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

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Abstract

The Early Triassic is generally portrayed as a time of various, high ecological stresses leading to a delayed biotic recovery after the devastating end-Permian mass extinction. This interval is notably characterized by repeated biotic crises (e.g., during the late Smithian), large-scale fluctuations of the global carbon, nitrogen and sulfur cycles as well as harsh marine conditions including a combination of ocean acidification, anoxia, extreme seawater temperatures and shifting productivity. Observations from different paleolatitudes suggest that sulfidic (H_2S -rich) conditions may have developed widely during the Early Triassic, possibly reaching up to ultra-shallow environments in some places. However, the existence and the spatio-temporal extent of such redox swings remain poorly constrained. In order to explore Early Triassic paleoceanographic redox changes and their potential influences on the biotic recovery, we analyzed multiple sulfur isotopes (^{32}S , ^{33}S , ^{34}S , and ^{36}S) of sedimentary pyrite and carbonate associated sulfate ($\delta^{34}\text{S}_{\text{CAS}}$) from the Mineral Mountains section, Utah. Sediments from this section were mainly deposited in shallow waters and span the Smithian and lower Spathian. We report a 68‰ range of variations in $\delta^{34}\text{S}_{\text{py}}$ associated with $\Delta^{33}\text{S}_{\text{py}}$ varying from -0.01‰ to +0.12‰, whereas the $\delta^{34}\text{S}_{\text{CAS}}$ varies between +19.5‰ and +34.8‰. We interpret the observed signal of multiple sulfur isotopes as reflecting the operation of pore-water syndimentary microbial sulfate reduction in open system with respect to sulfates before the late Smithian, evolving to a closed system, sulfate limited, Rayleigh-type distillation across the Smithian/Spathian boundary (SSB) and immediately after the SSB. We argue that this marked change is driven by the effectiveness of the connection between the sedimentary pore waters and the overlying water column, which is, in our case, controlled by the local sedimentological conditions such as the bioturbation intensity and the sedimentation rate. Therefore, our results suggest that changes in the sulfur cycle before and across the SSB at Mineral Mountains is probably a local consequence of the loss of the mixed sedimentary

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

1. Introduction

1.1. Smithian and Smithian/Spathian boundary events

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

Song et al., 2013; Thomazo et al., 2016; Caravaca et al., 2017a). The negative shift is usually attributed to a massive light carbon input and/or a major reorganization of the exogenous global carbon cycle, such as a decrease in the organic carbon flux buried in the sedimentary record. The negative shift has thus been linked to an episodic large-scale injection into the atmosphere of volcanic CO₂ and thermogenic CH₄ from the Siberian Traps (Payne et al., 2004; Payne and Kump, 2007; Meyer et al., 2011; Sobolev et al., 2011). Alternatively, local processes such as early diagenetic reactions in pore water producing authigenic carbonates also probably participate to generate this signal (Thomazo et al., 2016; Zhao et al., 2016). The negative isotopic excursion is followed by an abrupt positive $\delta^{13}\text{C}$ excursion of comparable magnitude beginning in the late Smithian and crossing the SSB. Such negative-positive swings in the carbon isotope record were suggested to characterize strong anoxic conditions (e.g., Retallack and Jahren, 2008; Song et al., 2012; 2014a). Positive covariation of this oscillation in the $\delta^{13}\text{C}_{\text{carb}}$ signal with existing $\delta^{34}\text{S}_{\text{CAS}}$ records has been interpreted to reflect changes in the burial rate of sedimentary sulfides during increased marine anoxia in an ocean with an extremely small sulfate reservoir (Song et al., 2010; 2014b). Late Smithian potential anoxic sediments were reported from various localities worldwide (e.g., Galfetti et al., 2008; Grasby et al., 2013) and anoxic conditions possibly reached ultra-shallow environments in some places (e.g., Wignall et al., 2016).

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

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

1.2. Potential underlying processes

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

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

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

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

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

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

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

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

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

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

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

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

2. Geological setting

2.1. The Sonoma Foreland Basin

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

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

2.2. The Mineral Mountains section

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

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

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

The local ammonoid biostratigraphy has been described in Brayard et al. (2011, 2013). The unit A is early Smithian in age (“*Vercherites undulatus* beds”; *V.u.* in Fig. 3). The unit B is latest early to middle Smithian in age (*Inyoites beaverensis* and *Owenites* beds, respectively; *I.b.* and *O.* in Fig. 3; Unitary Association Zones UAZ₃ and UAZ₄ in Jattiot et al., 2017). The SSB unit mainly corresponds to the late Smithian with the occurrence of typical prionitid and xenoceltitid ammonoid assemblages (*A.m.* and *Xe.* in Fig. 3; UAZ₅ and UAZ₆ in Jattiot et al., 2017). Although Spathian beds are not well identified above these late Smithian assemblages, the first Spathian dominant fauna likely corresponds to a regional bivalve bloom (Brayard et al., 2013; Hofmann et al., 2014).

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

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

3. Methods

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

3.1. Carbonate carbon isotopes

Carbonate carbon isotope analyses ($\delta^{13}\text{C}_{\text{carb}}$) were carried out at the Biogéosciences Laboratory, Dijon, France. The samples (90 to 300 μg) were loaded into septum screwed glass tubes, flushed via the autosampler with He to remove atmospheric gases. Each sample was reacted with 500 μl of $>100\%$ phosphoric acid at 90°C for 17 min using an online carbonate preparation line coupled to an IsoPrime stable isotope ratio mass spectrometer (IsoPrime, Manchester, UK). Inorganic carbonate content was quantified manometrically from the CO_2 yield; all isotopic values are reported in the standard δ -notation in permil (‰) relative to VPDB by assigning a $\delta^{13}\text{C}$ value of $+1.95\text{‰}$ to the NBS19 international standard. The long-term reproducibility of the NBS19 replicate analyses (three months) is better than $\pm 0.09\text{‰}$ (1σ) for carbon isotopes. H_3PO_4 blank tests were performed and evolved CO_2 was below the detection limit of our online-IRMS system.

3.2. Sulfide isotopes

Sulfide sulfur was retrieved using a conventional wet chemical extraction at the Biogéosciences Laboratory, Dijon, France. Acid volatile sulfide (AVS), representing monosulfides, and chromium reducible sulfur (CRS) consisting primarily of pyrite were extracted sequentially. First, AVS was liberated using cold concentrated HCl for 2 hours. If any, resulting hydrogen sulfide was precipitated as Ag₂S with a 0.3 M AgNO₃ solution. Subsequently, CRS was released using a hot and acidic 1.0 M CrCl₂ solution (Canfield et al., 1986). The resulting H₂S was precipitated as Ag₂S. After centrifugation, the silver sulfide precipitate was washed several times with deionized distilled water and dried at 50°C for 48 hours in an oven and weighted. Mass balance was used to calculate the amount of AVS and CRS. Concentrations in ppm are reported individually in Table 1 (note that monosulfides were below the detection limit in all samples). The silver sulfides were then fluorinated to produce SF₆ and analyzed for their multiple sulfur isotope compositions at the Stable Isotope Laboratory of the Institut de Physique du Globe de Paris, France. The isotope compositions were determined by dual-inlet gas-source mass spectrometry monitoring ion beams at m/z of 127, 128, 129, and 131 using a ThermoScientific MAT 253 gas source mass spectrometer (Labidi et al., 2012). Sulfur isotope ratios are reported in conventional delta notation with respect to VCDT as Eq. (1):

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

where i is either 3, 4 or 6;

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

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

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

The $\delta^{34}S$ values are presented with an analytical reproducibility of $\leq 0.1\text{‰}$. We used values for IAEA-S2 on the Vienna Cañon Diablo Troilite (VCDT) normalization of 5.224‰, 0.030‰ and -0.203‰ for $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$, respectively. Based on duplicate and triplicate analyses, uncertainties on $\Delta^{33}S$ and $\Delta^{36}S$ values by the SF_6 technique are estimated at 0.01‰ and 0.2‰ in 2σ , respectively.

Ten samples have been successfully cross calibrated (Table 1, Fig. 4) for their $\delta^{34}S_{py}$ with measurements performed at the Biogéosciences Laboratory, Dijon, France, on SO_2 molecules via combustion of $\sim 500 \mu g$ of silver sulfide homogeneously mixed with an equal amount of tungsten trioxide using a Vario PYRO cube (Elementar GmbH) connected online via an open split device to an IsoPrime IRMS system (Isoprime, Manchester, UK). International standards IAEA-S-1, IAEA-S-2 and IAEA-S-3 were used for calibration assuming $\delta^{34}S$ values of -0.3‰ , $+22.7\text{‰}$ and -32.3‰ (VCDT), respectively. Analytical reproducibility was better than $\pm 0.3\text{‰}$ (1σ) based on replicates for standard materials and samples.

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3.3. CAS sulfur isotopes

CAS sulfur was retrieved using a wet chemical extraction at the Laboratory Géosciences Océan, Brest, France. Fifty grams of carbonate samples (with carbonate contents typically $>70 \text{ wt. \%}$ of the total rock) were powdered, soluble sulfates being leached by a 1.7 M NaCl solution for 4 hours, followed by four rinses in deionized water. This step was repeated five times and the powder was then dissolved in 4 N HCl (12 h). The acidified samples were then filtered, on a $0.45\text{-}\mu m$ nitrocellulose paper and an excess of 250 g.l^{-1} of $BaCl_2$ solution was added to the filtrate to precipitate $BaSO_4$. After centrifugation, the barium

sulfate precipitate was washed several times with deionized distilled water and dried at 60°C for 24 hours in an oven. $\delta^{34}\text{S}$ measurements were performed at the Biogéosciences Laboratory, Dijon, France, on SO_2 molecules via combustion of ~500 μg of barium sulfate homogeneously mixed with 1/3 of vanadium pentoxide using a Vario PYRO cube (Elementar GmbH) connected online via an open split device to an IsoPrime IRMS system (Isoprime, Manchester, UK). International standard NBS 127 was used for calibration assuming a $\delta^{34}\text{S}$ value of +20.3‰ on the VCDT scale. Isotope results are reported in the standard delta notation against the Vienna Cañon Diablo Troilite standard (VCDT). Analytical reproducibility was better than $\pm 0.3\text{‰}$ (1σ) based on replicates for standard materials.

3.4. Major and trace elements

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

3.5. Petrographic observations

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

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

4. Results and discussion

4.1. Carbonate carbon isotopes

Except for samples MI169, MI197, MI202 and MI209, the $\delta^{13}\text{C}_{\text{carb}}$ values presented in this work have already been reported in Thomazo et al. (2016). All data are consistent with the expected $\delta^{13}\text{C}_{\text{carb}}$ decrease (by $\sim 3\text{‰}$) during the middle Smithian followed by an abrupt increase (of $\sim 4\text{‰}$) through the late Smithian and the SSB (Fig. 3). Samples from the upper part of unit A and from unit B (from 50.8 to 104.2 m) display a significant correlation of the $\delta^{13}\text{C}_{\text{carb}}$ signal with the Mn content and Mn/Sr ratio (see figure 3 in Thomazo et al., 2016). In this work, we also observe a covariation between the $\delta^{13}\text{C}_{\text{carb}}$ and the Mg/(Mg+Ca) ratios (Fig. 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 the units B, SSB and C (see figure 3 in Thomazo et al., 2016). Low $\delta^{13}\text{C}_{\text{carb}}$ values ($\sim -3\text{‰}$) associated with high Mn/Sr and high Mg/(Mg+Ca) ratios are interpreted to reflect early diagenetic authigenic precipitation of dolomicrites within reducing, Mn-bearing, ^{12}C enriched, fluids produced during the bacterially mediated degradation of OM close to the sediment water interface (Gilleaudeau and Kah, 2013; Schrag et al., 2013; Thomazo et al., 2016).

4.2. Major and trace elements

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

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

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

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

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

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

The TOC concentrations show variations from 0.02 to 0.37 wt. % with a mean value of 0.114 ± 0.099 wt. % (1σ) (Fig. 3, Table 1). Units B, SSB and C exhibit similar TOC concentrations with average values of 0.09 ± 0.04 , 0.06 and 0.06 ± 0.02 wt. % (1σ), respectively. Strongest variations in TOC content are observed in unit A and encompass the highest mean value: 0.169 ± 0.115 wt. % (1σ). Within this unit, the microbial deposits show a lower TOC concentration (0.04 ± 0.026 wt. %; 1σ) than the overlying calcarenite and siltstones (0.218 ± 0.094 wt. %; 1σ). A clear maximum in TOC content is documented atop the unit A, between MI72a and MI83 (Fig. 3). This maximum is associated with a negative carbon isotope shift in $\delta^{13}\text{C}_{\text{carb}}$ (Fig. 3) and $\delta^{13}\text{C}_{\text{org}}$ values (down to -30.46‰ ; Thomazo et al., 2016). Given the shallow depositional settings and the absence of evidence for anoxia in the water column (Vennin et al., 2015; Thomazo et al., 2016), these features may be interpreted as corresponding to a major perturbation of the global carbon cycle. It can result from a CO_2 released from volcanogenic (Sobolev et al., 2011) or thermogenic sources (Payne and Kump, 2007). However, changes in productivity and preservation of organic matter (i.e. the biological pump) due to increasing temperatures (Fig. 3; Sun et al., 2012; Romano et al., 2013) or changes in the relative contribution of the TOC between terrestrial and marine OM (Caravaca et al., 2017a) may also explain this signal.

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

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

4.3. Sulfide MSI results

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

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

petrographic observations of the samples. Instead, the lack of covariation between the $\delta^{34}\text{S}_{\text{py}}$ and sulfides content in all units (Table 1) and the observation of pyrite (FeS_2) in the form of framboids suggest that microbial sulfur cycling had a dominant role on the $\delta^{34}\text{S}_{\text{py}}$ signal, rather than the influence of secondary processes such as thermochemical sulfate reduction (Machel et al., 1995).

4.4. Interpretations of the sulfide MSI signal

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

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

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

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

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

In vitro laboratory experiments have shown that the MSI values of hydrogen sulfide produced during MSR under non-limiting sulfate conditions is higher in $\Delta^{33}\text{S}_{\text{py}}$ and lower in $\delta^{34}\text{S}_{\text{py}}$ compared to the substrate (Johnston et al., 2007; Sim et al, 2011a, 2011b). Therefore, 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

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

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

Isotopic data from the unit SSB and the lower part of unit C are largely consistent with the range of values in a closed system Rayleigh distillation (including the mixing line between accumulative sulfides and open system sulfides, Fig. 8). Importantly, they cannot be explained by the mixing of sulfides produced during sulfate reduction in an open system and produced during quantitative sulfate reduction in a closed system. Moreover, very highly ^{34}S -enriched (and positive $\Delta^{33}\text{S}_{\text{py}}$) sulfides in parts of units SSB and C may reflect (i) the evolution of the residual sulfate reservoirs from which sulfides precipitated and subsequent 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 hypotheses are in accordance with a closed-system Rayleigh distillation model. However, we cannot fully exclude here that the heaviest pyrite signal also reflect an H_2S pool produced under low sulfate concentration, where some of the H_2S would have been partially oxidized under aerobic conditions with an attendant effect resulting in sulfate that is lighter than the H_2S available for capture as pyrite (Ries et al., 2009). Further analyses using secondary-ion mass spectrometry will help to better address cumulative *versus* instantaneous isotopic effects associated with these processes in a future study. The sulfides of the units SSB and C are pyrite framboids of various sizes (Figs. 7E and 7F) consistent with MSR activity. According to the record of trace elements (Thomazo et al., 2016), these sediments were deposited under oxic conditions. A collapse in bioturbation and storm event occurrences are visible during the late Smithian and at the SSB (Figs. 2, 5D). We therefore suggest that pyrites of unit SSB and C precipitated syndementarily in pore water with a limited sulfate availability due to a rapid disconnection of top-layer sediments with the overlying seawater sulfate reservoir. Such a marked change may result from the absence of bioturbations at that time (see stratigraphic variations of bioturbation intensity in, Fig. 3 and illustration of non-biotic and non-bioturbated mudstones from the SSB unit in, Fig. 7D). This disappearance was coeval to, and could have been a consequence of, the global late Smithian event, which for instance

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

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

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

4.5. CAS sulfur isotopes results

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

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

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

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

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

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

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

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

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

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

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

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

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

Contrasting with Saitoh et al. (2017) we established here (Fig. 8, Section 4.3) a strong relationship between bioturbation and the MSI signal recorded within the permanently oxic bottom water conditions that developed at Mineral Mountains across the SSB. Bioturbation, which is a necessary driver to sustain intense iron and sulfur cycling in marine sediments through the suboxic zone (Van de Velde et al., 2016), likely continuously supplied sulfates into the sediments and stimulates the sulfate reduction and *in situ* sulfide precipitation in the sediments during the deposition of the middle Smithian unit B. During this period, open system MSR activity from pore water fluids connected to oceanic waters is in accordance with (i) the higher average concentration of sulfides, (ii) the observation of pyrite (FeS_2) in the form of framboids, and (iii) the MSI signatures. Moreover, unit B records low $\delta^{13}\text{C}_{\text{carb}}$ values associated with high Mn/Sr and high $\text{Mg}/(\text{Mg}+\text{Ca})$ ratios. Such variations are in agreement with a strong influence of the MSR activity on the geochemistry of the sediments. Indeed, MSR is well known for its role in promoting the precipitation of early diagenetic authigenic carbonates and secondary carbonates such as dolostones with low $\delta^{13}\text{C}_{\text{carb}}$ values through the consumption of excess protons (Vasconcelos and McKenzie, 1997; Zhang et al.,

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

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

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

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

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

6. Conclusions

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

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

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

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

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

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

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Captions

Table 1. Results of isotopic and elemental analyses.

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

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

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

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

Fig. 4: Cross calibration between SO₂-EA-IRMS and SF₆-IRMS on the $\delta^{34}\text{S}$ values of 10 samples from this study. Uncertainties are smaller than the symbol size.

Fig. 5: Relationship between the $\delta^{13}\text{C}_{\text{carb}}$ (VPDB, ‰) and the Mg/(Mg+Ca) ratio in units A, B, SSB and C.

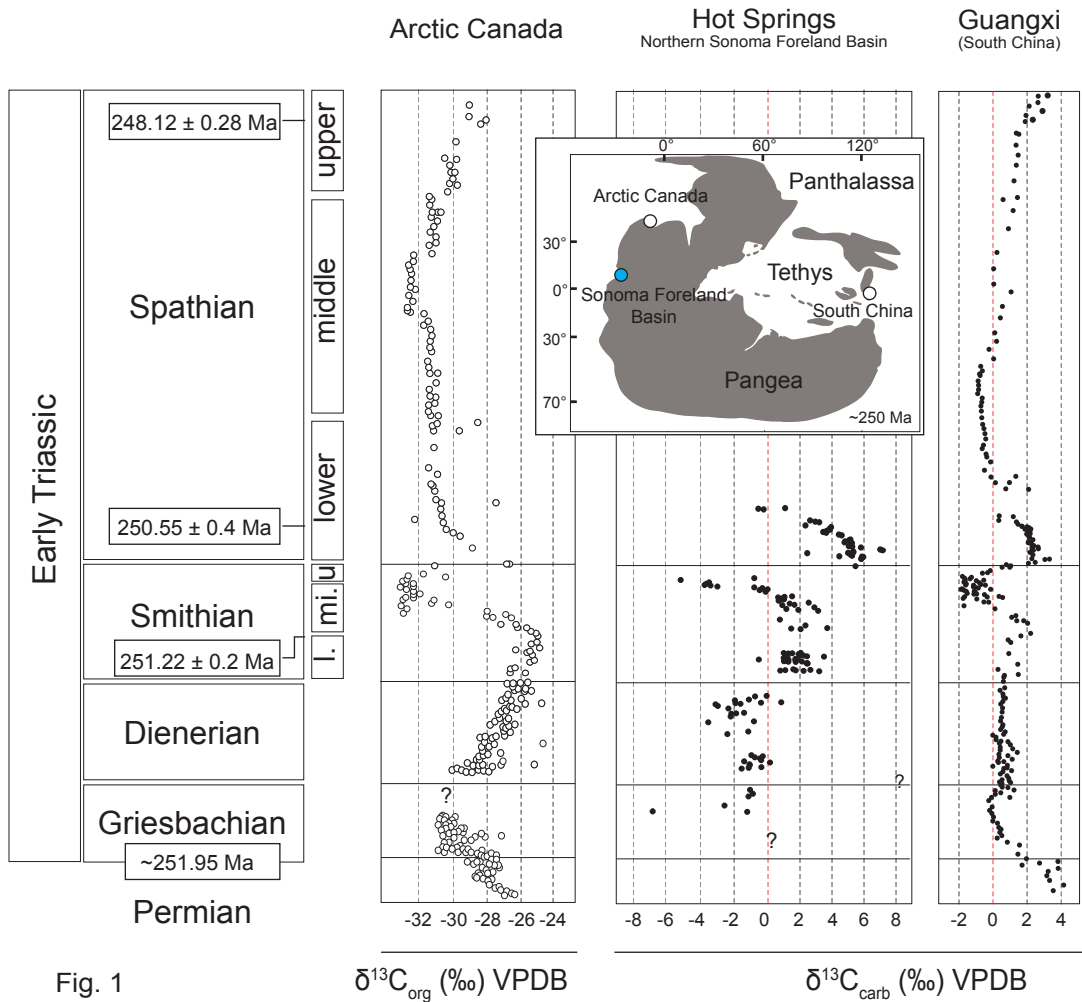
Fig. 6: Correlation relationship between the carbonate content (in wt. %) and the sum of calcium and magnesium content (in wt. %).

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

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

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



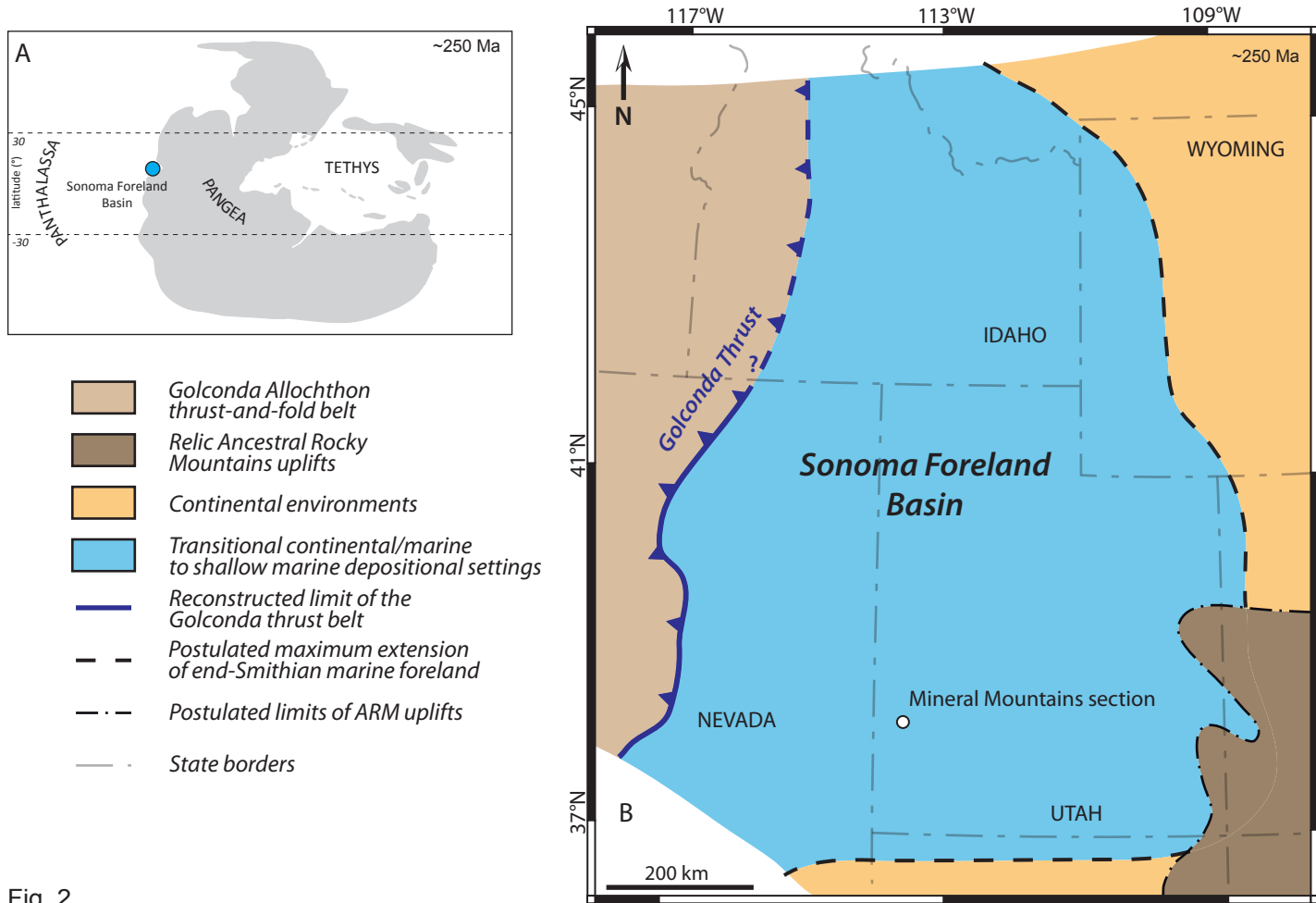


Fig. 2

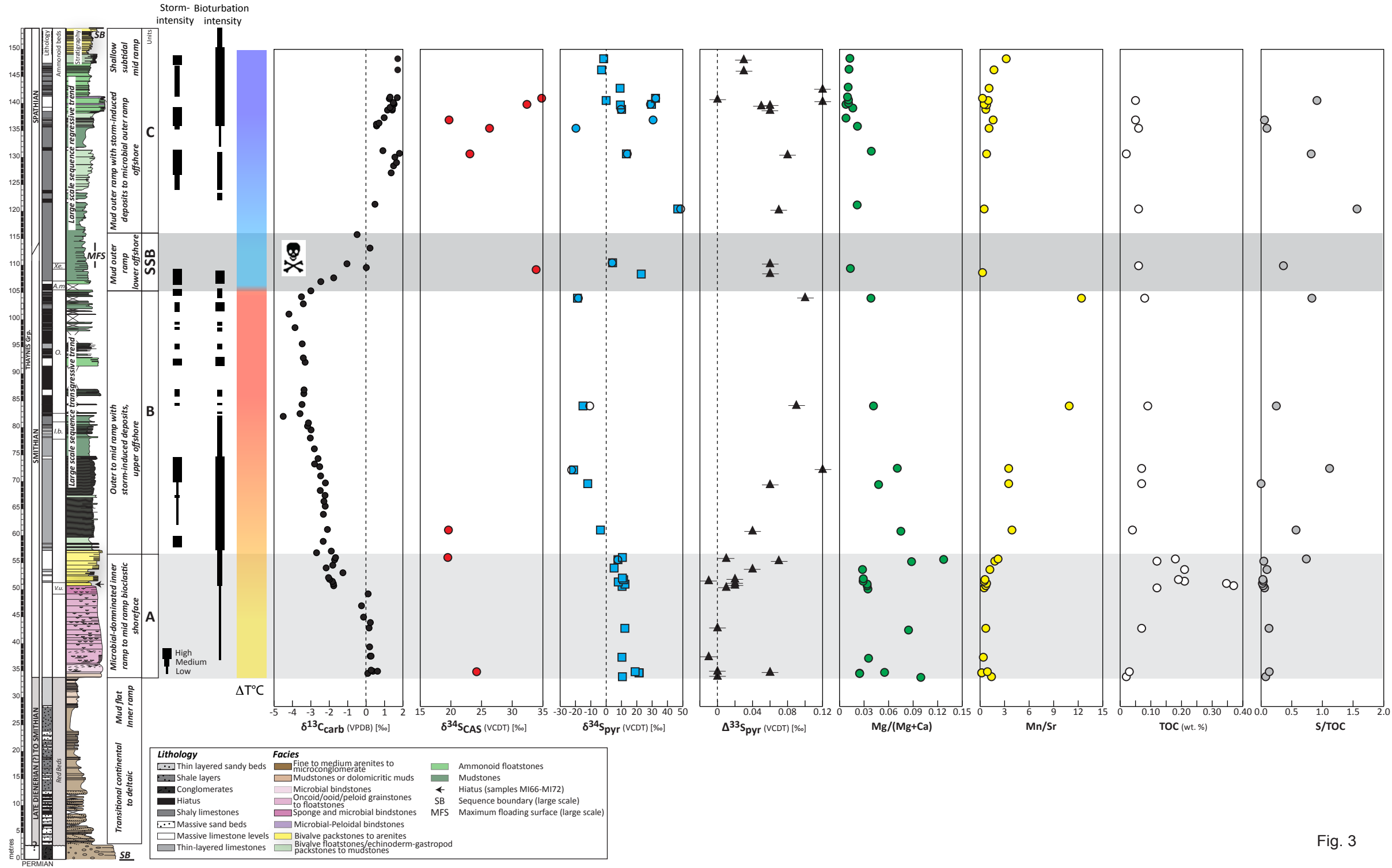


Fig. 3

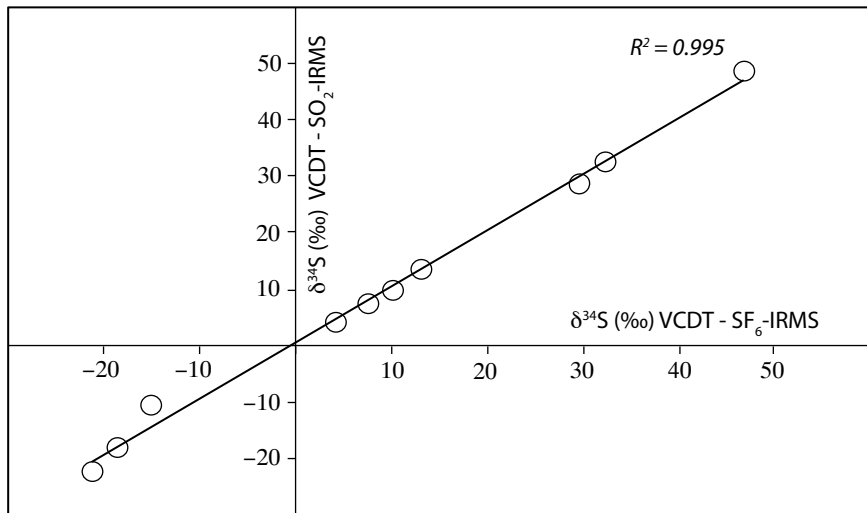


Fig. 4

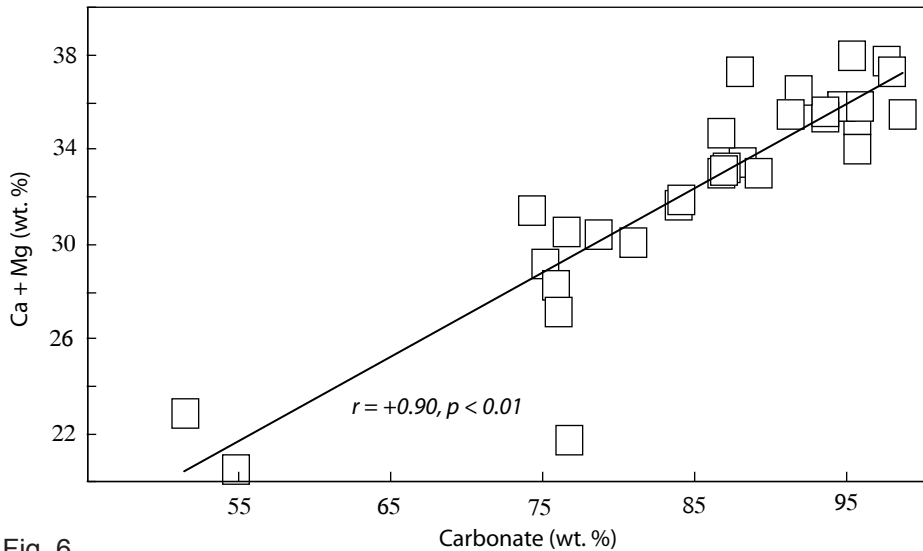
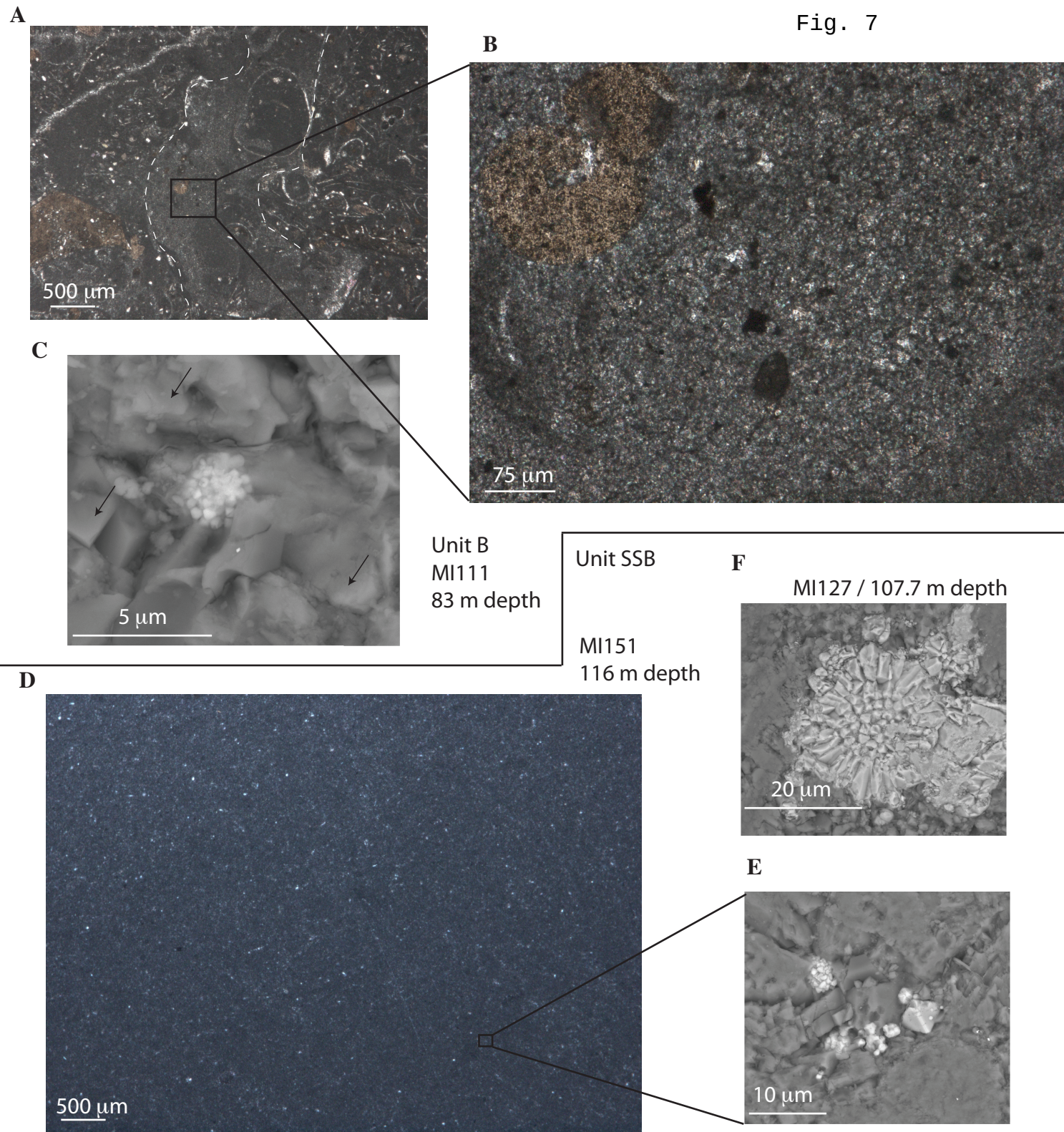


Fig. 6

Fig. 7



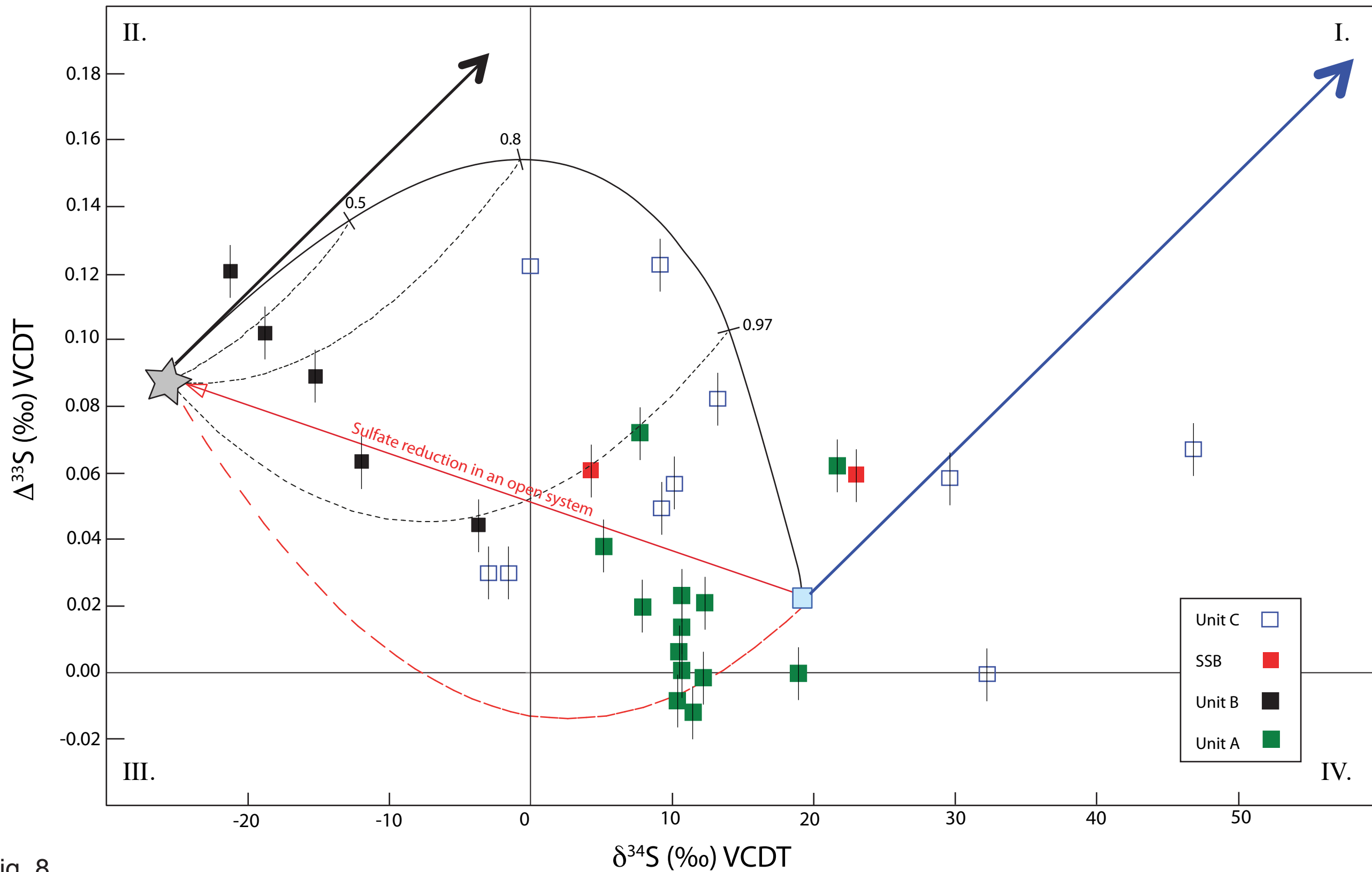


Fig. 8

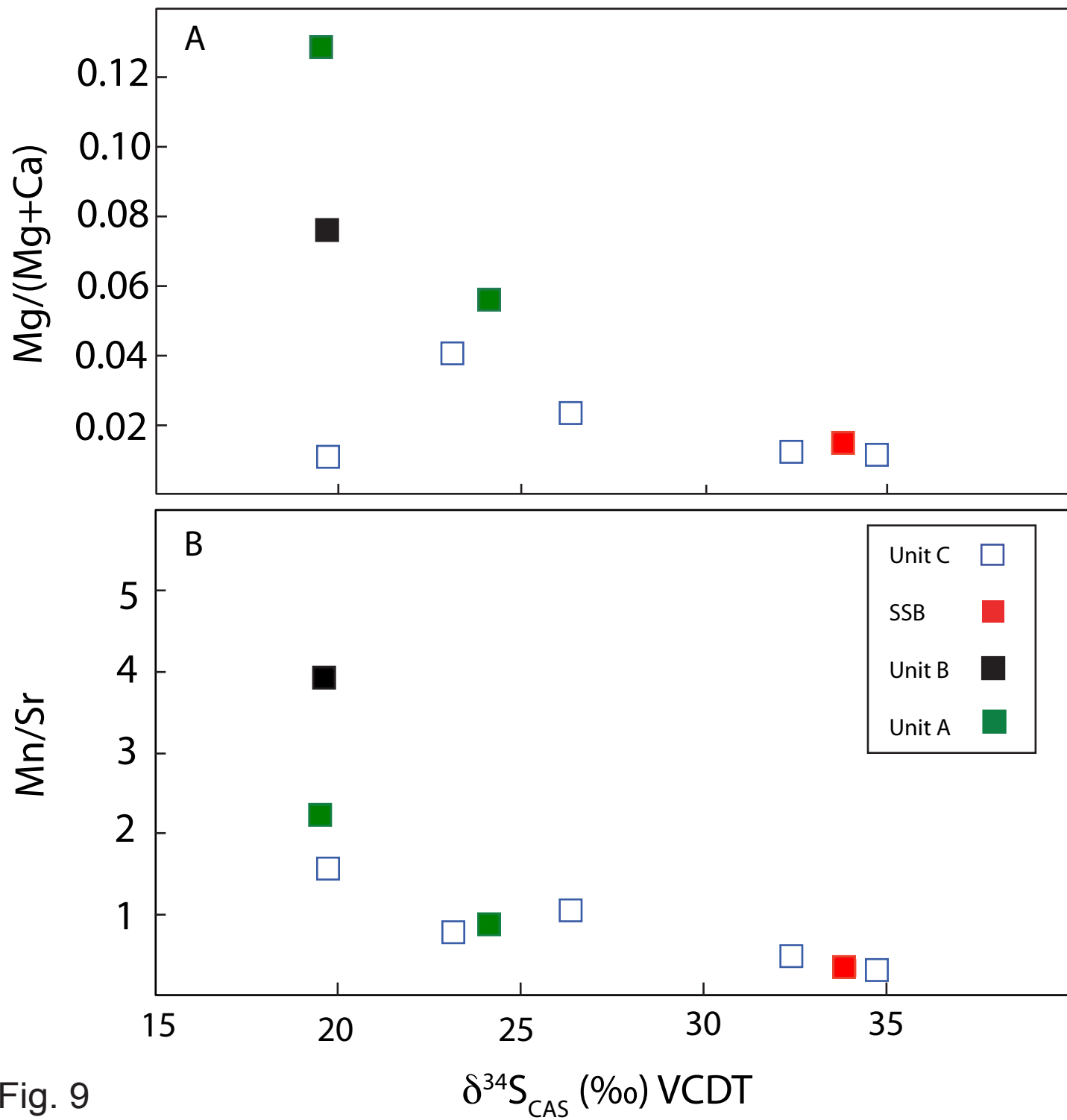


Fig. 9

Table 1 : Participant's baseline characteristics

	EIH (n = 10)	NEIH (n = 9)	Untrained (n = 10)
Age (years)	40.3 ± 1.2	39.1 ± 1.3	37.8 ± 1.7
Body mass (kg)	70.1 ± 2.3	71.1 ± 2.4	76.3 ± 1.9
Height (cm)	178 ± 2	179 ± 2	174 ± 1
Body mass index (kg·m⁻²)	22.2 ± 0.4 ^Ψ	22.3 ± 0.7 ^Ψ	24.9 ± 0.6
VO₂max (ml·min⁻¹·kg⁻¹)	60.1 ± 2.0 ^Ψ	58.3 ± 1.8 ^Ψ	43.3 ± 2.0
FEV₁ (% predicted)	119 ± 3	112 ± 7	114 ± 6
Training volume (hours·week⁻¹)	12.0 ± 1.7 ^Ψ	11.3 ± 1.1 ^Ψ	2 ± 0.5

Values are means ± SEM. EIH: athletes exhibiting O₂ desaturation; NEIH: athletes without O₂ desaturation

^Ψ, significantly different from untrained group (p < 0.05)