

1 **Multiple sulfur isotope signals associated with the late Smithian event and**  
2 **the Smithian/Spathian boundary**

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4 C. Thomazo<sup>1,\*</sup>, A. Brayard<sup>1</sup>, S. Elmeknassi<sup>1</sup>, E. Vennin<sup>1</sup>, N. olivier<sup>2</sup>, G. Caravaca<sup>1</sup>, G.  
5 Escarguel<sup>3</sup>, E. Fara<sup>1</sup>, K.G. Bylund<sup>4</sup>, J.F. Jenks<sup>5</sup>, D.A. Stephen<sup>6</sup>, B. Killingsworth<sup>7</sup>, P.  
6 Sansjofre<sup>7</sup>, P. Cartigny<sup>8</sup>

7  
8 <sup>1</sup>Laboratoire Biogéosciences, UMR 6282, CNRS, Université Bourgogne Franche-Comté,  
9 21000 Dijon, France

10 <sup>2</sup>Université Clermont Auvergne, CNRS, Laboratoire Magmas et Volcans, F-63000 Clermont-  
11 Ferrand, France

12 <sup>3</sup>Laboratoire d'Ecologie des Hydrosystèmes Naturels et Anthropisés, UMR 5023, CNRS,  
13 Université de Lyon, 69622 Villeurbanne Cedex, France.

14 <sup>4</sup>140 South 700 East, Spanish Fork, Utah 84660, USA

15 <sup>5</sup>1134 Johnson Ridge Lane, West Jordan, Utah 84084, USA

16 <sup>6</sup>Department of Earth Science, Utah Valley Univ., Orem, Utah 84058, USA

17 <sup>7</sup>CNRS-UMR6538 Lab. Géosciences Océan, Université de Bretagne Occidentale, 29280  
18 Plouzané, France

19 <sup>8</sup>Institut de Physique du Globe de Paris, Sorbonne-Paris Cité, Univ. Paris Diderot, CNRS,  
20 75238 Paris Cedex 05, France

21

22 \*Corresponding author: [christophe.thomazo@u-bourgogne.fr](mailto:christophe.thomazo@u-bourgogne.fr)

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## 26 **Abstract**

27         The Early Triassic is generally portrayed as a time of various, high ecological stresses  
28 leading to a delayed biotic recovery after the devastating end-Permian mass extinction. This  
29 interval is notably characterized by repeated biotic crises (e.g., during the late Smithian),  
30 large-scale fluctuations of the global carbon, nitrogen and sulfur cycles as well as harsh  
31 marine conditions including a combination of ocean acidification, anoxia, extreme seawater  
32 temperatures and shifting productivity. Observations from different paleolatitudes suggest  
33 that sulfidic (H<sub>2</sub>S-rich) conditions may have developed widely during the Early Triassic,  
34 possibly reaching up to ultra-shallow environments in some places. However, the existence  
35 and the spatio-temporal extent of such redox swings remain poorly constrained. In order to  
36 explore Early Triassic paleoceanographic redox changes and their potential influences on the  
37 biotic recovery, we analyzed multiple sulfur isotopes (<sup>32</sup>S, <sup>33</sup>S, <sup>34</sup>S, and <sup>36</sup>S) of sedimentary  
38 pyrite and carbonate associated sulfate ( $\delta^{34}\text{S}_{\text{CAS}}$ ) from the Mineral Mountains section, Utah.  
39 Sediments from this section were mainly deposited in shallow waters and span the Smithian  
40 and lower Spathian. We report a 68‰ range of variations in  $\delta^{34}\text{S}_{\text{py}}$  associated with  $\Delta^{33}\text{S}_{\text{py}}$   
41 varying from -0.01‰ to +0.12‰, whereas the  $\delta^{34}\text{S}_{\text{CAS}}$  varies between +19.5‰ and +34.8‰.  
42 We interpret the observed signal of multiple sulfur isotopes as reflecting the operation of  
43 pore-water syndimentary microbial sulfate reduction in open system with respect to sulfates  
44 before the late Smithian, evolving to a closed system, sulfate limited, Rayleigh-type  
45 distillation across the Smithian/Spathian boundary (SSB) and immediately after the SSB. We  
46 argue that this marked change is driven by the effectiveness of the connection between the  
47 sedimentary pore waters and the overlying water column, which is, in our case, controlled by  
48 the local sedimentological conditions such as the bioturbation intensity and the sedimentation  
49 rate. Therefore, our results suggest that changes in the sulfur cycle before and across the SSB  
50 at Mineral Mountains is probably a local consequence of the loss of the mixed sedimentary

51 layer during the late Smithian extinction event, as opposed to reflecting the development of a  
52 lethal anoxic ocean at the global scale.

53

## 54 **1. Introduction**

### 55 *1.1. Smithian and Smithian/Spathian boundary events*

56 The recovery of marine and terrestrial ecosystems after the end-Permian mass  
57 extinction (EPME, ~252 Ma) is usually described as a slow and delayed process resulting  
58 from the effects of sustained or recurrent environmental stresses during the Early Triassic,  
59 such as extreme climatic warmings (Sun et al., 2012; Romano et al., 2013), intensified water-  
60 column stratifications (Horacek et al., 2007; Song et al., 2013) and expansions of oceanic  
61 oxygen-minimum zones (Algeo et al., 2010, 2011; Winguth and Winguth, 2012). Although  
62 oxygen deficiency was probably a major biotic stressor in the thermocline and deep-ocean,  
63 shallow-marine environments were generally well-oxygenated except for brief anoxic  
64 episodes (Algeo et al., 2007, 2008; Beatty et al., 2008; Zonneveld et al., 2010). Specifically,  
65 extremely harsh environmental conditions were suggested during the late Smithian (~1.4 Ma  
66 after the Permian/Triassic boundary, PTB; Galfetti et al., 2007a) as this short time interval  
67 (~100 kyr, Brühwiler et al., 2010) records a severe extinction of the nekton (e.g., Orchard,  
68 2007, Brayard et al., 2006, 2009; Stanley, 2009). Major disturbances in the global carbon  
69 cycle in the Smithian and through the Smithian/Spathian boundary (SSB) are documented by  
70 a strong negative-positive couplet of carbon isotope excursions respectively before and during  
71 the late Smithian. This couplet of excursions is documented worldwide in both carbonate  
72 ( $\delta^{13}\text{C}_{\text{carb}}$ ) and organic ( $\delta^{13}\text{C}_{\text{org}}$ ) carbon reservoirs (Payne et al., 2004; Galfetti et al., 2007a and  
73 b; Tong et al., 2007; Horacek et al., 2009; Hermann et al., 2011; Clarkson et al., 2013;  
74 Komatsu et al., 2016; Fig. 1). However, the magnitude differs from section to section and  
75 depends on the reservoir that has been measured (e.g., Meyer et al., 2011; Grasby et al., 2013;

76 Song et al., 2013; Thomazo et al., 2016; Caravaca et al., 2017a). The negative shift is usually  
77 attributed to a massive light carbon input and/or a major reorganization of the exogenous  
78 global carbon cycle, such as a decrease in the organic carbon flux buried in the sedimentary  
79 record. The negative shift has thus been linked to an episodic large-scale injection into the  
80 atmosphere of volcanic CO<sub>2</sub> and thermogenic CH<sub>4</sub> from the Siberian Traps (Payne et al.,  
81 2004; Payne and Kump, 2007; Meyer et al., 2011; Sobolev et al., 2011). Alternatively, local  
82 processes such as early diagenetic reactions in pore water producing authigenic carbonates  
83 also probably participate to generate this signal (Thomazo et al., 2016; Zhao et al., 2016). The  
84 negative isotopic excursion is followed by an abrupt positive  $\delta^{13}\text{C}$  excursion of comparable  
85 magnitude beginning in the late Smithian and crossing the SSB. Such negative-positive  
86 swings in the carbon isotope record were suggested to characterize strong anoxic conditions  
87 (e.g., Retallack and Jahren, 2008; Song et al., 2012; 2014a). Positive covariation of this  
88 oscillation in the  $\delta^{13}\text{C}_{\text{carb}}$  signal with existing  $\delta^{34}\text{S}_{\text{CAS}}$  records has been interpreted to reflect  
89 changes in the burial rate of sedimentary sulfides during increased marine anoxia in an ocean  
90 with an extremely small sulfate reservoir (Song et al., 2010; 2014b). Late Smithian potential  
91 anoxic sediments were reported from various localities worldwide (e.g., Galfetti et al., 2008;  
92 Grasby et al., 2013) and anoxic conditions possibly reached ultra-shallow environments in  
93 some places (e.g., Wignall et al., 2016).

94 The late Smithian and the SSB are also marked by a major shift in climate, changing  
95 from hot to cool conditions (Sun et al., 2012; Romano et al., 2013). This event corresponds to  
96 major changes in marine and terrestrial organisms (Tozer, 1982; Dagys, 1988; Galfetti et al.,  
97 2007a and b; Hermann et al., 2011; Schneebli-Hermann et al., 2012), including for instance a  
98 severe drop in taxonomic richness and disparity among ammonoids (Stanley, 2009; Brayard  
99 et al., 2009; Brosse et al., 2013), and a major restructuring of their biogeographical  
100 distributions (e.g. Brayard et al., 2006, 2007; Jattiot et al., 2016). The late Smithian extinction



101 was at least of equal magnitude to the EPME for ammonoids (e.g., Brühwiler et al., 2010;  
102 Jattiot et al., 2016). However, recent works showed that in some shallow-water settings of the  
103 Panthalassa, environmental conditions were favorable to the development of diversified and  
104 complex ecosystems during the earliest Spathian, i.e., immediately after the SSB (Brayard et  
105 al., 2017).

106

### 107 *1.2. Potential underlying processes*

108 Carbon isotopic trends during the Smithian-Spathian transition have been interpreted  
109 in various ways. A first scenario suggests that emissions of  $^{12}\text{C}$ -enriched carbon dioxide  
110 associated with the Siberian Traps (Payne et al., 2004; Payne and Kump, 2007), causing an  
111 acidification, a warming trend and an oceanic anoxia (Galfetti et al., 2008; Grasby et al.,  
112 2013; Song et al., 2014a; Clarkson et al., 2016). The subsequent enhanced burial of  
113 isotopically light organic carbon in anoxic sediments would have generated the positive  $\delta^{13}\text{C}$   
114 trend documented across the SSB (Galfetti et al., 2007a). In a second model, Meyer et al.  
115 (2011) argued that the positive  $\delta^{13}\text{C}$  shift records an increased productivity in the water  
116 column thereby generating a steeper surface-to-deep isotopic gradient. In a third alternative,  
117 Horacek et al. (2007) interpreted the initial negative shift as reflecting the overturn of a  
118 previously well-stratified ocean water column causing the release of light dissolved inorganic  
119 carbon, derived from remineralized organic matter (OM) into the upper water column. Finally,  
120 local early diagenetic reactions in pore water producing  $^{12}\text{C}$ -enriched authigenic carbonates  
121 during the suboxic remineralization of OM due to microbial sulfate reduction have also been  
122 suggested (Thomazo et al., 2016; Zhao et al., 2016). All these hypotheses differ in their  
123 predictions on the relative timing of the carbon isotope excursions and anoxia. The scenario  
124 of Galfetti et al.'s (2007a) implies that anoxia developed concomitantly to the positive shift  
125 during the late Smithian; the Meyer et al.'s (2011) scenario corresponds to an anoxia peaking

126 later when  $\delta^{13}\text{C}$  reaches maximum values; the Horacek et al.'s (2007) model suggests that  
127 anoxia peaked just prior to the minimum in  $\delta^{13}\text{C}$ . Finally, the diagenetic hypothesis supports  
128 the synsedimentary co-occurrence of suboxic conditions and of the minimum  $\delta^{13}\text{C}$  values,  
129 which do not involve a water-column process. Therefore, the relationships between redox  
130 changes,  $\delta^{13}\text{C}$  fluctuations, and biotic events around the SSB needs further investigations and  
131 better discrimination between synsedimentary *versus* water-column chemical processes.

132

### 133 *1.3. The biogeochemical sulfur cycle, oceanic redox conditions and sulfur isotopes*

134 The biogeochemical sulfur cycle is a key process in regulating Earth's surface  
135 environment through the activity of several microbial metabolisms including primarily sulfate  
136 reduction, disproportionation, and sulfide oxidation. These metabolic activities transform the  
137 oxidation state of sulfur and are tightly linked to the global carbon cycle and climate, through  
138 the remineralization of organic carbon in marine sediments. The burial of oxidized (sulfate)  
139 relative to reduced (sulfide) minerals on the geological time scale, in marine sediments and  
140 sedimentary rocks, regulates marine redox conditions (Berner and Raiswell, 1983; Canfield,  
141 2001). The various microbial pathways that drive the sulfur cycle can be recognized using  
142 their diagnostic stable isotopic fractionations of sulfur species (Chambers et al., 1975; Fry et  
143 al., 1984; Canfield and Thamdrup, 1994; Habicht and Canfield, 1997; Habicht et al., 1998;  
144 Brunner and Bernasconi, 2005; Johnston et al., 2005a; Sim et al., 2011a, b). In modern  
145 environments, the isotopic compositions of aqueous sulfide and sulfate have been  
146 successfully used to demonstrate specific biological sulfur cycling activities (e.g. Canfield et  
147 al., 2010; Fike et al., 2008, 2009; Gomes and Hurtgen, 2013). In ancient sediments, the  
148 isotopic record of sulfur-bearing phases, predominantly sulfate minerals in the form of barite  
149 and CAS as well as sulfides in the form of pyrite, can be also used to trace sulfur metabolisms  
150 (Canfield and Teske, 1996; Shen et al., 2001; Johnston et al., 2005b; Philippot et al., 2007;

151 Leavitt et al., 2013) and to reconstruct the past ocean chemistry and oxidation state (Claypool  
152 et al., 1980; Canfield and Teske, 1996; Johnston et al., 2005b; Fike et al., 2006; Gill et al.,  
153 2007; Fike and Grotzinger, 2008; Hurtgen et al., 2009; Jones and Fike, 2013).

154 The two main components driving the long-term secular fluctuation of  $\delta^{34}\text{S}$  of sulfur  
155 species over geological time are variations in the net flux of sulfate reduced to sulfide,  
156 subsequently precipitated as pyrite in marine sediments, and the mean isotopic fractionation  
157 between marine sulfate and sedimentary pyrite produced during the microbial metabolic  
158 activities (Fike et al., 2015). For example, during times of increased pyrite burial enhanced by  
159 protracted marine anoxia, the  $\delta^{34}\text{S}$  of marine sulfates would increase generating a positive  
160 isotopic excursion imprint in both sulfate and sulfide reservoirs. Modulation of sedimentary  
161 sulfides burial can also influence the size of the oceanic dissolved sulfate reservoir, and hence,  
162 the kinetic of sulfur isotope variations (Bottrell and Newton, 2006). When the oceanic sulfate  
163 reservoir is small, rapid  $\delta^{34}\text{S}$  variations can thus be driven by relatively small flux imbalances.

164 Meanwhile, depositional environment and sediment remobilization can have  
165 considerable impacts on the isotopic composition of both pore water and sedimentary sulfate  
166 and sulfide phases (Aller et al., 2008, 2010). Bioturbation and the local sedimentation rate can  
167 also impact the sulfur isotope records by decoupling the evolution of sedimentary pyrite  $\delta^{34}\text{S}$   
168 to the overlying water column (Pasquier et al., 2017). Moreover, both sulfate and pyrite sulfur  
169 isotope signals can be muted during diagenesis. Record of the  $\delta^{34}\text{S}_{\text{CAS}}$  can notably be altered  
170 by circulating fluids (e.g., meteoric fluids) during diagenetic secondary carbonate  
171 precipitation and can obscure the signal of the primary oceanic sulfate isotopic composition.  
172 Additionally, post-depositional processes can impact the  $\delta^{34}\text{S}_{\text{py}}$  records. For instance,  $\delta^{34}\text{S}_{\text{py}}$   
173 signatures can be overprinted during late-stage diagenesis when sulfide-bearing fluids migrate  
174 through strata that contain reactive iron (Fike et al., 2015). Due to these various possible  
175 secondary imprints on the sedimentary sulfur isotope signals, a full characterization of the

176 depositional environment in which the sample formed is mandatory, as well as an evaluation  
177 of its connection to the open ocean, and of its diagenetic history (Fike et al., 2015).

178 In addition to the  $\delta^{34}\text{S}$  record of sulfur species, the measurement of multiple sulfur  
179 isotopes (MSI) recently becomes increasingly important to further constrain the Phanerozoic  
180 evolution of the biogeochemical sulfur cycle (Wu et al., 2010), as well as in modern  
181 environments (e.g., Tostevin et al., 2014). The use of pyrite  $\delta^{33}\text{S}$  in addition to  $\delta^{34}\text{S}$  can  
182 provide additional ways to evaluate the involvement of different sulfur metabolisms, as well  
183 as variations in sulfur fluxes through geologic time (Johnston et al., 2005a, 2005b, 2007,  
184 2008a, b; Ono et al., 2006; Li et al., 2010; Wu et al., 2010; Zerkle et al., 2010; Shen et al.,  
185 2011; Leavitt et al., 2013; Sansjofre et al., 2016). Furthermore, MSI is a robust tool to  
186 investigate Phanerozoic paleoredox conditions even when the pyrite and contemporaneous  
187 seawater sulfate  $\delta^{34}\text{S}$  measurements are not paired in the same samples (Shen et al., 2011;  
188 Zhang et al., 2015, 2017; Saitoh et al., 2017). For paleoenvironmental reconstructions,  
189 measurements of minor sulfur isotopes ( $^{33}\text{S}$  and  $^{36}\text{S}$ ) can provide additional information on  
190 local and global processes and can be helpful for differentiating between these two cases  
191 (Johnston et al., 2006; Saitoh et al., 2017).

192 Therefore, the MSI composition of seawater sulfates and precipitated sulfides (i.e.,  
193 pyrite) can be an important proxy to discuss the Smithian-Spathian transition processes.  
194 Previous studies focusing on this time interval and aiming to reconstruct the biogeochemical  
195 sulfur cycle were based on analyses of pyrite framboids and trace metal elements from South  
196 China (Tian et al., 2014; Sun et al., 2015), iron mineral speciation from the Arabian margin  
197 (Clarkson et al., 2016), carbonate associated sulfate (CAS)  $\delta^{34}\text{S}$  signal from South China  
198 (Zhang et al., 2015) and the western USA (Marenco et al., 2008), sulfide  $\delta^{34}\text{S}$  signal from  
199 Japan (Takahashi et al., 2013), barite and evaporite  $\delta^{34}\text{S}$  signal from Italy (Cortecci et al.,  
200 1981; Horacek et al., 2010), and paired sulfur isotopes (CAS and pyrite) signals from South

201 Central China (Song et al., 2014b). Although the CAS  $\delta^{34}\text{S}$  values in recent sediments are in  
202 agreement with the sulfur isotopic composition of modern seawater sulfates (Lyons et al.,  
203 2004), and while the record of ancient carbonates is more complete than the record of marine  
204 evaporites, the fidelity of CAS signals in rocks that have undergone variable degrees of  
205 secondary processes (e.g., early or burial diagenesis, hydrothermal alteration) needs to be  
206 carefully testified for each measured section and sample (Present et al., 2015). For instance,  
207 Marengo et al. (2008) performed  $\delta^{34}\text{S}_{\text{CAS}}$  measurements on samples from the Early Triassic  
208 Moenkopi Formation of the Sonoma Foreland (western USA) basin and showed that an  
209 alteration of the isotopic signal during late stage dolomitization could not be fully excluded.

210 In this study, we test the existence of anoxia during the late Smithian and its  
211 relationships with the Smithian-Spathian  $\delta^{13}\text{C}$  curve by measuring the MSI of sedimentary  
212 sulfides and  $^{34}\text{S}/^{32}\text{S}$  sulfur isotopes of CAS in the shallow water deposits of the Mineral  
213 Mountains section, Utah, USA. This section has been previously studied for its sedimentary  
214 and fossil contents, as well as for its paired carbon isotope signal (Brayard et al., 2011, 2015;  
215 Hofmann et al., 2014; Vennin et al., 2015; Thomazo et al., 2016). We discuss results of our  
216 sulfur isotope analyses in the light of detailed sedimentological constraints on depositional  
217 environments, within global C cycle perturbations typical of the late Smithian and SSB, to  
218 provide new insights into the nature of oceanic and sedimentary environmental changes at  
219 that time.

220

## 221 **2. Geological setting**

### 222 *2.1. The Sonoma Foreland Basin*

223 During the Permian-Triassic transition, the Sonoma orogeny led to the formation of  
224 the Sonoma Foreland Basin (SFB) (Fig. 2; Burchfiel and Davis, 1975; Ingersoll, 2008;  
225 Dickinson, 2013; Caravaca et al., 2017b). This sedimentary basin extends from the modern

226 states of Idaho and Wyoming to Utah and eastern Nevada. The SFB was located in the  
227 northern intertropical zone on the western Pangea margin during the Early Triassic (Fig. 2).  
228 The SFB shows detailed and well-preserved Lower Triassic fossil and sedimentary records  
229 with mainly transitional continental/marine terrigenous conglomerates and sandstones of the  
230 Moenkopi Group to shallow marine carbonates of the Thaynes Group (e.g., Kummel, 1954,  
231 1957, Paull and Paull, 1993; Lucas et al., 2007). A robust, high-resolution, Smithian  
232 biostratigraphic framework based on ammonoids is available for most parts of the basin  
233 (Brayard et al., 2009, 2013; Jattiot et al., 2016, 2017; Jenks and Brayard, 2018).

234

## 235 2.2. *The Mineral Mountains section*

236 The alternating carbonates and marls of the Lower Triassic Thaynes Group (*sensu*  
237 Lucas et al., 2007) reflect sedimentary deposition in epicontinental marine environments and  
238 rest unconformably on middle to upper Permian rocks with a major sedimentary hiatus  
239 corresponding to the Permian-Triassic transition (e.g., McKee, 1954; Collinson et al., 1976).  
240 In western and central Utah, the late Permian, Griesbachian and Dienerian are usually not  
241 observed. The historical middle and late Smithian time markers of the Thaynes Group within  
242 the SFB are respectively the *Meekoceras* and *Anasibirites* ammonoid zones, but these zones  
243 can be further subdivided (see discussion in Brayard et al., 2009, 2013; Jattiot et al. 2016;  
244 Jenks and Brayard, 2018).

245 The present study has been carried out on the Smithian to Spathian sedimentary  
246 succession in the Mineral Mountains, thoroughly described for its sedimentological  
247 characteristics by Vennin et al. (2015; Figs. 2, 3). The basal unit A mostly consists of  
248 microbially-dominated carbonates with sponge-microbe bioconstructions deposited on a  
249 mudflat inner ramp, intertidal to supratidal, environments evolving upward into bioclastic  
250 sediments deposited in tidal-dominated shoreface environments. Mudstone-rich sediments of

251 the unit B are finely laminated and reflect homogenous upper offshore depositional conditions  
252 of outer to mid-ramp environments. They were episodically influenced by storm-induced  
253 events (Fig. 3). The unit including the SSB (“unit SSB”) is composed of marls representing  
254 outer ramp, lower offshore, environments. This unit corresponds to the deepest deposits,  
255 below the storm wave base. The overlying unit C evolves from mudstones deposited in outer  
256 ramp (with local storm-induced deposits) to subtidal microbial carbonates deposited in outer  
257 to mid ramp environments. The evolution prior to the SSB unit thus shows a progressive  
258 deepening, whereas the lower Spathian corresponds to shallowing-upward conditions.

259         The local ammonoid biostratigraphy has been described in Brayard et al. (2011, 2013).  
260 The unit A is early Smithian in age (“*Vercherites undulatus* beds”; *V.u.* in Fig. 3). The unit B  
261 is latest early to middle Smithian in age (*Inyoites beaverensis* and *Owenites* beds,  
262 respectively; *I.b.* and *O.* in Fig. 3; Unitary Association Zones UAZ<sub>3</sub> and UAZ<sub>4</sub> in Jattiot et al.,  
263 2017). The SSB unit mainly corresponds to the late Smithian with the occurrence of typical  
264 prionitid and xenoceltitid ammonoid assemblages (*A.m.* and *Xe.* in Fig. 3; UAZ<sub>5</sub> and UAZ<sub>6</sub> in  
265 Jattiot et al., 2017). Although Spathian beds are not well identified above these late Smithian  
266 assemblages, the first Spathian dominant fauna likely corresponds to a regional bivalve bloom  
267 (Brayard et al., 2013; Hofmann et al., 2014).

268         The Early Triassic is marked by a global long-term rise in sea level with several  
269 second- and third-order transgressive-regressive (T–R) sequences (Haq et al., 1987). Within  
270 the SFB, a Spathian T-R cycle is recognized together with two older T-R cycles that  
271 developed during the Griesbachian–Dienerian and the Smithian (e.g., Paull and Paull, 1993;  
272 Lucas et al., 2007). The Smithian transgression proceeded southward in a complex pathway  
273 resulting from the multifaceted subsidence of the basin and paleotopographic highs within  
274 and on each side of the basin (e.g. Lucas et al., 2007; Caravaca et al., 2017b). The maximum  
275 extent of this transgression within the basin was reached during the late Smithian (Paull and

276 Paull 1993; Lucas et al., 2007; Brayard et al., 2013). It corresponds to the deepest  
277 environmental conditions recorded at Mineral Mountains, i.e., the unit SSB (Vennin et al.,  
278 2015).

279

### 280 **3. Methods**

281 A total of 34 bulk rock samples of the Mineral Mountains section were investigated  
282 for their major and trace elements, carbonate carbon isotopes, sulfide major ( $^{32}\text{S}$ ,  $^{33}\text{S}$ ) and  
283 minor ( $^{33}\text{S}$ ,  $^{36}\text{S}$ ) sulfur isotopes and CAS major sulfur isotopes (Table 1). All measurements  
284 were performed on bulk rock samples which were at start powdered to  $< 60 \mu\text{m}$  using a ring  
285 and puck mill at the Biogéosciences Laboratory, Dijon, France.

286

#### 287 *3.1. Carbonate carbon isotopes*

288 Carbonate carbon isotope analyses ( $\delta^{13}\text{C}_{\text{carb}}$ ) were carried out at the Biogéosciences  
289 Laboratory, Dijon, France. The samples (90 to 300  $\mu\text{g}$ ) were loaded into septum screwed  
290 glass tubes, flushed via the autosampler with He to remove atmospheric gases. Each sample  
291 was reacted with 500  $\mu\text{l}$  of  $>100\%$  phosphoric acid at  $90^\circ\text{C}$  for 17 min using an online  
292 carbonate preparation line coupled to an IsoPrime stable isotope ratio mass spectrometer  
293 (Isoprime, Manchester, UK). Inorganic carbonate content was quantified manometrically  
294 from the  $\text{CO}_2$  yield; all isotopic values are reported in the standard  $\delta$ -notation in permil ( $\text{‰}$ )  
295 relative to VPDB by assigning a  $\delta^{13}\text{C}$  value of  $+1.95\text{‰}$  to the NBS19 international standard.  
296 The long-term reproducibility of the NBS19 replicate analyses (three months) is better than  $\pm$   
297  $0.09\text{‰}$  ( $1\sigma$ ) for carbon isotopes.  $\text{H}_3\text{PO}_4$  blank tests were performed and evolved  $\text{CO}_2$  was  
298 below the detection limit of our online-IRMS system.

299



300 3.2. Sulfide isotopes

301 Sulfide sulfur was retrieved using a conventional wet chemical extraction at the  
 302 Biogéosciences Laboratory, Dijon, France. Acid volatile sulfide (AVS), representing  
 303 monosulfides, and chromium reducible sulfur (CRS) consisting primarily of pyrite were  
 304 extracted sequentially. First, AVS was liberated using cold concentrated HCl for 2 hours. If  
 305 any, resulting hydrogen sulfide was precipitated as Ag<sub>2</sub>S with a 0.3 M AgNO<sub>3</sub> solution.  
 306 Subsequently, CRS was released using a hot and acidic 1.0 M CrCl<sub>2</sub> solution (Canfield et al.,  
 307 1986). The resulting H<sub>2</sub>S was precipitated as Ag<sub>2</sub>S. After centrifugation, the silver sulfide  
 308 precipitate was washed several times with deionized distilled water and dried at 50°C for 48  
 309 hours in an oven and weighted. Mass balance was used to calculate the amount of AVS and  
 310 CRS. Concentrations in ppm are reported individually in Table 1 (note that monosulfides  
 311 were below the detection limit in all samples). The silver sulfides were then fluorinated to  
 312 produce SF<sub>6</sub> and analyzed for their multiple sulfur isotope compositions at the Stable Isotope  
 313 Laboratory of the Institut de Physique du Globe de Paris, France. The isotope compositions  
 314 were determined by dual-inlet gas-source mass spectrometry monitoring ion beams at m/z of  
 315 127, 128, 129, and 131 using a ThermoScientific MAT 253 gas source mass spectrometer  
 316 (Labidi et al., 2012). Sulfur isotope ratios are reported in conventional delta notation with  
 317 respect to VCDT as Eq. (1):

$$318 \quad \delta^{3i}S = \left( \frac{\left( \frac{{}^{3i}S}{{}^{32}S} \right)_{sample}}{\left( \frac{{}^{3i}S}{{}^{32}S} \right)_{V-CDT}} - 1 \right) \times 1000 \quad (1)$$

319 where *i* is either 3, 4 or 6;

320 and as Eqs. (2) and (3) for capital delta notation (following Johnston et al., 2008a):

$$321 \quad \Delta^{33}S = \delta^{33}S - 1000 \cdot \left( \left( 1 + \frac{\delta^{34}S}{1000} \right)^{0.515} - 1 \right) \quad (2)$$

322 
$$\Delta^{36}S = \delta^{36}S - 1000 \cdot \left( \left( 1 + \frac{\delta^{34}S}{1000} \right)^{1.90} - 1 \right) \quad (3)$$

323 The  $\delta^{34}S$  values are presented with an analytical reproducibility of  $\leq 0.1\text{‰}$ . We used values for  
324 IAEA-S2 on the Vienna Cañon Diablo Troilite (VCDT) normalization of 5.224‰, 0.030‰  
325 and  $-0.203\text{‰}$  for  $\delta^{34}S$ ,  $\Delta^{33}S$ , and  $\Delta^{36}S$ , respectively. Based on duplicate and triplicate  
326 analyses, uncertainties on  $\Delta^{33}S$  and  $\Delta^{36}S$  values by the SF<sub>6</sub> technique are estimated at 0.01‰  
327 and 0.2‰ in 2 $\sigma$ , respectively.

328 Ten samples have been successfully cross calibrated (Table 1, Fig. 4) for their  $\delta^{34}S_{py}$   
329 with measurements performed at the Biogéosciences Laboratory, Dijon, France, on SO<sub>2</sub>  
330 molecules via combustion of ~500  $\mu\text{g}$  of silver sulfide homogeneously mixed with an equal  
331 amount of tungsten trioxide using a Vario PYRO cube (Elementar GmbH) connected online  
332 via an open split device to an IsoPrime IRMS system (Isoprime, Manchester, UK).  
333 International standards IAEA-S-1, IAEA-S-2 and IAEA-S-3 were used for calibration  
334 assuming  $\delta^{34}S$  values of  $-0.3\text{‰}$ ,  $+22.7\text{‰}$  and  $-32.3\text{‰}$  (VCDT), respectively. Analytical  
335 reproducibility was better than  $\pm 0.3\text{‰}$  (1 $\sigma$ ) based on replicates for standard materials and  
336 samples.

337

### 338 3.3. CAS sulfur isotopes

339 CAS sulfur was retrieved using a wet chemical extraction at the Laboratory  
340 Géosciences Océan, Brest, France. Fifty grams of carbonate samples (with carbonate contents  
341 typically  $>70\text{ wt. \%}$  of the total rock) were powdered, soluble sulfates being leached by a 1.7  
342 M NaCl solution for 4 hours, followed by four rinses in deionized water. This step was  
343 repeated five times and the powder was then dissolved in 4 N HCl (12 h). The acidified  
344 samples were then filtered, on a 0.45- $\mu\text{m}$  nitrocellulose paper and an excess of 250 g.l<sup>-1</sup> of  
345 BaCl<sub>2</sub> solution was added to the filtrate to precipitate BaSO<sub>4</sub>. After centrifugation, the barium

346 sulfate precipitate was washed several times with deionized distilled water and dried at 60°C  
347 for 24 hours in an oven.  $\delta^{34}\text{S}$  measurements were performed at the Biogéosciences Laboratory,  
348 Dijon, France, on  $\text{SO}_2$  molecules via combustion of ~500  $\mu\text{g}$  of barium sulfate  
349 homogeneously mixed with 1/3 of vanadium pentoxide using a Vario PYRO cube (Elementar  
350 GmbH) connected online via an open split device to an IsoPrime IRMS system (Isoprime,  
351 Manchester, UK). International standard NBS 127 was used for calibration assuming a  $\delta^{34}\text{S}$   
352 value of +20.3‰ on the VCDT scale. Isotope results are reported in the standard delta  
353 notation against the Vienna Cañon Diablo Troilite standard (VCDT). Analytical  
354 reproducibility was better than  $\pm 0.3\text{‰}$  ( $1\sigma$ ) based on replicates for standard materials.

355

#### 356 *3.4. Major and trace elements*

357 Major and trace elements analyses were performed on selected samples by ICP-MS at  
358 the Activation Laboratory (Actlabs) in Ancaster, Canada. The method used is Lithium  
359 Metaborate/Tetraborate Fusion ICP and ICP-MS. Reproducibility was estimated by seven  
360 replicate analyses of laboratory standards, and is better than 2% ( $1\sigma$ ) for major and trace  
361 elements.

362

#### 363 *3.5. Petrographic observations*

364 Photonic observations of Mineral Mountains samples were performed using a Leica  
365 MZ205c at the Biogéosciences Laboratory, Dijon. High-resolution images were obtained with  
366 a JEOL JSM 6400F Field Emission SEM equipped with an Oxford INCA Energy 300 X-ray  
367 Energy Dispersive Spectrometer (EDS) system for all chemical analyses at the ARCEN  
368 platform (Laboratory Institut Carnot de Bourgogne in Dijon, Université de Bourgogne,  
369 France). The thin sections were prepared for SEM analyses and were subsequently coated  
370 with ~10 nm of graphite using a High Resolution Ion Beam Coater GATAN 681. The high-

371 resolution images were taken in back-scatter electron imaging mode to enhance the  
372 compositional contrast. These facilities were used to identify rock textures and to examine  
373 pyrite morphologies in samples from the studied section.

374

## 375 **4. Results and discussion**

### 376 *4.1. Carbonate carbon isotopes*

377 Except for samples MI169, MI197, MI202 and MI209, the  $\delta^{13}\text{C}_{\text{carb}}$  values presented in  
378 this work have already been reported in Thomazo et al. (2016). All data are consistent with  
379 the expected  $\delta^{13}\text{C}_{\text{carb}}$  decrease (by  $\sim 3\text{‰}$ ) during the middle Smithian followed by an abrupt  
380 increase (of  $\sim 4\text{‰}$ ) through the late Smithian and the SSB (Fig. 3). Samples from the upper  
381 part of unit A and from unit B (from 50.8 to 104.2 m) display a significant correlation of the  
382  $\delta^{13}\text{C}_{\text{carb}}$  signal with the Mn content and Mn/Sr ratio (see figure 3 in Thomazo et al., 2016). In  
383 this work, we also observe a covariation between the  $\delta^{13}\text{C}_{\text{carb}}$  and the Mg/(Mg+Ca) ratios (Fig.  
384 5). There is however no covariation between the  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{org}}$  signals at MI throughout  
385 the units B, SSB and C (see figure 3 in Thomazo et al., 2016). Low  $\delta^{13}\text{C}_{\text{carb}}$  values ( $\sim -3\text{‰}$ )  
386 associated with high Mn/Sr and high Mg/(Mg+Ca) ratios are interpreted to reflect early  
387 diagenetic authigenic precipitation of dolomicrites within reducing, Mn-bearing,  $^{12}\text{C}$  enriched,  
388 fluids produced during the bacterially mediated degradation of OM close to the sediment  
389 water interface (Gilleaudeau and Kah, 2013; Schrag et al., 2013; Thomazo et al., 2016).

390

### 391 *4.2. Major and trace elements*

392 The Mg/(Mg+Ca) ratio varies from 0.01 to 0.13 with a mean value of  $0.04 \pm 0.03$  ( $1\sigma$ )  
393 (Table 1). The units A and B exhibit high ratios of  $0.05 \pm 0.03$  and  $0.05 \pm 0.02$  ( $1\sigma$ ),  
394 respectively. The unit C displays the lowest Mg/(Mg+Ca) ratio with an average of  $0.02 \pm 0.01$

395 (1 $\sigma$ ). Mg/(Mg+Ca) ratios decrease within the unit SSB (Fig. 3) and most likely provide a  
396 direct record of the relative amount of dolomicrite versus carbonates in the samples. Indeed,  
397 the carbonate concentration is strongly correlated to the sum of Ca plus Mg contents (Fig. 6, r  
398 = +0.90, p < 0.01, n = 32). The dolomitization most likely occurred early in the studied  
399 section leading to the formation of nano to micro-meter-sized granular structures, poorly  
400 preserved spherical dolomite and euhedral rhombs (Fig. 7A, 7B and 7C). Dolomite is often  
401 observed in association with sheet-like mat and microbial structures. The formation of these  
402 morphologies and structures has been interpreted as reflecting, microbially mediated, early  
403 precipitation of dolomites (Lin et al., 2017) and their evolution into crystalline dolomite may  
404 be explained by subsequent burial diagenesis (Rodriguez-Blanco et al., 2015).

405         The Mn/Sr ratio varies from 0.2 to 12.4 with a mean value of  $2.2 \pm 3.2$  (1 $\sigma$ ) (Table 1).  
406 The units A and C show the smallest ratios with average values of  $0.9 \pm 0.6$  and  $1.1 \pm 0.8$  (1 $\sigma$ ),  
407 respectively, whereas units B and SSB display highest ratios with respective average values  
408 of  $6.8 \pm 4.4$  and  $6.0 \pm 8.0$ . Samples MI97 to MI127 (from 56 to 107.7 m), encompassing the  
409 units B, SSB and the lowermost samples of the unit C (Fig. 3) show Mn/Sr values > 2. Due to  
410 the high responsiveness of the Mn/Sr ratio to record reducing fluids during diagenesis  
411 (Kaufman and Knoll, 1995), samples with Mn/Sr > 2 are considered here to have undergone  
412 significant water-rock interactions during early diagenetic secondary processes (Pakhomova  
413 et al., 2007; Thomazo et al., 2016).

414         Sulfur sulfide concentrations vary throughout the section, from 15 to 1329 ppm with a  
415 mean value of  $216 \pm 301$  ppm (1 $\sigma$ ) (Table 1). These concentrations vary over a short time  
416 scale and a well-defined trend across sedimentary deposits is not recognized. The Unit A  
417 shows the strongest variations encompassing the total range of values, with a mean value of  
418  $163 \pm 339$  ppm (1 $\sigma$ ). The microbial deposits from unit A are remarkably poor in sulfides  
419 (only  $48 \pm 25$  ppm; 1 $\sigma$ ) compared to calcarenite and siltstones from the same unit or samples

420 from overlying units. Unit B shows the highest mean value,  $474 \pm 290$  ppm ( $1\sigma$ ), while the  
421 unit SSB exhibits the lowest mean value,  $131 \pm 124$  ppm ( $1\sigma$ ). Concentrations in the unit C  
422 are similar to those of the unit A, with a mean value of  $206 \pm 257$  ppm ( $1\sigma$ ).

423 Only nine samples yielded enough materials for CAS quantification of sulfate contents.  
424 The concentrations vary from 23 to 72 ppm with a mean value of  $35 \pm 17$  ppm ( $1\sigma$ ). This  
425 dataset is restricted and we did not attempt to outline any special trend along the section.

426 The TOC concentrations show variations from 0.02 to 0.37 wt. % with a mean value  
427 of  $0.114 \pm 0.099$  wt. % ( $1\sigma$ ) (Fig. 3, Table 1). Units B, SSB and C exhibit similar TOC  
428 concentrations with average values of  $0.09 \pm 0.04$ , 0.06 and  $0.06 \pm 0.02$  wt. % ( $1\sigma$ ),  
429 respectively. Strongest variations in TOC content are observed in unit A and encompass the  
430 highest mean value:  $0.169 \pm 0.115$  wt. % ( $1\sigma$ ). Within this unit, the microbial deposits show a  
431 lower TOC concentration ( $0.04 \pm 0.026$  wt. %;  $1\sigma$ ) than the overlying calcarenite and  
432 siltstones ( $0.218 \pm 0.094$  wt. %;  $1\sigma$ ). A clear maximum in TOC content is documented atop  
433 the unit A, between MI72a and MI83 (Fig. 3). This maximum is associated with a negative  
434 carbon isotope shift in  $\delta^{13}\text{C}_{\text{carb}}$  (Fig. 3) and  $\delta^{13}\text{C}_{\text{org}}$  values (down to  $-30.46\text{‰}$ ; Thomazo et al.,  
435 2016). Given the shallow depositional settings and the absence of evidence for anoxia in the  
436 water column (Vennin et al., 2015; Thomazo et al., 2016), these features may be interpreted  
437 as corresponding to a major perturbation of the global carbon cycle. It can result from a  $\text{CO}_2$   
438 released from volcanogenic (Sobolev et al., 2011) or thermogenic sources (Payne and Kump,  
439 2007). However, changes in productivity and preservation of organic matter (i.e. the  
440 biological pump) due to increasing temperatures (Fig. 3; Sun et al., 2012; Romano et al.,  
441 2013) or changes in the relative contribution of the TOC between terrestrial and marine OM  
442 (Caravaca et al., 2017a) may also explain this signal.

443 The S/C ratio fluctuates from 0.02 to 1.56 with a mean value of  $0.38 \pm 0.45$  ( $1\sigma$ ) (Fig.  
444 3, Table 1). Units B, SSB and C show the highest ratios with values of  $0.69 \pm 0.37$ , 0.36 and

445  $0.69 \pm 0.36$  ( $1\sigma$ ), respectively. Excluding MI83 ( $S/C = 0.74$ ; similar to values observed in  
446 units B, SSB and C), unit A displays the lowest ratios with a mean of  $0.07 \pm 0.36$  ( $1\sigma$ ). S/C  
447 ratio fluctuations in the units B, SSB and C are controlled by variations in the S content,  
448 whereas unit A samples (except MI83) do not exhibit any covariation with either the TOC or  
449 S content. The behavior of the sulfur and carbon contents through the section suggest that the  
450 activity of microbial sulfate reduction (MSR) activity and ensuing sulfur sulfide precipitations  
451 were probably not limited by sedimentary OM availability.

452

### 453 *4.3. Sulfide MSI results*

454 The  $\delta^{34}\text{S}_{\text{py}}$  signal of sedimentary pyrites is highly variable with values ranging from -  
455  $21.2\text{‰}$  to  $+46.7\text{‰}$  (Fig. 3, Table 1). Positive values are recorded in units A, SSB and C. The  
456 unit A shows positive, little variable,  $\delta^{34}\text{S}_{\text{py}}$  values with an average isotopic composition of  
457  $12.2 \pm 5.0\text{‰}$  ( $1\sigma$ ). The unit B documents strictly negative  $\delta^{34}\text{S}_{\text{py}}$  values with an average  
458 isotopic composition of  $-14.2 \pm 6.8\text{‰}$  ( $1\sigma$ ). SSB samples yield positive  $\delta^{34}\text{S}_{\text{py}}$  values of  
459  $+22.9\text{‰}$  and  $+4.2\text{‰}$ . The unit C exhibits mostly positive  $\delta^{34}\text{S}_{\text{py}}$  values but cover an extended  
460 range of values ( $-3.0\text{‰}$  to  $46.7\text{‰}$ ) with short time scale variations (mean  $\delta^{34}\text{S}_{\text{py}}$  is  $4.5 \pm$   
461  $16.4\text{‰}$ ;  $1\sigma$ ; Fig. 3).

462 Overall, the  $\Delta^{33}\text{S}_{\text{py}}$  signal varies from  $-0.01\text{‰}$  to  $+0.12\text{‰}$  with an average value of  
463  $0.05 \pm 0.04\text{‰}$  ( $1\sigma$ ) (Fig. 3, Table 1). At its base, unit A shows values close to zero with an  
464 average isotopic composition of  $0.02 \pm 0.03\text{‰}$  (Table 1, Fig. 3). More positive values are  
465 recorded in units B, SSB and C with average values of  $0.08 \pm 0.03\text{‰}$ ,  $0.06 \pm 0.00\text{‰}$  and  $0.06$   
466  $\pm 0.04\text{‰}$  ( $1\sigma$ ), respectively. Small-scale variations of the  $\Delta^{33}\text{S}_{\text{py}}$  signal (from  $0.00\text{‰}$  to  
467  $0.12\text{‰}$ ) are recorded in unit C between 139.2 m and 148.3 m (Fig. 3). In this section, there is  
468 no evidence of secondary hydrothermal or metamorphic alteration of the MSI record based on

469 petrographic observations of the samples. Instead, the lack of covariation between the  $\delta^{34}\text{S}_{\text{py}}$   
470 and sulfides content in all units (Table 1) and the observation of pyrite ( $\text{FeS}_2$ ) in the form of  
471 framboids suggest that microbial sulfur cycling had a dominant role on the  $\delta^{34}\text{S}_{\text{py}}$  signal,  
472 rather than the influence of secondary processes such as thermochemical sulfate reduction  
473 (Machel et al., 1995).

474

#### 475 *4.4. Interpretations of the sulfide MSI signal*

476 Most previous studies focusing on the Smithian-Spathian transition considered the  
477 oceanic sulfur cycle under a steady state hypothesis where sulfides are precipitated after MSR  
478 under open-system conditions (here defined as oceanic sulfate supply > microbial sulfate  
479 reduction). However, at Mineral Mountains, this hypothesis cannot account for the high-  
480 magnitude (from  $-21.2\text{‰}$  to  $+46.7\text{‰}$ ) and rapid (probably  $\ll 50$  kyr; see Brühwiler et al.,  
481 2010) swings in  $\delta^{34}\text{S}_{\text{py}}$  values between the units A and B and between units B and SSB. The  
482 most positive  $\Delta^{33}\text{S}_{\text{py}}$  values (up to  $+0.12\text{‰}$ ) are also significantly above expected  $\Delta^{33}\text{S}_{\text{py}}$  under  
483 a steady state approximation (Wu et al., 2010). Instead, we suggest here that the observed  
484 high-magnitude and rapid swings in  $\delta^{34}\text{S}_{\text{py}}$  values can reflect deviations from the canonical  
485 Phanerozoic  $\delta^{34}\text{S}_{\text{py}}$  value ( $-20\text{‰}$ ) produced under steady state open-system conditions (as  
486 observed in unit B) to either (i) a Rayleigh-type distillation of the residual pore water sulfate  
487 pool, or (ii) a partial or complete re-oxidation of the reduced sulfur pools produced during  
488 MSR (units A, SSB and C) (see Fike et al., 2015 and references therein). Taking into account  
489 the positive  $\delta^{34}\text{S}_{\text{py}}$  values in units A, SSB and C, hypotheses (i) and (ii) have fundamentally  
490 different paleoenvironments implications. If a Rayleigh distillation drove increasing  $\delta^{34}\text{S}_{\text{py}}$   
491 values, this implies that the residual sulfate pool might have evolved during the course of  
492 sulfate reduction in a closed system with a disconnection between the pore water and the



493 overlying seawater (Fike et al., 2015). On the contrary, pyrites with heavy  $\delta^{34}\text{S}$  that  
494 precipitated in shallow marine settings characterized by frequent and repeated abiotic  
495 oxidative reworking due to physical (e.g., through storm or tide activity) or biological (e.g.  
496 bioturbation) mixing of sediments can be produced during abiotic oxidation of sulfides  
497 (fractionation up to 5‰; Fry et al., 1988). The pyrite  $^{34}\text{S}$  enrichment is in this case controlled  
498 by unsteady diagenetic processes and primarily reflects the efficiency of solute diffusion  
499 (pumping) and re-precipitation (refluxing) in the suboxic zone (Aller et al., 2008, 2010; Gao  
500 et al., 2013). Transport conditions and sedimentary dynamics indeed play a major role on the  
501 observed sulfur isotope pattern by promoting exchanges of sulfur and iron pools between the  
502 reduced deep layers and oxidized surface layers of unconsolidated sediments as shown in both  
503 the modern (Aller et al., 2010) and the geological sedimentary record (Pasquier et al., 2017).  
504 This process can result in geochemical records that preserve small or negative isotopic offsets  
505 between sulfate and sulfide (Sansjofre et al., 2016); these differences can be substantially less  
506 than the isotopic fractionation associated with microbial sulfur cycling in sediments (Fike et  
507 al., 2015). Finally, observed swings in  $\delta^{34}\text{S}_{\text{py}}$  values can also reflect variations in the  
508 fractionation with reduced MSR  $\epsilon^{34}$  associated with lowering sulfate concentrations or  
509 increasing cell-specific reduction rates (Leavitt et al., 2013).

510 In order to discriminate among these mechanisms, the use of the minor isotope of  
511 sulfur ( $^{33}\text{S}$ ) in combination with the  $\delta^{34}\text{S}_{\text{py}}$  signal has been previously successfully applied to  
512 various Phanerozoic sediments by some authors (e.g. Shen et al., 2011; Zhang et al., 2015,  
513 2017; Saitoh et al., 2017). MSI analyses were first applied to the EPME context by Shen et al.  
514 (2011). They analyzed carbonate rocks across the PTB at the GSSP Meishan section, South  
515 China and based on a negative  $\Delta^{33}\text{S}_{\text{py}}$  shift, they suggested that the episodic shoaling of  
516 anoxic deep-water caused the EPME. Recently, Zhang et al. (2015) analyzed the quadruple  
517 sulfur isotopic composition of carbonates across the end-Guadalupian extinction from two

518 sections in South China. They also suggested that the shoaling of sulfidic deep-waters  
519 contributed to this extinction based on negative  $\Delta^{33}\text{S}_{\text{py}}$  signatures. Both studies interpreted  
520 negative  $\Delta^{33}\text{S}_{\text{py}}$  signals as indicating the mixing of  $^{34}\text{S}$ -enriched and  $^{34}\text{S}$ -depleted sulfur from  
521 two different sources. The shutdown of bioturbation in the sediments caused by shoaling of  
522 toxic (anoxic/sulfidic) deep-waters was put forward to support this interpretation. However,  
523 this inference was challenged by Saitoh et al. (2017). Based on an additional MSI record of  
524 the end-Guadalupian event at Chaotian, China, these authors proposed that in shallow marine  
525 limestones deposited in oxic conditions, a negative  $\Delta^{33}\text{S}_{\text{py}}$  shift can be also recorded and  
526 reflects the mixing of two distinct types of pyrites precipitating from MSR in an open and  
527 closed system. They subsequently suggested that bioturbation at Chaotian promoted MSR and  
528 enhanced pyrite burial within the sediments. Thus, while these studies both agreed on the  
529 mixing of different pools of sulfides to account for observed negative  $\Delta^{33}\text{S}_{\text{py}}$  shifts, the link  
530 with the bioturbation intensity and ensuing redox conditions was interpreted in opposite ways.

531 In the frame of these previous works, we report here the first MSI record across the  
532 Smithian and the SSB (Fig. 8). The measured MSI correlate remarkably with the  
533 lithostratigraphic units of the Mineral Mountains section and its  $\delta^{13}\text{C}_{\text{carb}}$  record (Fig. 3). We  
534 notably document steadily high  $\Delta^{33}\text{S}_{\text{py}}$  values associated with low negative  $\delta^{34}\text{S}_{\text{pyr}}$  in unit B,  
535 while unit A shows low  $\Delta^{33}\text{S}_{\text{py}}$  values associated with positive  $\delta^{34}\text{S}_{\text{py}}$ . In the units SSB and C,  
536 the  $\Delta^{33}\text{S}_{\text{py}}$  signal remains high and is associated with positive  $\delta^{34}\text{S}_{\text{py}}$ . Strong small-scale  
537 fluctuations of the MSI signal are recorded in the unit C (Fig. 3).

538 *In vitro* laboratory experiments have shown that the MSI values of hydrogen sulfide  
539 produced during MSR under non-limiting sulfate conditions is higher in  $\Delta^{33}\text{S}_{\text{py}}$  and lower in  
540  $\delta^{34}\text{S}_{\text{py}}$  compared to the substrate (Johnston et al., 2007; Sim et al, 2011a, 2011b). Therefore,  
541 the high  $\Delta^{33}\text{S}_{\text{py}}$  values associated with low negative  $\delta^{34}\text{S}_{\text{py}}$  values of unit B (data in quadrant II

542 of figure 8) relative to contemporaneous seawater sulfate estimated by model calculation (Wu  
543 et al., 2010) is consistent with sulfate reduction in an open system (i.e. sulfate supply > sulfate  
544 reduction) with respect to sulfate. This is supported by evidence that most sulfides of unit B  
545 are small pyrite framboids (Fig. 7C) congruent with MSR activity. Moreover, the likely  
546 absence of an anoxic water column (Thomazo et al., 2016) and the abundant occurrences of  
547 bioturbations and storm events (Figs. 3, 7A) recorded during the deposition of the unit B  
548 suggest that pyrites precipitated syngedimentarily and that sediments were continuously  
549 replenished in sulfates. In other words, the connectivity of the sedimentary pore water, where  
550 MSR proceeded with the overlying water column, was probably strong during the deposition  
551 of unit B. This MSI signal corresponds to an open system sulfate reduction. We hypothesize  
552 that this connection was favored by a sustained sedimentary remobilization. Additionally, we  
553 estimate that sulfur isotope fractionations during MSR in the unit B of Mineral Mountains  
554 reflect values of  $^{34}\epsilon$  and  $^{33}\lambda$  of 44.8‰ and 0.512, respectively, based on the sedimentary  
555 sulfides and seawater sulfate isotopic compositions proposed by Wu et al. (2010; Fig. 8).

556 The  $\delta^{34}\text{S}_{\text{py}}$  values of the unit SSB and most of unit C show highly positive values  
557 associated with positive  $\Delta^{33}\text{S}_{\text{py}}$  (Fig. 3, Table 1). These data mostly occurred in the quadrant I  
558 of the figure 8 and fall above the regression line expected during open-system MSR.  
559 Therefore, these positive  $\delta^{34}\text{S}_{\text{py}}$  and  $\Delta^{33}\text{S}$  values cannot be solely explained by variations in  
560 MSR (a decrease in the MSR fractionation being accompanied by a decrease in the  $\Delta^{33}\text{S}$   
561 signal; Bradley et al., 2016) or sulfur disproportionation activities (Shen et al., 2011; Sim et  
562 al., 2015; Zhang et al., 2015). In order to infer potential underlying mechanisms, we  
563 superimposed on figure 8 (i) the mixing line of the sedimentary sulfide and seawater sulfate  
564 endmembers, as well as the expected isotopic compositions of accumulative sulfides  
565 produced during sulfate reduction in a closed system. Arrows in figure 8 show the evolution  
566 of the residual sulfate and instantaneous sulfides during a closed-system Rayleigh distillation.

567 Isotopic data from the unit SSB and the lower part of unit C are largely consistent with the  
568 range of values in a closed system Rayleigh distillation (including the mixing line between  
569 accumulative sulfides and open system sulfides, Fig. 8). Importantly, they cannot be  
570 explained by the mixing of sulfides produced during sulfate reduction in an open system and  
571 produced during quantitative sulfate reduction in a closed system. Moreover, very highly  $^{34}\text{S}$ -  
572 enriched (and positive  $\Delta^{33}\text{S}_{\text{py}}$ ) sulfides in parts of units SSB and C may reflect (i) the  
573 evolution of the residual sulfate reservoirs from which sulfides precipitated and subsequent  
574 MSR, or (ii) the precipitation of super heavy pyrite (i.e.,  $\delta^{34}\text{S}_{\text{py}} > \delta^{34}\text{S}_{\text{CAS}}$ ). Both of these  
575 hypotheses are in accordance with a closed-system Rayleigh distillation model. However, we  
576 cannot fully exclude here that the heaviest pyrite signal also reflect an  $\text{H}_2\text{S}$  pool produced  
577 under low sulfate concentration, where some of the  $\text{H}_2\text{S}$  would have been partially oxidized  
578 under aerobic conditions with an attendant effect resulting in sulfate that is lighter than the  
579  $\text{H}_2\text{S}$  available for capture as pyrite (Ries et al., 2009). Further analyses using secondary-ion  
580 mass spectrometry will help to better address cumulative *versus* instantaneous isotopic effects  
581 associated with these processes in a future study. The sulfides of the units SSB and C are  
582 pyrite framboids of various sizes (Figs. 7E and 7F) consistent with MSR activity. According  
583 to the record of trace elements (Thomazo et al., 2016), these sediments were deposited under  
584 oxic conditions. A collapse in bioturbation and storm event occurrences are visible during the  
585 late Smithian and at the SSB (Figs. 2, 5D). We therefore suggest that pyrites of unit SSB and  
586 C precipitated syndepositionally in pore water with a limited sulfate availability due to a rapid  
587 disconnection of top-layer sediments with the overlying seawater sulfate reservoir. Such a  
588 marked change may result from the absence of bioturbations at that time (see stratigraphic  
589 variations of bioturbation intensity in, Fig. 3 and illustration of non-biotic and non-  
590 bioturbated mudstones from the SSB unit in, Fig. 7D). This disappearance was coeval to, and  
591 could have been a consequence of, the global late Smithian event, which for instance

592 corresponds to a major diversity loss in nektonic organisms (e.g., Brayard et al., 2009; Jattiot  
593 et al. 2016). It may have also been generated by a strong increase in the sedimentation rate  
594 (Pasquier et al., 2017), as observed regionally during the SSB and lower Spathian (Caravaca  
595 et al., 2017b).

596 Finally, most of the samples from the unit A show MSI values in-between quadrant I  
597 and IV of figure 8, close to, or aligned with, the mixing line between two different pools ( $^{34}\text{S}$ -  
598 enriched and  $^{34}\text{S}$ -depleted sulfur) of pyrites precipitating from MSR in an open and closed  
599 systems. In this case, when MSR occurs in an open system with respect to sulfates, pyrites  
600 with substantially low  $\delta^{34}\text{S}_{\text{py}}$  and high  $\Delta^{33}\text{S}_{\text{py}}$  values are formed. In contrast, when sulfate  
601 reduction goes to completion in a closed system, the sulfates are fully reduced and the  $\delta^{34}\text{S}_{\text{py}}$   
602 and  $\Delta^{33}\text{S}_{\text{py}}$  values of the precipitated pyrites become equal to those of sulfates (Shen et al.,  
603 2011; Sim et al., 2015; Zhang et al., 2015; Saitoh et al., 2017). The unit A samples are mainly  
604 composed of dolomicrites and microbial limestones deposited in very shallow water  
605 environments (Fig. 3). Burrows observed in the unit A may indicate that bioturbation activity  
606 supplied sulfates into the limestone deposits and promoted MSR leading to the low  $\delta^{34}\text{S}_{\text{py}}$  and  
607 high  $\Delta^{33}\text{S}_{\text{py}}$  values. However, the TOC in unit A is largely higher than in the unit B. The  
608 sulfate reduction rate in the unit A may have been even higher than in unit B and perhaps also  
609 to the rate of diffusive sulfate supply into the sediments due to the large amount of available  
610 OM (Ohmoto, 1992; Ohmoto and Goldhaber, 1997) promoting “seawater sulfate like”  $\delta^{34}\text{S}$   
611 and  $\Delta^{33}\text{S}$  values. Therefore, the observed variations in the  $\delta^{34}\text{S}_{\text{py}}$  and  $\Delta^{33}\text{S}_{\text{py}}$  values in unit A  
612 probably better reflect the rate of mixing between the two types of pyrites. Because unit A  
613 contained microbial limestones and dolomicrites corresponding to the development of  
614 complex microbial ecosystems with the possible involvement of microbial sulfide oxidizers,  
615 the processes that led to its MSI signal may also have been more complex by involving

616 several cycles of oxidation-reduction reactions (e.g., Canfield and Farquhar, 2009; Zerkle et  
617 al., 2009, 2016; Johnston, 2011; Fike et al., 2015).

618

#### 619 4.5. CAS sulfur isotopes results

620 Only nine samples over the twenty initially selected as part of this study yielded  
621 enough material for CAS isotopic analyses. Results are therefore not subdivided with respect  
622 to units of the studied section. No temporal trend can be documented. The  $\delta^{34}\text{S}$  values of CAS  
623 vary between +19.5‰ and +34.8‰ (mean value of  $+25.9 \pm 6.3\%$ ,  $1\sigma$ ) (Fig. 3, Table 1).  
624 Results indicate a strong relationship between  $\delta^{34}\text{S}_{\text{CAS}}$  and the Mg/(Mg+Ca) ratio ( $r = -0.64$ ,  $p$   
625  $= 0.06$ ,  $n = 9$ , including all samples but increasing to  $r = -0.84$ ,  $p < 0.01$ ,  $n = 8$ , without MI163,  
626 Fig. 9A), and between the  $\delta^{34}\text{S}_{\text{CAS}}$  and the Mn/Sr ratio ( $r = -0.75$ ,  $p < 0.02$ ,  $n = 9$ , Fig. 9B).  
627 Limestones with low Mg/(Mg+Ca) ratios show  $\delta^{34}\text{S}_{\text{CAS}}$  of around +35‰, whereas  
628 dolomicrites with high Mg/(Mg+Ca) ratios exhibit  $^{32}\text{S}$ -enriched sulfur isotope compositions  
629 around +20‰. There are no significant correlations between  $\delta^{34}\text{S}_{\text{CAS}}$  and carbonate  
630 concentration,  $\delta^{13}\text{C}_{\text{carb}}$ ,  $\delta^{34}\text{S}_{\text{py}}$  and CAS concentrations (Table 1).

631

#### 632 4.5. Fidelity and comparisons with other documented $\delta^{34}\text{S}$ signals from the Smithian-Spathian 633 transition.

634 The observed range of  $\delta^{34}\text{S}_{\text{CAS}}$  values are in agreement with previous measurements  
635 from Spathian strata of the Moenkopi Formation, in the southernmost part of the SFB, that  
636 yield values between +25‰ and +38‰ (Marenco et al., 2008), and more generally with most  
637 Spathian sulfate  $\delta^{34}\text{S}$  values falling between +25‰ and +30‰ VCDT (e.g., Cortecci et al.,  
638 1981; Holser, 1984; Holser and Magaritz, 1987; Holser et al., 1988; Strauss, 1997; Luo et al.,  
639 2010; Song et al., 2014b). Highly  $^{34}\text{S}$ -enriched sulfates are characteristic of the Early Triassic

640 with maximum values of about +35‰ compared with values of ~+10‰ in the late Permian  
641 (Holser et al., 1977; Claypool et al., 1980; Cortecci et al., 1981; Wilgus, 1981; Scholle, 1995;  
642 Strauss, 1997; Kampschulte and Strauss, 2004; Longinelli and Flora, 2010; Song et al.,  
643 2014b). However, the exact timing of the positive +35‰ maximum during the Early Triassic  
644 differs from study to study with some authors suggesting that this maximum is restricted to  
645 the Spathian (Wilgus, 1981; Marenco et al., 2008) or occurs across or immediately above the  
646 PTB (Newton et al., 2004; Gorjan et al., 2007; Luo et al., 2010; Horacek et al., 2010; Song et  
647 al., 2014b). Interestingly, some of the Early Triassic  $\delta^{34}\text{S}_{\text{CAS}}$  records show large and rapid  
648 variations within a section (Newton et al., 2004; Riccardi et al., 2006; Luo et al., 2010; Song  
649 et al., 2014b). These behaviors have been interpreted to reflect a drawdown in seawater  
650 sulfate concentration associated with a shortened residence time. Coupled variations in the  
651 carbon and sulfur cycles are suggested and might be traced back using the  $\delta^{13}\text{C}$  and  $\delta^{34}\text{S}$   
652 records when such paleoenvironmental conditions developed. Covariations between  $\delta^{13}\text{C}$  and  
653  $\delta^{34}\text{S}$  signals during periods of low seawater sulfate concentration have been hypothesized for  
654 the Early Triassic in South China (Luo et al., 2010; Song et al., 2014b), but also during the  
655 Paleozoic (Gill et al., 2007; Gill et al., 2011) and the Cretaceous (Adams et al., 2010). Such a  
656 relationship between the  $\delta^{34}\text{S}_{\text{CAS}}$  and  $\delta^{13}\text{C}_{\text{carb}}$  signals cannot be identified in our dataset.

657         Several authors postulated that a gradient in sulfate  $\delta^{34}\text{S}$  potentially developed within  
658 water column depth during the Early Triassic (Newton et al., 2004; Kump et al., 2005;  
659 Riccardi et al., 2006; Marenco, 2007). The advection of deep  $^{34}\text{S}$ -enriched sulfate water  
660 masses that formed during periods of prolonged global deep-ocean anoxia into shallow water  
661 environments may explain variable sulfate  $\delta^{34}\text{S}$  and deleterious biotic conditions due to  
662 ensuing shallow marine euxinia (Isozaki, 1997; Newton et al., 2004; Grice et al., 2005; Kump  
663 et al., 2005; Riccardi et al., 2006; Marenco, 2007). The observed stratigraphic variations in  
664  $\text{Mg}/(\text{Mg}+\text{Ca})$  ratios (Fig. 3) and the negative correlation between the degree of dolomitization

665 and the  $\delta^{34}\text{S}_{\text{CAS}}$  (Fig. 9A) suggest that the dolomitization process and associated  $\delta^{34}\text{S}_{\text{CAS}}$  could  
666 be facies-dependent, with shallowest sediments experiencing a higher degree of  
667 dolomitization compared to deepest sediments. These observations are consistent with the  
668 hypothesis of a gradient in sulfate  $\delta^{34}\text{S}$ , with the dolomitized samples recording the lower  
669  $\delta^{34}\text{S}_{\text{CAS}}$ . However, (i) a water column anoxia is not documented at Mineral Mountains and the  
670 advection of anoxic water masses to the shallowest part of the SFB is not kinetically-  
671 supported by the carbon isotopes record (Thomazo et al., 2016), and (ii) the relationships  
672 observed between the  $\delta^{34}\text{S}_{\text{CAS}}$  and both  $\text{Mg}/(\text{Mg}+\text{Ca})$  and  $\text{Mn}/\text{Sr}$  ratios (Fig. 9A and 9B)  
673 indicate that the sulfur isotope signal of CAS mostly reflects variations in early diagenetic  
674 processes including the degree of dolomitization. Accordingly, we postulate that only samples  
675 exhibiting  $\text{Mn}/\text{Sr}$  below 0.5 record primary CAS-derived  $\delta^{34}\text{S}$  sulfate with values between  
676 +32.4‰ and +34.8‰. This approximation is in agreement with the estimates by Marenco et al.  
677 (2008) interpreting a weaker altered signal in the Moenkopi Formation of the southern SFB,  
678 which exhibits sulfate  $\delta^{34}\text{S}$  values between +31‰ and +38‰.

679 Nevertheless, several early diagenetic reactions associated with secondary fluids can  
680 be deduced from the  $\delta^{34}\text{S}_{\text{CAS}}$  record at Mineral Mountains. Indeed, during early diagenesis,  
681 the MSR activity tends to produce a  $^{34}\text{S}$ -enriched CAS record (Marenco et al., 2008),  
682 especially if reduction occurred under a Rayleigh-type distillation in a closed system with  
683 respect to sulfates, as deduced from the MSI signal in samples from units SSB and C (Fig. 8).  
684 However, because OM fuels MSR a positive relationship between TOC and  $\delta^{34}\text{S}_{\text{CAS}}$  and an  
685 increasing S/C ratio associated with  $^{34}\text{S}$ -enriched CAS might be expected (Raiswell and  
686 Canfield, 2012). No such relationship between the  $\delta^{34}\text{S}_{\text{CAS}}$  and TOC or between the  $\delta^{34}\text{S}_{\text{CAS}}$   
687 and S/C can be documented using our restricted available data set.

688 In the unit C (between MI159 and MI169) significant small-scale  $\delta^{34}\text{S}_{\text{CAS}}$  variations  
689 (15‰ in amplitude) are also observed independently of the TOC, S/C ratio and paired  $\delta^{34}\text{S}$  of



690 pyrites. Such high-frequency fluctuations of the  $\delta^{34}\text{S}_{\text{CAS}}$  signal are difficult to explain by  
691 secular variations in seawater sulfate sulfur isotopic composition in a steady-state global  
692 sulfur cycle. Indeed, these variations are much more rapid ( $\ll 50$  kyr, Brühwiler et al., 2010)  
693 than the sulfate residence time in the ocean (i.e., 13 Myr in the modern ocean, Kah et al.,  
694 2004; but probably reduced to 1.3 Myr during the Triassic due to lower sulfate concentration,  
695 Horita et al., 2002). Rapid changes of the  $\delta^{34}\text{S}_{\text{CAS}}$  signal during the Griesbachian to Smithian  
696 interval have nonetheless been interpreted to reflect very low sulfate concentrations ( $\leq 4$  mM)  
697 with a residence time of oceanic sulfate reduced to  $\leq 200$  kyr (Song et al., 2014b). Thus, a  
698 partial influence of a global signal cannot be completely discarded in our case.

699 Finally, the strong correlation between the  $\delta^{34}\text{S}_{\text{CAS}}$  and the degree of dolomitization  
700 and the Mn/Sr ratio, as well as the identification of a closed system Rayleigh-type distillation  
701 of sulfur species, makes a compelling case for synsedimentary early diagenetic processes as  
702 the main control for the CAS sulfur isotope signal observed at Mineral Mountains.

703

## 704 **5. Perspectives on the use of MSI record in its sedimentological context**

705 The Mineral Mountains MSI signal is slightly different from previous observations for  
706 the sedimentary sulfur cycle associated with bioturbation during the Phanerozoic. In Shen et  
707 al. (2011), negative sulfide  $\Delta^{33}\text{S}$  values measured across the PTB were suggested to reflect the  
708 mixing of two types of pyrite formed during both an open system and a quantitative closed  
709 system MSR. Shen et al. (2011) linked this mixing to a shutdown of bioturbation resulting  
710 from the shoaling of anoxic deep waters that led to the EPME. According to this model, the  
711 pore water exchanged continuously with oceanic sulfate under oxic conditions because of the  
712 enhanced bioturbation (associated with low  $\delta^{34}\text{S}$  and high  $\Delta^{33}\text{S}$ ). On the contrary, bioturbation  
713 would have disappeared during anoxia and the sulfate supply into sediments was suppressed,  
714 leading to quantitative pore water sulfate reduction (high  $\delta^{34}\text{S}_{\text{py}}$  and low  $\Delta^{33}\text{S}_{\text{py}}$ ). A similar

715 scenario was proposed by Zhang et al. (2015), who interpreted negative  $\Delta^{33}\text{S}-\delta^{34}\text{S}$  values of  
716 pyrites around the PTB as corresponding to pyrites produced in a shoaling sulfidic water  
717 column. More recently, these interpretations have been challenged by Saitoh et al. (2017)  
718 based on the MSI record across the Guadalupian-Lopingian (Late Permian) boundary at  
719 Chaotian (China). They showed that the setting of pore water sediments under oxic conditions  
720 are not always an open system with respect to sulfates, even if bioturbation is associated.  
721 Therefore, the development of anoxic conditions and consequent shutdown of bioturbation are  
722 not required to produce negative  $\Delta^{33}\text{S}_{\text{py}}$  values and processes linking the sedimentary sulfur  
723 cycle to bioturbation are more complicated than previously thought.

724         Contrasting with Saitoh et al. (2017) we established here (Fig. 8, Section 4.3) a strong  
725 relationship between bioturbation and the MSI signal recorded within the permanently oxic  
726 bottom water conditions that developed at Mineral Mountains across the SSB. Bioturbation,  
727 which is a necessary driver to sustain intense iron and sulfur cycling in marine sediments  
728 through the suboxic zone (Van de Velde et al., 2016), likely continuously supplied sulfates  
729 into the sediments and stimulates the sulfate reduction and *in situ* sulfide precipitation in the  
730 sediments during the deposition of the middle Smithian unit B. During this period, open  
731 system MSR activity from pore water fluids connected to oceanic waters is in accordance  
732 with (i) the higher average concentration of sulfides, (ii) the observation of pyrite ( $\text{FeS}_2$ ) in  
733 the form of framboids, and (iii) the MSI signatures. Moreover, unit B records low  $\delta^{13}\text{C}_{\text{carb}}$   
734 values associated with high Mn/Sr and high Mg/(Mg+Ca) ratios. Such variations are in  
735 agreement with a strong influence of the MSR activity on the geochemistry of the sediments.  
736 Indeed, MSR is well known for its role in promoting the precipitation of early diagenetic  
737 authigenic carbonates and secondary carbonates such as dolostones with low  $\delta^{13}\text{C}_{\text{carb}}$  values  
738 through the consumption of excess protons (Vasconcelos and McKenzie, 1997; Zhang et al.,

739 2012; Thomazo et al., 2016), within reducing Mn-bearing,  $^{12}\text{C}$ -enriched, fluids produced  
740 during the bacterially mediated degradation of OM in the suboxic/anoxic zone.

741 On the contrary, during the deposition of both unit SSB and the lower part of unit C,  
742 the disappearance of bioturbation (see stratigraphic variations of bioturbation intensity in Fig.  
743 3 and illustration of non-biotic and non-bioturbated mudstones from the SSB unit in Fig. 7D), ,  
744 may have strongly reduced the pore water replenishment in sulfates, therefore leading to; (i)  
745 reduced *in situ* sulfide precipitation, (ii) MSI signatures typical of a closed system Rayleigh-  
746 type distillation, and (iii) reduced early diagenetic remineralization processes (i.e., lower  
747 Mn/Sr and lower Mg/(Mg+Ca) ratios, higher  $\delta^{13}\text{C}_{\text{carb}}$ ) due to the shortage in oxidant  
748 availability.

749 The relationship between secular trends in bioturbation patterns and the sedimentary  
750 geochemical signatures observed at Mineral Mountains, together with the absence of anoxia,  
751 support the primary influence of local processes as an important driver of isotopic trends  
752 observed before and across the SSB. Worldwide correlation of the Smithian-Spathian  $\delta^{13}\text{C}$   
753 signal (Fig. 1) is more easily explained by modifications of the global carbon cycle if the  
754 primary driver of the muted  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{34}\text{S}_{\text{py}}$  signatures across the SSB reflects the collapse  
755 of biogenic sediment mixing and subsequent changes in the connectivity of sedimentary pore  
756 waters with the overlying water column. These have likely influenced the geochemical  
757 properties of sediments over large distances and may have also generated a global pattern  
758 (Hofmann et al., 2015; Pasquier et al, 2017). If these hypotheses are confirmed, they also  
759 suggest that many commonly used proxies to infer Early Triassic seawater anoxia may rather  
760 reflect the poor sediment oxygenation arising from the extinction of organisms performing  
761 bioturbation.

762 Finally, the use of MSI geochemistry, together with strong sedimentological  
763 constraints, show that changes in the sulfur cycle before and across the SSB at Mineral

764 Mountains is most probably a local consequence of the late Smithian extinction event rather  
765 than recording the development of a lethal global anoxic ocean. Therefore, the data reported  
766 in this study demonstrate that the sulfide MSI signal can be a valuable proxy for assessing  
767 local paleoenvironmental and sedimentological processes throughout Earth history.

768

## 769 **6. Conclusions**

770 The study of the multiple sulfur isotope records before and across the SSB at Mineral  
771 Mountains provides new insights into the Early Triassic sulfur cycle and its temporal and  
772 mechanistic relationships with local sedimentological conditions, the  $\delta^{13}\text{C}$  curve variations  
773 and the decrease in diversity and abundance among benthic organisms. We notably show that:

774 1. The  $\Delta^{33}\text{S}-\delta^{34}\text{S}$  signals reflect the operation of MSR in two different regimes. Before  
775 the late Smithian, open system sulfate reduction in sediments pore water connected to the  
776 seawater is prevailing, while during the late Smithian and after the SSB, a closed-system,  
777 sulfate-limited, Rayleigh-type distillation is recorded in the MSI signals.

778 2. No change in the oxygenation of the water column accompanied this evolution of  
779 the MSI record and all pyrite framboids formed in the sediment pore water were precipitated  
780 under an overlying oxygenated water column.

781 3. The connection of pore waters to the overlying water column is locally controlled  
782 by sedimentological conditions such as bioturbation intensity and sedimentation rate. This led  
783 to a constant replenishment in pore water sulfates during the middle Smithian, and an  
784 impoverishment during the late Smithian and across the SSB.

785 4. Both the C and S isotope signals at Mineral Mountains are therefore best explained  
786 by the extent to which MSR and associated early diagenetic remineralization proceeded  
787 within the sediments.

788 Finally, we suggest that the muted sulfur isotope record at Mineral Mountains is a  
789 consequence of the late Smithian extinction and the associated loss of the sedimentary mixed  
790 layer. Future isotopic studies on other sections across the SSB in various sedimentological  
791 contexts should be used to further test in detail these inferences and help to improve our  
792 understanding of the importance of local synsedimentary processes for paleoenvironmental  
793 reconstructions during the EPME recovery and, more generally, over geological times.

794

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803

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1351

## 1352 **Captions**

1353 **Table 1.** Results of isotopic and elemental analyses.

1354

1355 **Fig. 1:** Chronostratigraphic subdivisions of the Early Triassic (radiometric ages by  
1356 Ovtcharova et al., 2006, Galfetti et al., 2007a and Burgess et al., 2014) with previously  
1357 published carbon isotope trends after Galfetti et al., 2007; Grasby et al., 2013 and Caravaca et  
1358 al., 2017a showing that similar fluctuations are observed worldwide from various localities  
1359 (see palaeogeographic map modified after Brayard et al., 2006). Subdivisions of the Smithian  
1360 and Spathian follow the ammonoid zonation from Brühwiler et al. (2010) and Guex et al.  
1361 (2010). l.: lower; mi.: middle; u.: upper. The definition of the Dienerian/Smithian Boundary  
1362 (DSB) follows biostratigraphical data published in e.g., Galfetti et al. (2007) and Romano et  
1363 al. (2013). A formal definition of the DSB is under discussion and some authors have  
1364 proposed to place this boundary at, or just below, the “P2”  $\delta^{13}\text{C}$  isotopic maximum (e.g., Song  
1365 et al., 2013). The middle-late Smithian and Smithian-Spathian Boundary (SSB) correlation

1366 among localities is primarily based on high-resolution ammonoid zonations (see synthesis in  
1367 Jenks et al., 2015).

1368

1369 **Fig. 2:** (A) Early Triassic paleogeographic map and location of the Sonoma Foreland Basin  
1370 (SFB), modified after Brayard et al. (2013). (B) Simplified paleogeographic map of the SFB  
1371 with location of the Mineral Mountains section (after Caravaca et al., 2017b).

1372

1373 **Fig. 3:** Mineral Mountains section with corresponding lithological units and  
1374 chemostratigraphic parameters. See Vennin et al. (2015) for detailed information on facies  
1375 and depositional environments. Abbreviations for the sequential framework: SB: sequence  
1376 boundary; MFS: maximum flooding surface. Abbreviations for the ammonoid zones: *V.u.*:  
1377 *Vercherites undulatus* bed; *I.b.*: *Inyoites beaverensis* beds; *O.*: *Owenites* beds; *A.m.*:  
1378 *Anasibirites multiformis* beds; Xe: Xenoceltitidae “*gen. indet.*” A. beds (see Brayard et al.,  
1379 2013 and Jattiot et al., 2016). Relative variations of sea surface temperatures are depicted  
1380 using color gradient and underlined a major cooling event across the Smithian/Spathian  
1381 Boundary (interpreted from Sun et al., 2012 and Romano et al., 2013). A prolonged absence  
1382 of bioturbation occurred in the SSB and lower unit C intervals. These deposits correspond to  
1383 mud outer ramp lower offshore environment (Vennin et al., 2015). Below and above, the  
1384 depositional environment is the same but shows a more intense bioturbation.

1385

1386 **Fig. 4:** Cross calibration between SO<sub>2</sub>-EA-IRMS and SF<sub>6</sub>-IRMS on the δ<sup>34</sup>S values of 10  
1387 samples from this study. Uncertainties are smaller than the symbol size.

1388

1389 **Fig. 5:** Relationship between the δ<sup>13</sup>C<sub>carb</sub> (VPDB, ‰) and the Mg/(Mg+Ca) ratio in units A, B,  
1390 SSB and C.

1391

1392 **Fig. 6:** Correlation relationship between the carbonate content (in wt. %) and the sum of  
1393 calcium and magnesium content (in wt. %).

1394

1395 **Fig. 7:** Selected thin sections from the Mineral Mountains section under a photonic and  
1396 scanning electron microscope. **(A-B-C)** Burrows underlying a strong remobilization of the  
1397 sediments during bioturbation (white-dash line) and pervasive microdolomitization (black  
1398 arrows) in sample from a micropackstone of the unit B mudstone. **(D)** Non-biotic and non-  
1399 bioturbated mudstone from the SSB unit. **(C, F-E)** SEM backscattered electron images of  
1400 pyrite framboids from units B and SSB.

1401

1402 **Fig. 8:** Graphic showing the sulfides  $\delta^{34}\text{S}$  and  $\Delta^{33}\text{S}$  relationship in units A, B, SSB and C. The  
1403 grey stars and the pale blue square respectively represent the average Early Triassic  
1404 sedimentary sulfides and seawater sulfate multiple sulfur isotope signatures estimated by  
1405 model calculations (Wu et al., 2010). The red dashed curve represents the mixing line of these  
1406 two endmembers. The black solid curve displays isotopic values of accumulative sulfides  
1407 produced during a Rayleigh-type distillation of the residual sulfate pool (assuming values  
1408 estimated by the model calculations) in a closed system, with MSR  $^{34}\epsilon$  and  $^{33}\lambda$  values of  
1409 44.8‰ and 0.512 (red arrow), respectively. Numbers on this black solid curve correspond to  
1410 the fraction of sulfates converted to sulfides. The dashed black curves depict mixing lines of  
1411 accumulative sulfides produced in closed system and sulfides produced in an open system  
1412 with respect to sulfates. The black and blue arrows respectively represent the evolution of  
1413 instantaneously produced hydrogen sulfides and the residual sulfates during a Rayleigh-type  
1414 distillation in closed system.

1415

1416 **Fig. 9:** Relationships between the  $\delta^{34}\text{S}_{\text{CAS}}$  (VCDT, ‰) and the Mg/(Mg+Ca) ratio (**A**), and  
1417 the Mn/Sr ratio (**B**) in units A, B, SSB and C.

1418

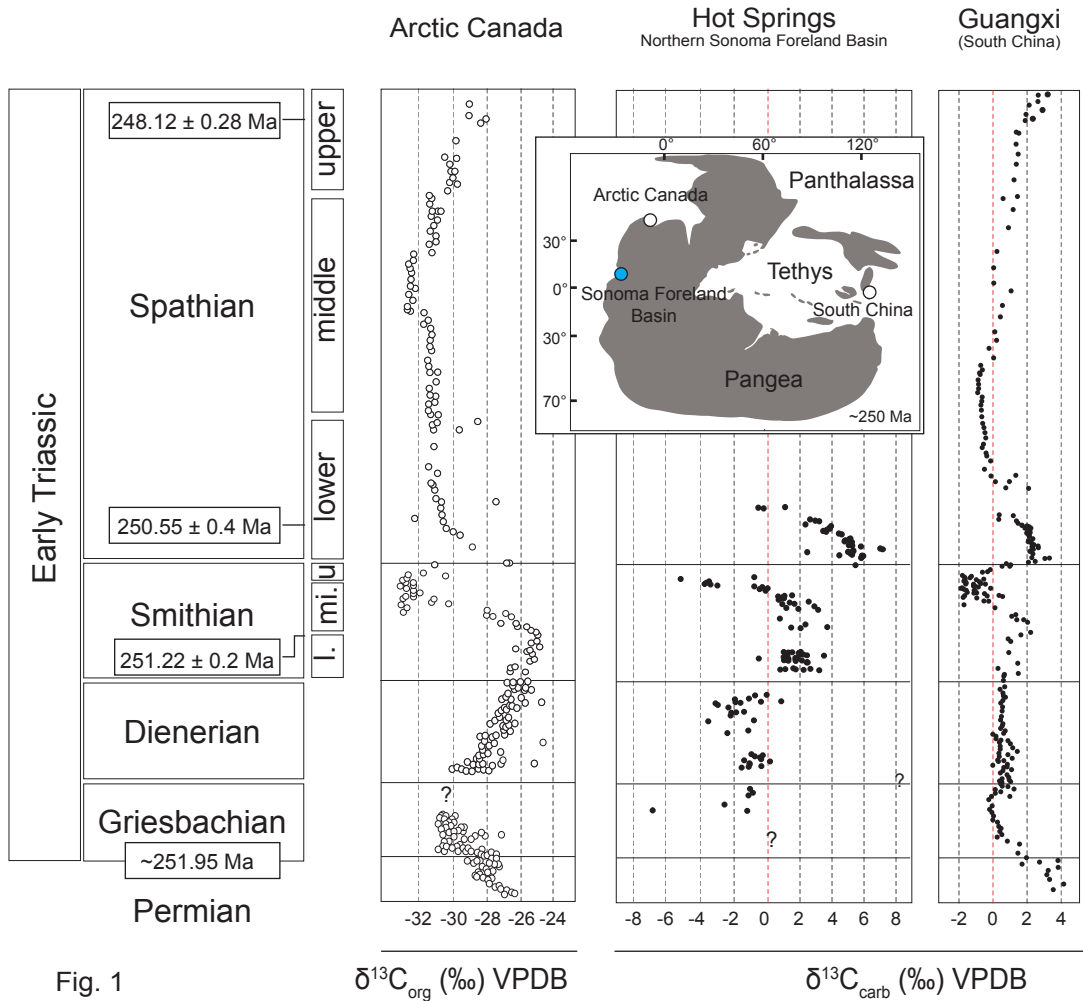
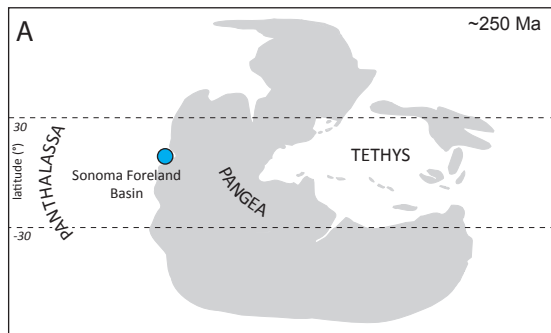










Fig. 1





-  *Golconda Allochthon thrust-and-fold belt*
-  *Relic Ancestral Rocky Mountains uplifts*
-  *Continental environments*
-  *Transitional continental/marine to shallow marine depositional settings*
-  *Reconstructed limit of the Golconda thrust belt*
-  *Postulated maximum extension of end-Smithian marine foreland*
-  *Postulated limits of ARM uplifts*
-  *State borders*

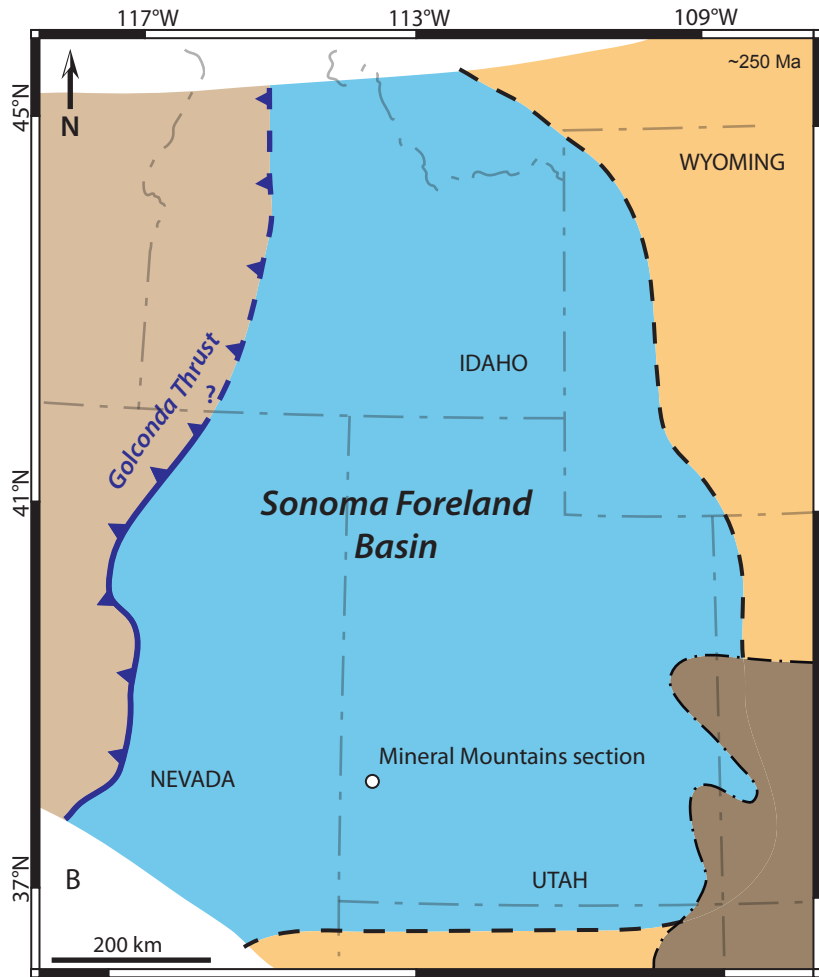


Fig. 2

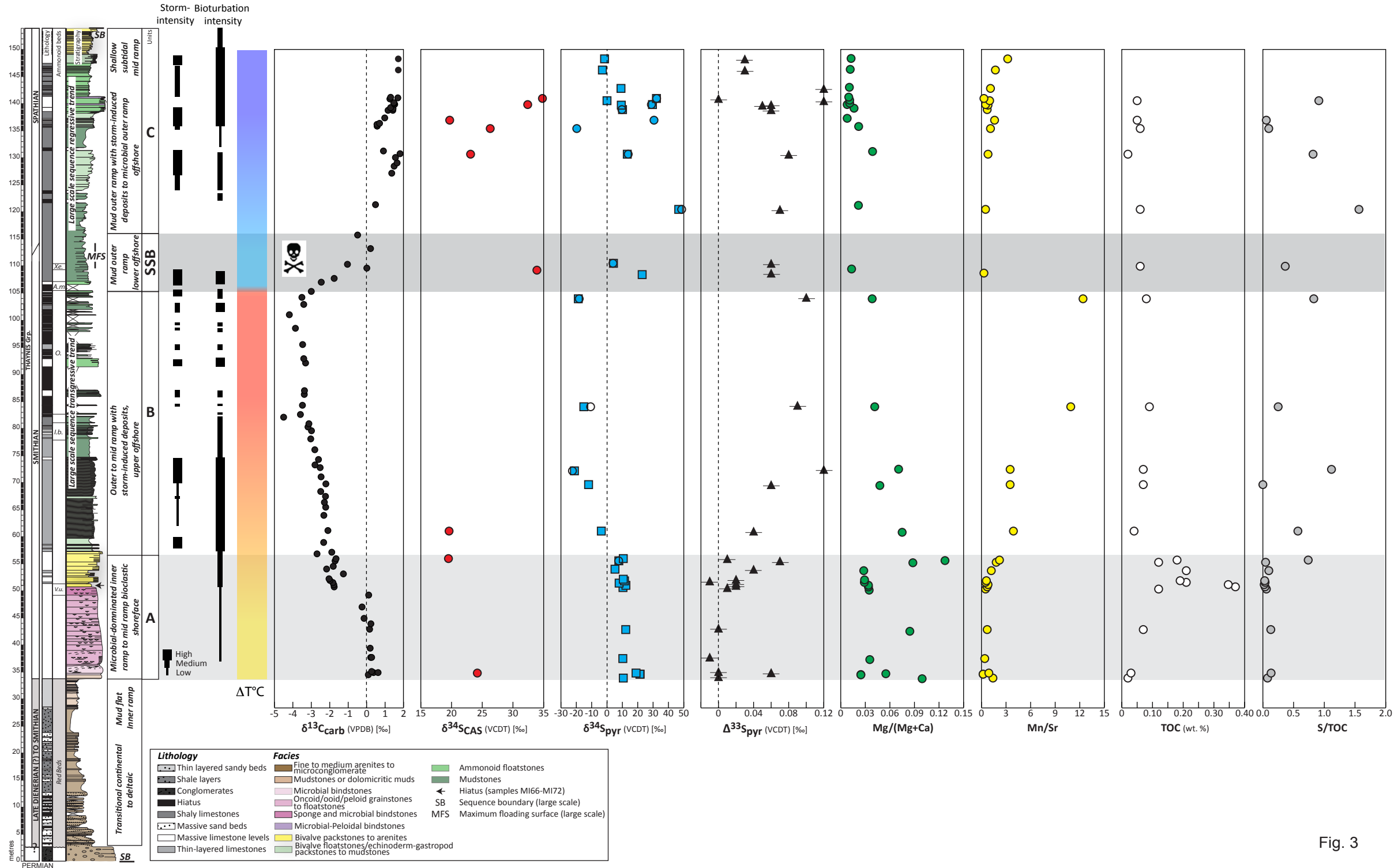


Fig. 3

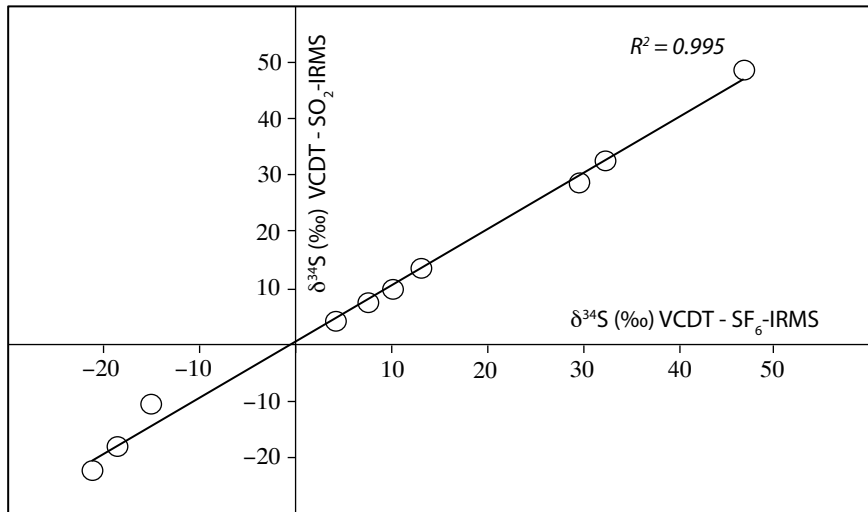


Fig. 4

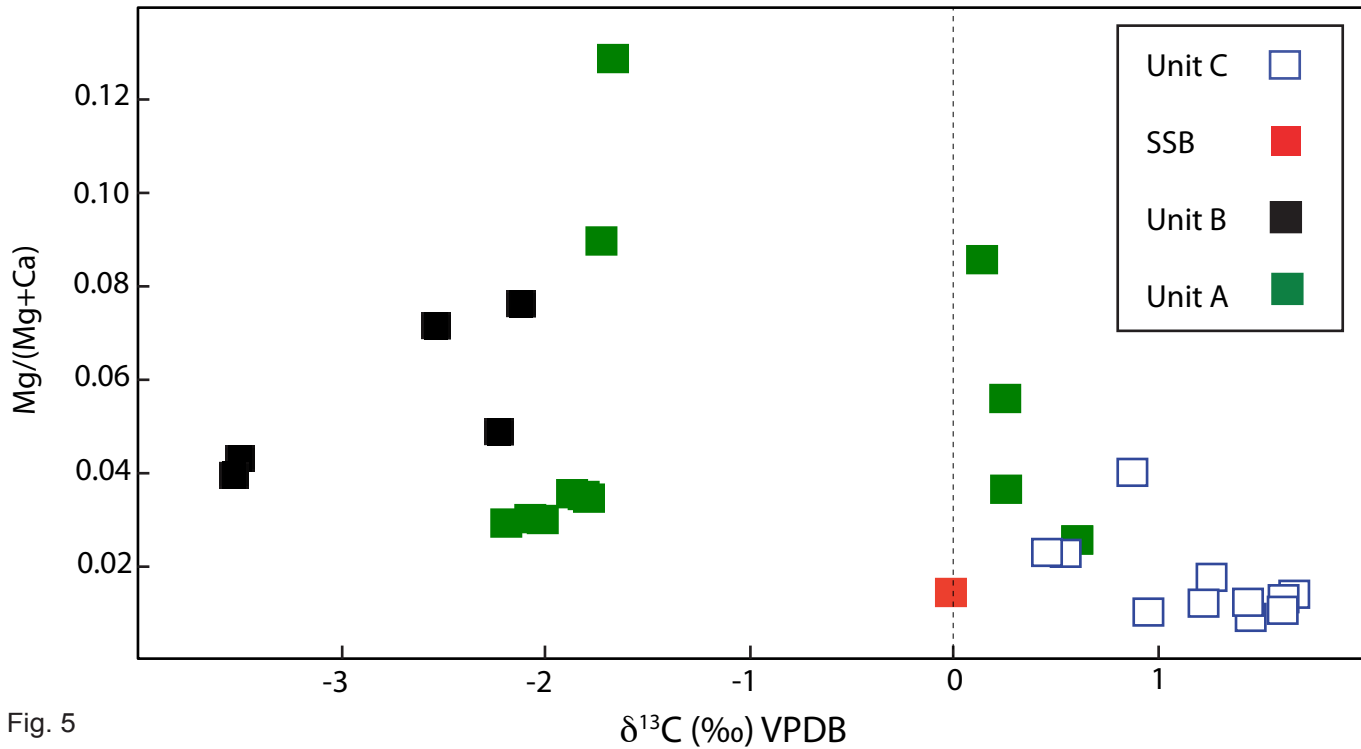


Fig. 5

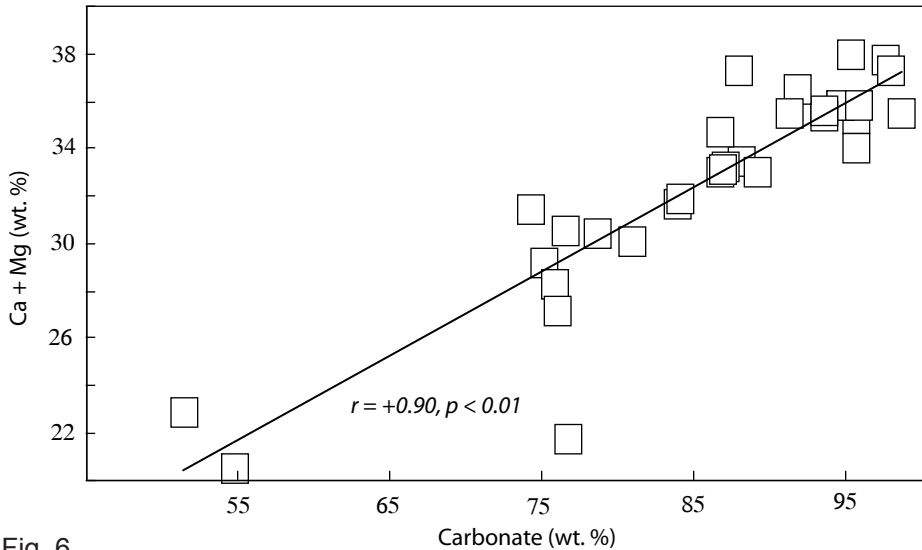
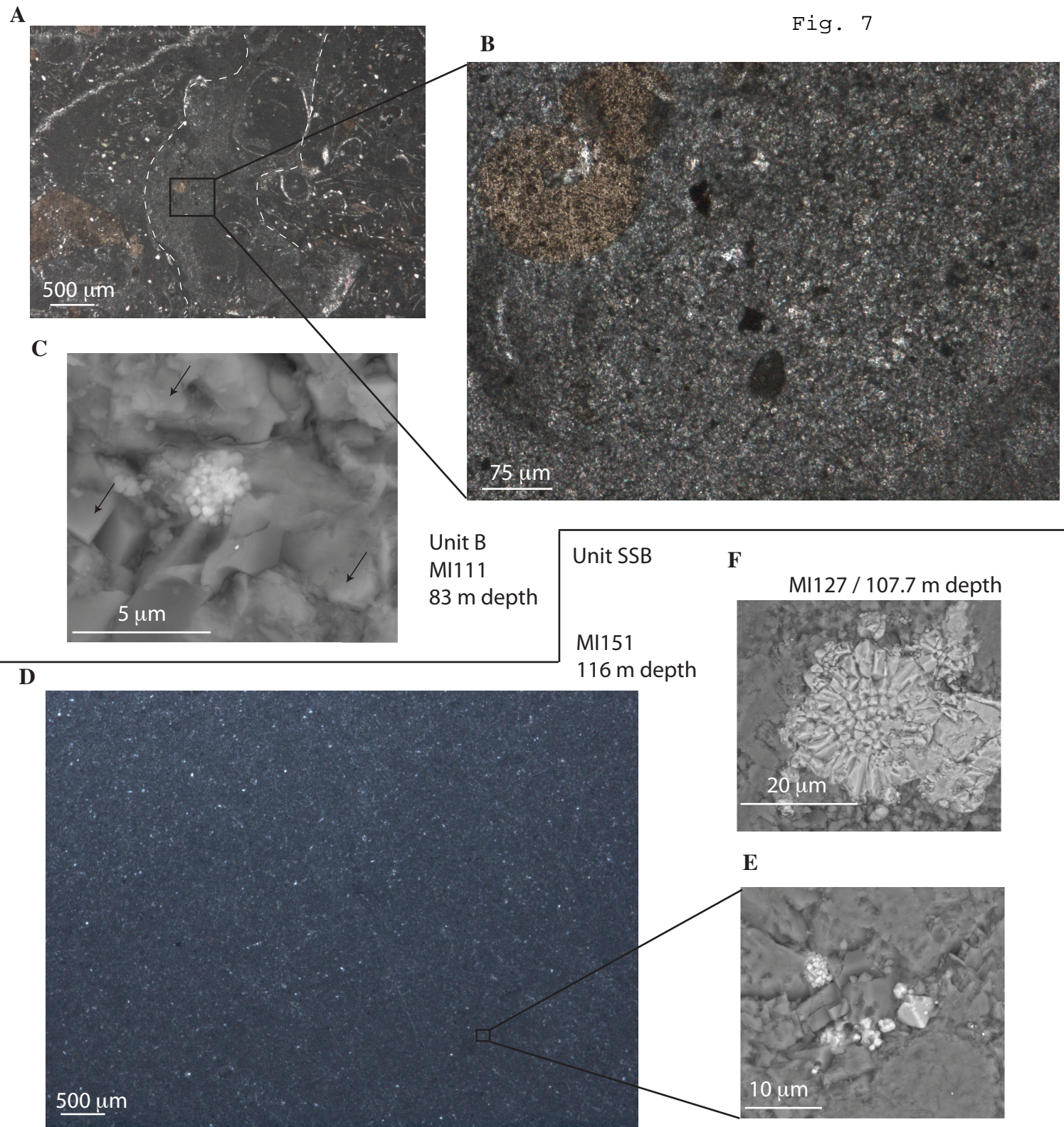


Fig. 6

Fig. 7





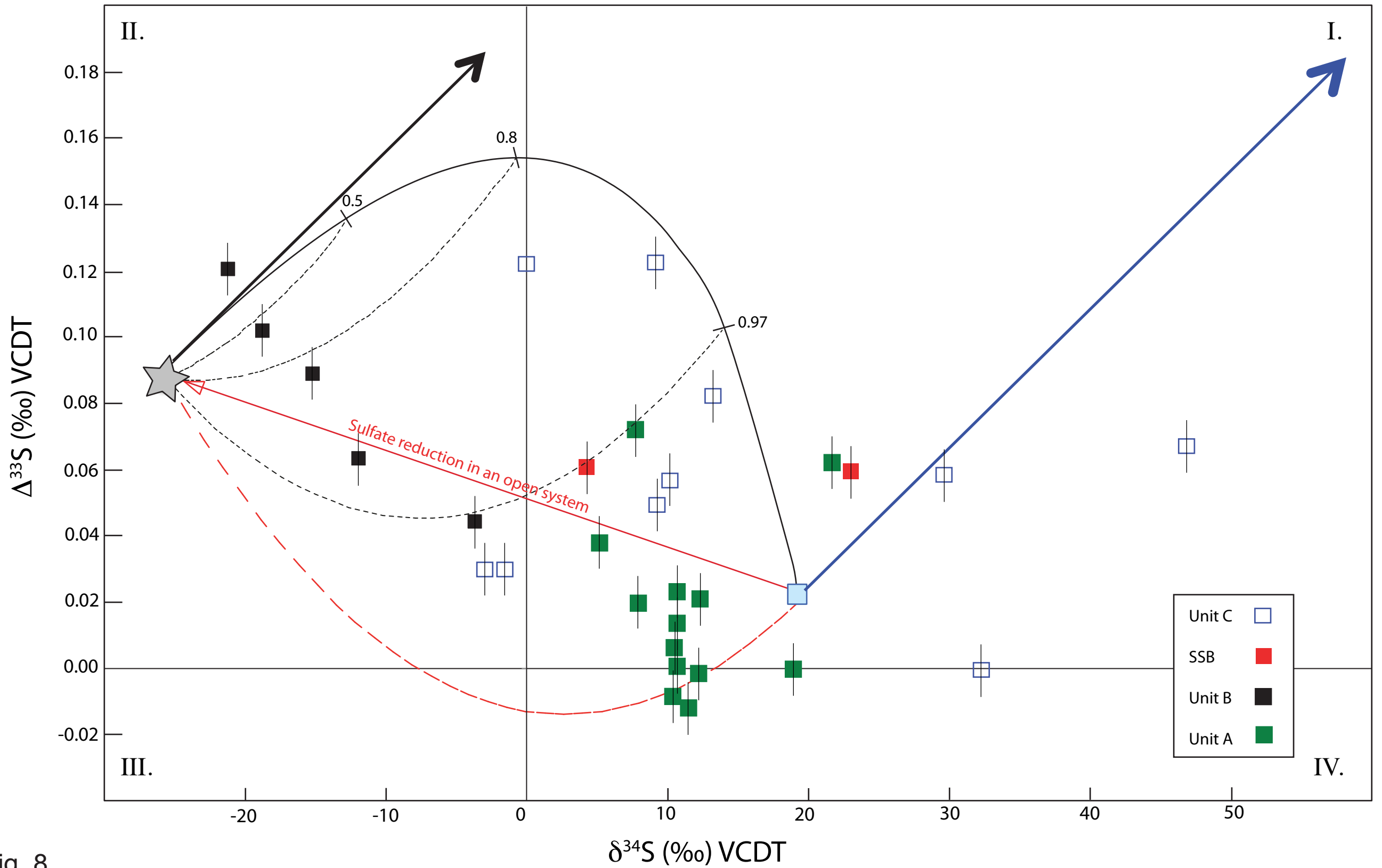


Fig. 8

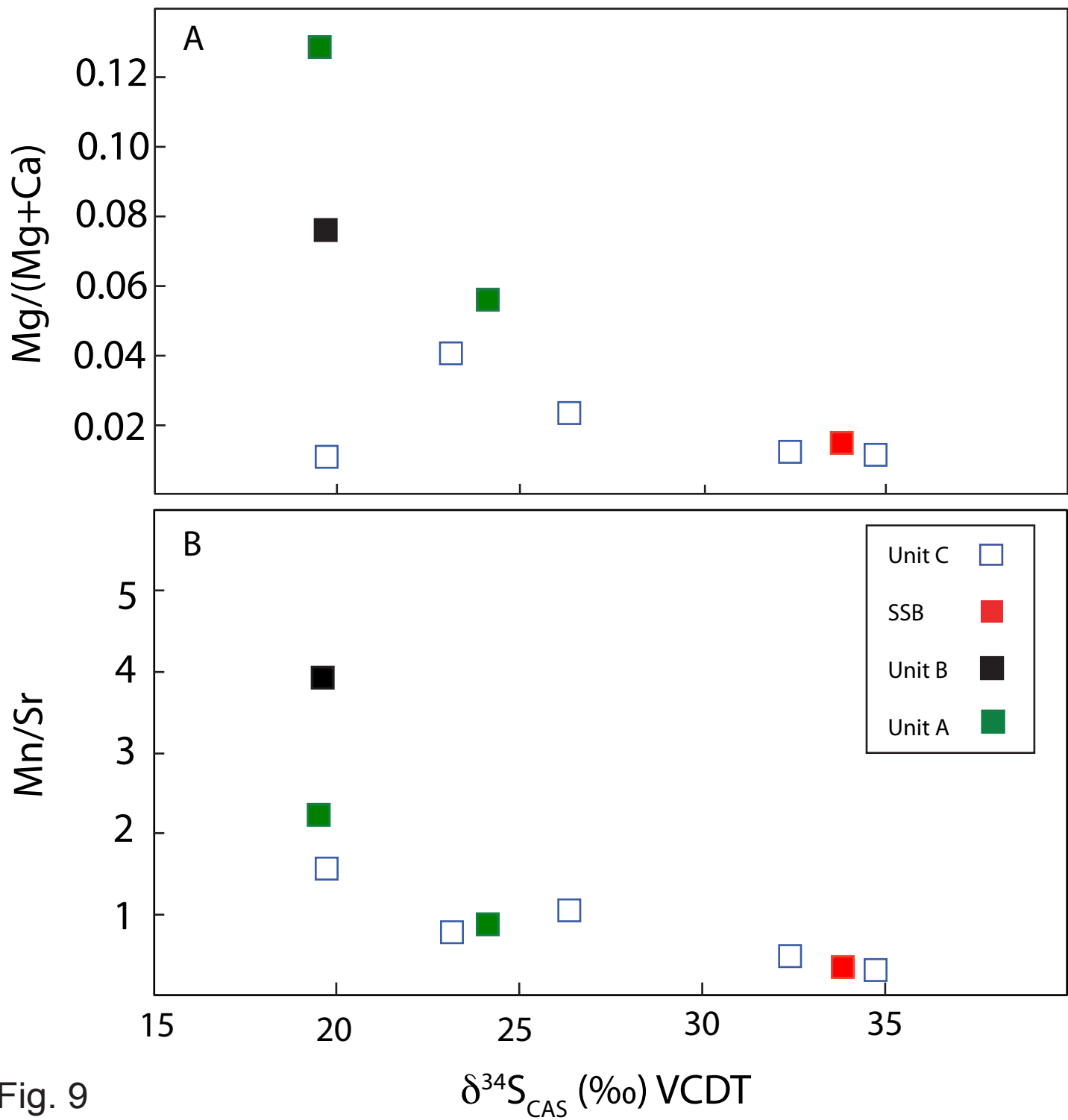


Fig. 9



Table 1 : Participant's baseline characteristics

	<b>EIH</b> <b>(n = 10)</b>	<b>NEIH</b> <b>(n = 9)</b>	<b>Untrained</b> <b>(n = 10)</b>
<b>Age (years)</b>	40.3 ± 1.2	39.1 ± 1.3	37.8 ± 1.7
<b>Body mass (kg)</b>	70.1 ± 2.3	71.1 ± 2.4	76.3 ± 1.9
<b>Height (cm)</b>	178 ± 2	179 ± 2	174 ± 1
<b>Body mass index (kg·m<sup>-2</sup>)</b>	22.2 ± 0.4 <sup>Ψ</sup>	22.3 ± 0.7 <sup>Ψ</sup>	24.9 ± 0.6
<b>VO<sub>2</sub>max (ml·min<sup>-1</sup>·kg<sup>-1</sup>)</b>	60.1 ± 2.0 <sup>Ψ</sup>	58.3 ± 1.8 <sup>Ψ</sup>	43.3 ± 2.0
<b>FEV<sub>1</sub> (% predicted)</b>	119 ± 3	112 ± 7	114 ± 6
<b>Training volume (hours·week<sup>-1</sup>)</b>	12.0 ± 1.7 <sup>Ψ</sup>	11.3 ± 1.1 <sup>Ψ</sup>	2 ± 0.5

Values are means ± SEM. EIH: athletes exhibiting O<sub>2</sub> desaturation; NEIH: athletes without O<sub>2</sub> desaturation

<sup>Ψ</sup>, significantly different from untrained group (p < 0.05)