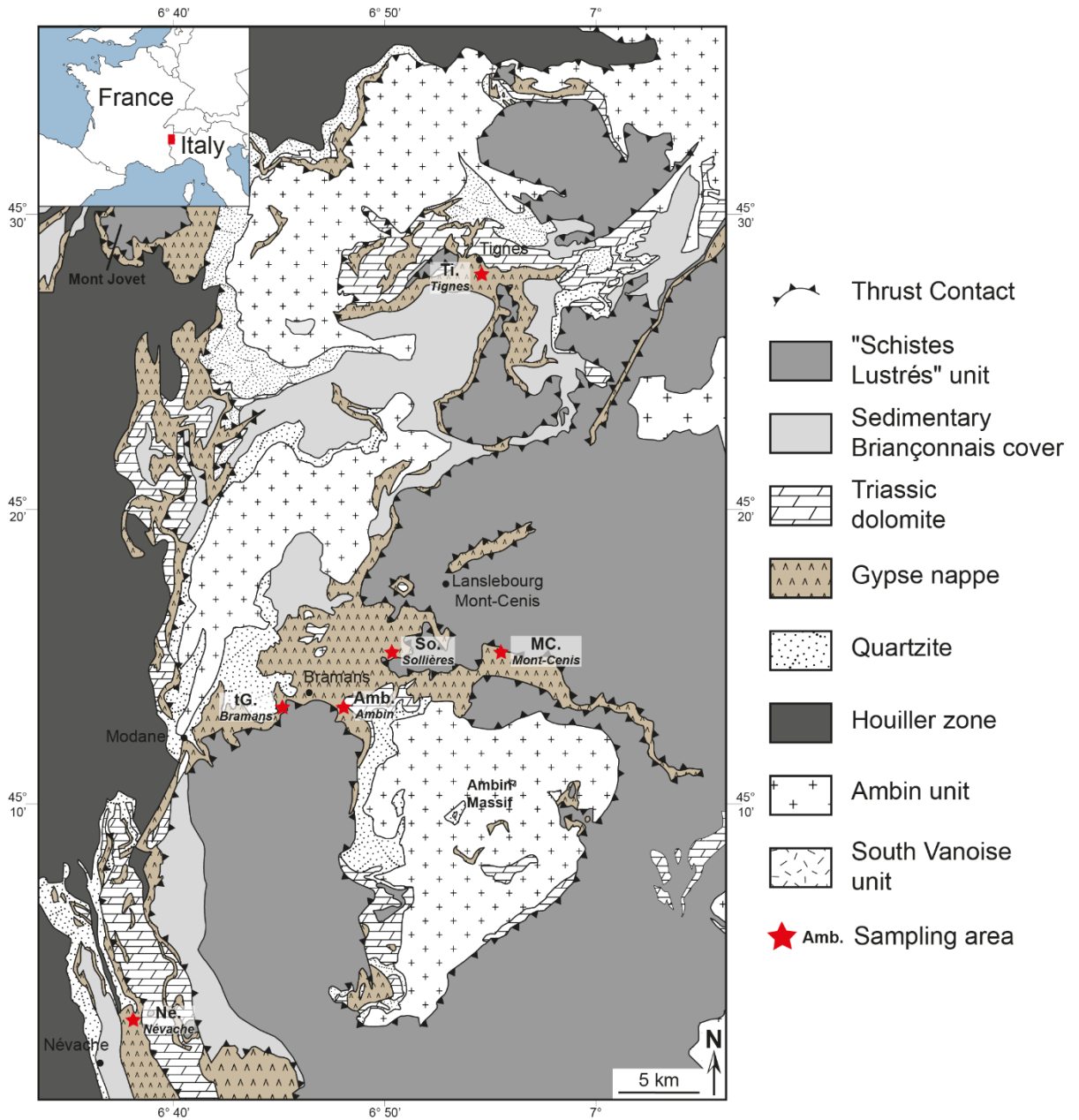


Figure 2

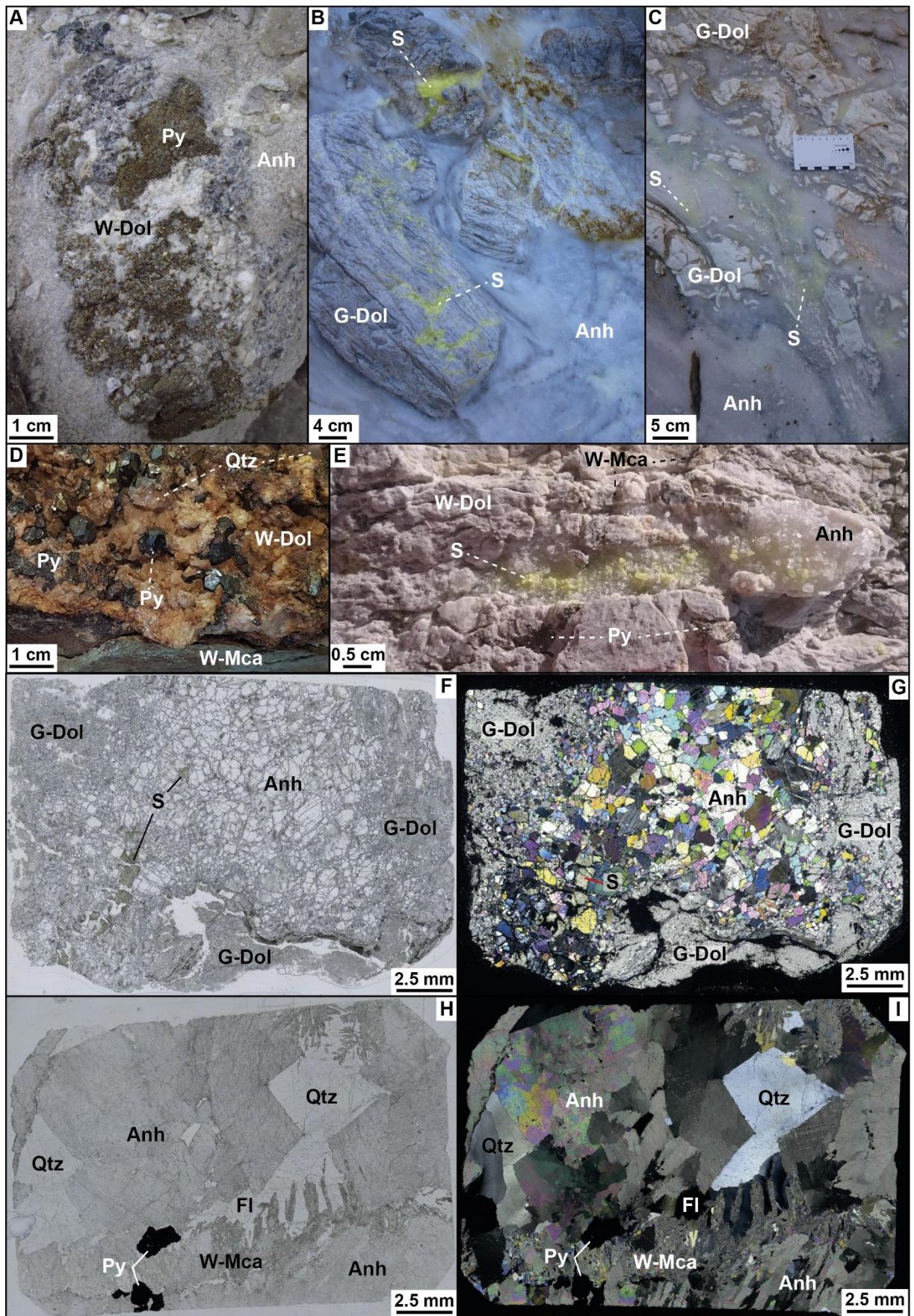


Figure 3

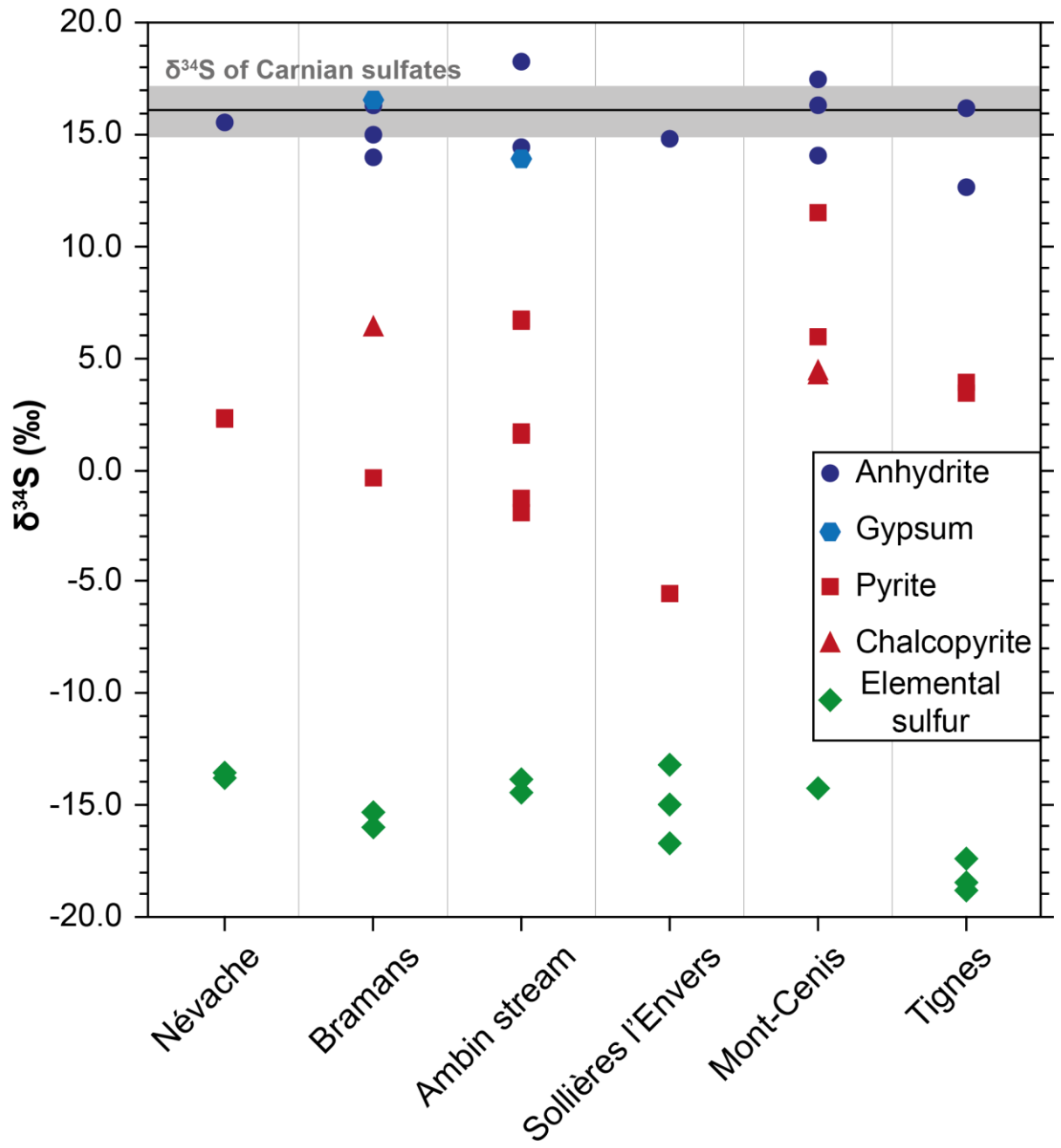
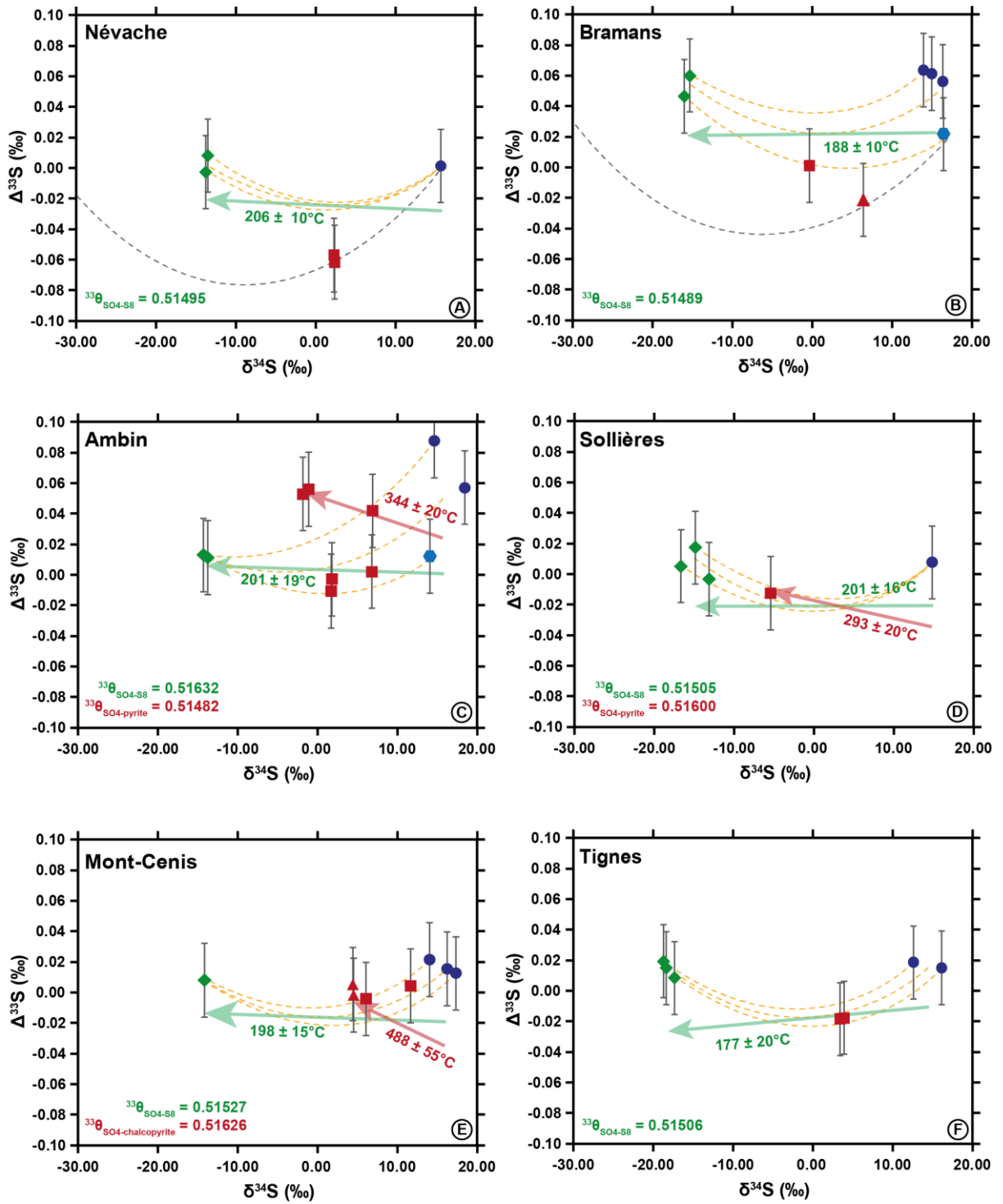
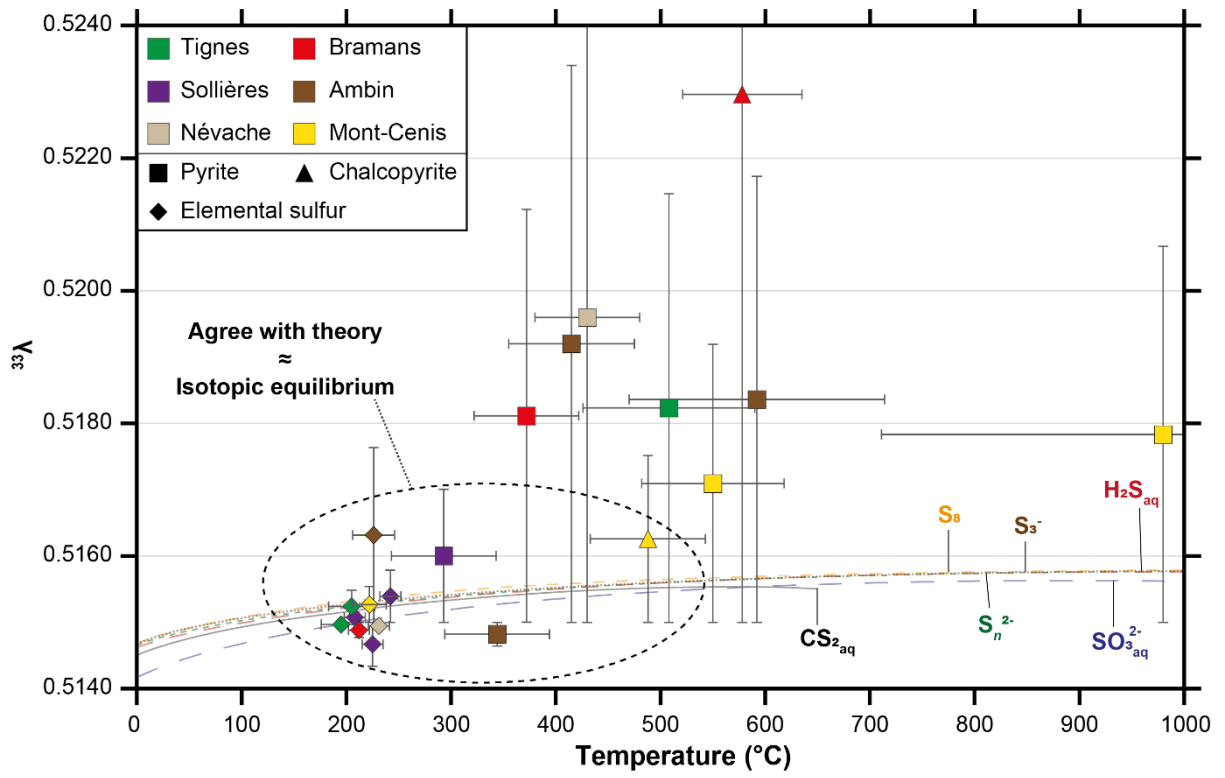


Figure 4



765

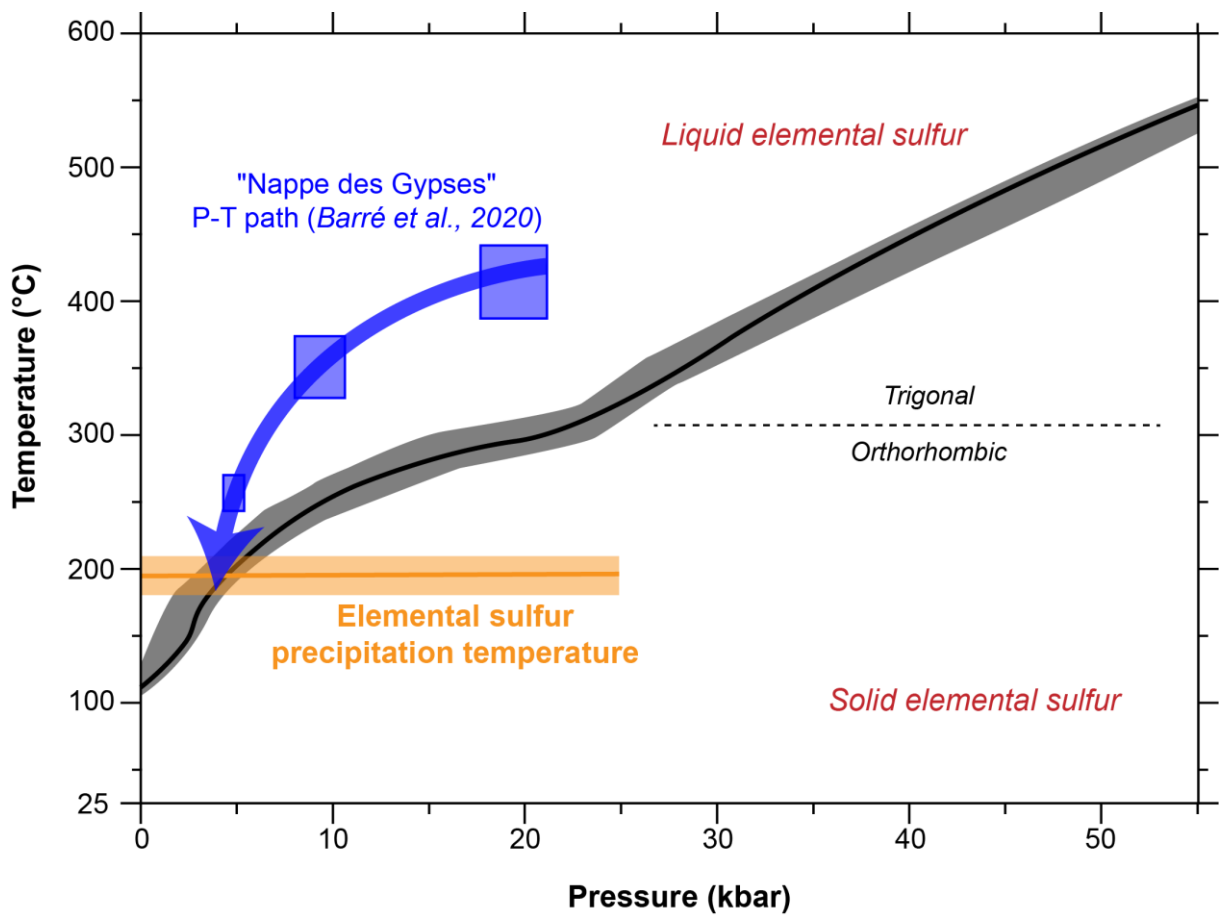
Figure 5



766

767

768 Figure 6



769

770

Figure 7

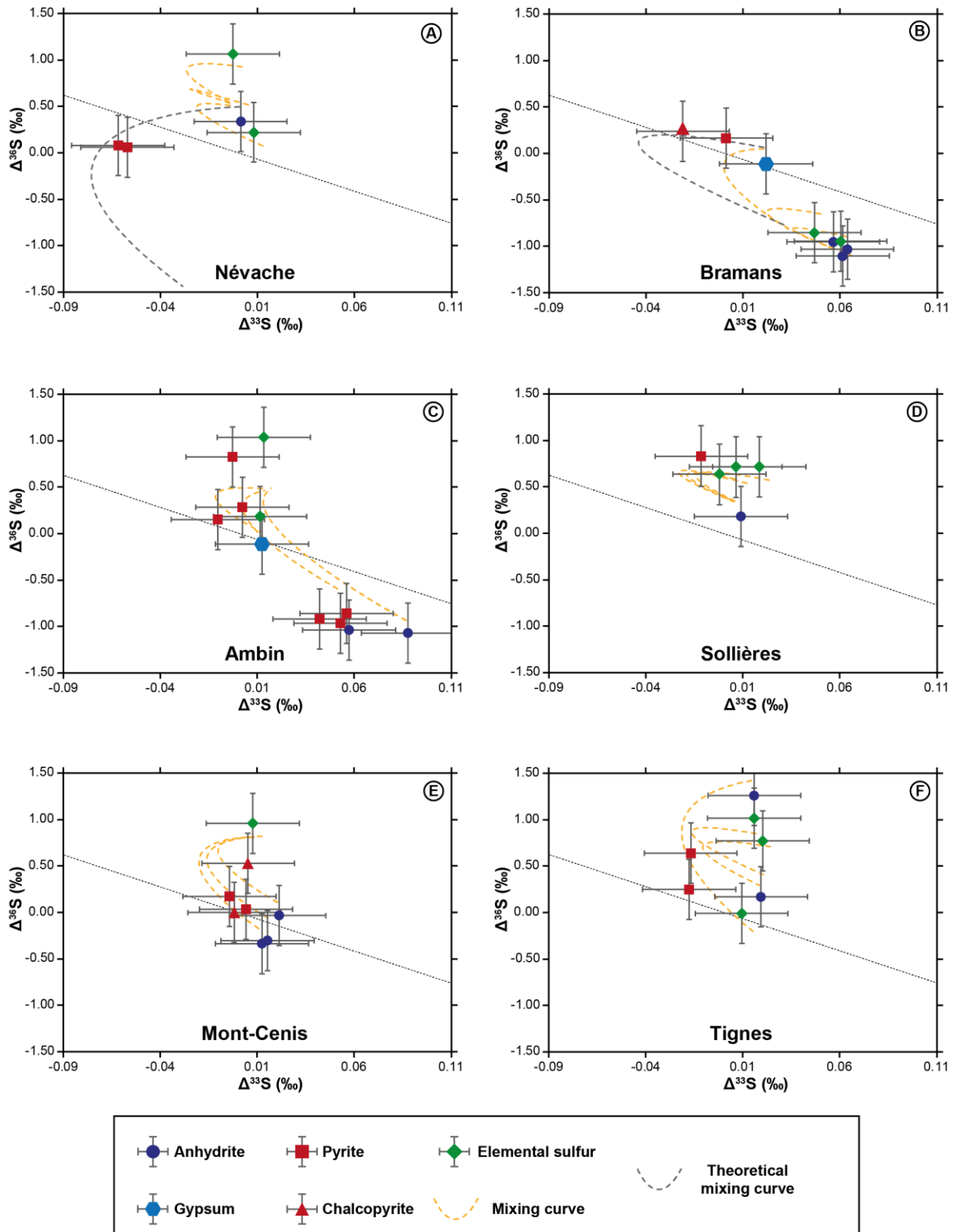


Figure 8

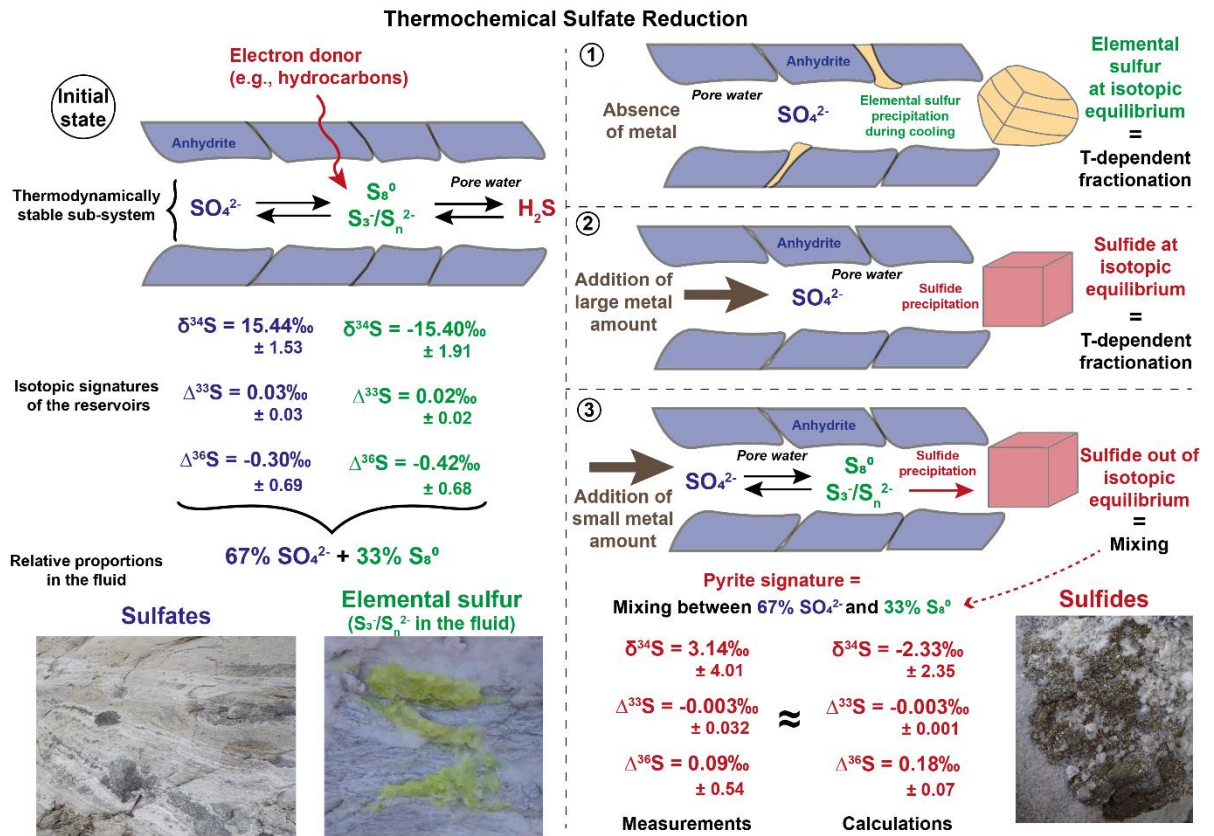




Table 1

Sample	Mineral	$\delta^{33}\text{S}$ (‰) $\pm \sigma$	$\delta^{34}\text{S}$ (‰) $\pm \sigma$	$\delta^{36}\text{S}$ (‰) $\pm \sigma$	$\Delta^{33}\text{S}$ (‰)	$\Delta^{36}\text{S}$ (‰)			
<b>Névache</b>									
Né.1.2	Anhydrite	8.02	0.012	15.64	0.007	30.26	0.030	0.00	0.34
Né.3.1	Pyrite	1.15	0.008	2.34	0.006	4.52	0.092	-0.06	0.06
Né.3.2	Pyrite	1.15	0.010	2.36	0.005	4.56	0.083	-0.06	0.08
Né.S8.1	Elemental sulfur	-7.09	0.013	-13.71	0.008	-24.82	0.255	0.00	1.06
Né.S8.2	Elemental sulfur	-6.97	0.008	-13.51	0.006	-25.29	0.070	0.01	0.22
<b>Bramans</b>									
tG.1.1	Anhydrite	8.49	0.019	16.43	0.035	30.50	0.115	0.06	-0.95
tG.1.2	Anhydrite	7.80	0.014	15.08	0.011	27.74	0.091	0.06	-1.11
tG.11	Anhydrite	7.29	0.012	14.07	0.012	25.88	0.075	0.06	-1.04
tG.16.1	Gypsum	8.52	0.006	16.57	0.012	31.60	0.162	0.02	-0.11
tG.12.1	Pyrite	-0.15	0.009	-0.30	0.002	-0.41	0.128	0.00	0.16
tG.16.S2	Chalcopyrite	3.31	0.013	6.47	0.006	12.57	0.132	-0.02	0.23
tG.S0.1	Elemental sulfur	-8.22	0.011	-16.00	0.009	-31.03	0.111	0.05	-0.85
tG.S0.2	Elemental sulfur	-7.83	0.013	-15.26	0.004	-29.74	0.030	0.06	-0.95
<b>Ambin</b>									
Amb.4.SO.1	Anhydrite	7.54	0.036	14.52	0.041	26.70	0.178	0.09	-1.07
Amb.4.SO.2	Anhydrite	9.49	0.012	18.39	0.011	34.19	0.064	0.06	-1.04
Amb.1	Gypsum	7.19	0.014	13.99	0.004	26.63	0.084	0.01	-0.11
Amb.4.S2.1	Pyrite	-0.91	0.006	-1.88	0.006	-4.53	0.092	0.05	-0.97
Amb.4.S2.2	Pyrite	-0.55	0.015	-1.18	0.022	-3.10	0.098	0.06	-0.86
Amb.2.1	Pyrite	3.56	0.017	6.84	0.017	12.12	0.105	0.04	-0.92
Amb.2.2	Pyrite	3.48	0.009	6.77	0.002	13.17	0.089	0.00	0.28
Amb.B.S.1	Pyrite	0.91	0.009	1.77	0.006	4.18	0.358	0.00	0.82
Amb.B.S.2	Pyrite	0.82	0.005	1.62	0.003	3.23	0.066	-0.01	0.15
Amb.3.1	Elemental sulfur	-7.40	0.007	-14.34	0.007	-26.03	0.324	0.01	1.03
Amb.3.2	Elemental sulfur	-7.10	0.010	-13.77	0.005	-25.82	0.133	0.01	0.18
<b>Sollières</b>									
$\alpha$ So.3	Anhydrite	7.66	0.006	14.91	0.008	28.70	0.217	0.01	0.18
$\alpha$ So.2.2	Pyrite	-2.82	0.008	-5.44	0.011	-9.49	0.273	-0.01	0.82
So.D.1.S8	Elemental sulfur	-8.64	0.006	-16.72	0.005	-30.82	0.217	0.01	0.71
$\alpha$ So.2.3	Elemental sulfur	-6.80	0.011	-13.17	0.003	-24.24	0.191	0.00	0.63
So.4	Elemental sulfur	-7.68	0.010	-14.90	0.002	-27.42	0.204	0.02	0.71
<b>Mont-Cenis</b>									
MC.4.SO.1	Anhydrite	7.21	0.011	14.00	0.004	26.74	0.111	0.02	-0.03
MC.4.SO.2	Anhydrite	8.88	0.011	17.28	0.005	32.76	0.074	0.01	-0.33
MC.2	Anhydrite	8.33	0.008	16.20	0.008	30.71	0.122	0.02	-0.30
MC.3.1.1	Pyrite	3.10	0.005	6.04	0.006	11.68	0.076	0.00	0.17
MC.3.1.4	Pyrite	5.96	0.005	11.60	0.004	22.20	0.050	0.00	0.04
MC.3.1.2	Chalcopyrite	2.29	0.007	4.45	0.004	8.47	0.111	0.00	0.00
MC.3.1.3	Chalcopyrite	2.24	0.012	4.34	0.005	8.79	0.192	0.01	0.53
MC.4.S8	Elemental sulfur	-7.36	0.010	-14.25	0.004	-25.95	0.220	0.01	0.96
<b>Tignes</b>									
Ti.1.SO	Anhydrite	8.36	0.007	16.27	0.006	32.40	0.093	0.02	1.26
Ti.2.SO	Anhydrite	6.56	0.015	12.74	0.006	24.52	0.052	0.02	0.17
Ti.3.1	Pyrite	2.06	0.007	4.03	0.010	8.31	0.171	-0.02	0.64
Ti.3.2	Pyrite	1.77	0.010	3.48	0.008	6.87	0.081	-0.02	0.25
Ti.1.S8.1	Elemental sulfur	-9.52	0.009	-18.43	0.006	-33.71	0.230	0.02	1.01
Ti.1.S8.2	Elemental sulfur	-9.72	0.005	-18.82	0.004	-34.69	0.175	0.02	0.77
Ti.2.S8	Elemental sulfur	-8.98	0.011	-17.39	0.005	-32.79	0.123	0.01	-0.01

779 Table 2

Locality	Sample	Mineral	$^{33}\lambda$	$1\sigma$	$^{36}\lambda$	$1\sigma$	T°C	$1\sigma$	Valid temperature?
Névache	Né.3	Pyrite	0.51960	0.00460	1.91973	0.02973	430	20	No
	Né.S8	Elemental sulfur	0.51495	0.00005	1.88873	0.00134	206	10	Yes
Bramans	tG.12.1	Pyrite	0.51812	0.00311	1.84051	0.04949	372	20	No
	tG.16.S2	Chalcopyrite	0.52296	0.00796	1.78740	0.10260	578	57	No
	tG.S0	Elemental sulfur	0.51489	0.00012	1.90484	0.01484	188	10	Yes
Ambin	Amb.4.S2	Pyrite	0.51482	0.00018	1.91167	0.02167	344	20	Yes
	Amb.2	Pyrite	0.51836	0.00336	1.85402	0.03599	592	122	No
	Amb.B.S	Pyrite	0.51920	0.00420	1.81325	0.07675	415	60	No
	Amb.3	Elemental sulfur	0.51632	0.00132	1.85488	0.03512	201	19	Yes
Sollières	$\alpha$ So.2.2	Pyrite	0.51600	0.00100	1.86761	0.02239	293	20	Yes
	So.D.1.S8	Elemental sulfur	0.51508	0.00008	1.88250	0.00751	185	10	Yes
	$\alpha$ So.2.3	Elemental sulfur	0.51539	0.00039	1.88320	0.00682	217	10	Yes
	So.4	Elemental sulfur	0.51467	0.00033	1.88139	0.00862	200	10	Yes
Mont-Cenis	MC.3.1.1	Pyrite	0.51710	0.00210	1.86016	0.02984	550	68	No
	MC.3.1.4	Pyrite	0.51783	0.00283	1.84000	0.05000	980	269	No
	MC.3.2	Chalcopyrite	0.51626	0.00126	1.85803	0.03197	488	55	Yes
	MC.4.S8	Elemental sulfur	0.51527	0.00027	1.86009	0.02991	198	15	Yes
Tignes	Ti.3	Pyrite	0.51823	0.00323	1.92388	0.03388	508	82	No
	Ti.1.S8	Elemental sulfur	0.51497	0.00004	1.89314	0.00317	172	18	Yes
	Ti.2.S8	Elemental sulfur	0.51524	0.00024	1.92214	0.03215	182	21	Yes

