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**Sulfur isotope evidence for low and fluctuating sulfate levels in the
Late Devonian ocean and the potential link with the mass extinction
event**

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26 Abstract

27 High amplitude positive carbon isotope excursions in the Late Devonian, the *punctata* and Kellwasser
28 events, reflect major perturbations in the global carbon cycle that have been attributed to increased
29 continental weathering and subsequent ocean eutrophication. Despite the comparable carbon isotope
30 anomalies, however, a major extinction has been reported only for the Kellwasser Events, while the
31 *punctata* Event is marked by low extinction intensity. This study presents multiple sulfur isotope records
32 of carbonate-associated sulfate (CAS) and pyrite from Late Devonian sections in the Great Basin, USA,
33 in order to document changes in the coupled (or decoupled) geochemical cycles of carbon and sulfur
34 during the *punctata* and Upper Kellwasser events. A positive sulfur isotope shift in both CAS and pyrite
35 accompanies the onset of the *punctata* Event, but to a larger extent in the latter. As a result, the sulfur
36 isotope offset between CAS and pyrite ($\Delta^{34}\text{S}_{\text{CAS-py}}$) dropped to less than 10‰. In the middle of the
37 *punctata* Event, a sharp negative $\delta^{34}\text{S}_{\text{CAS}}$ excursion and negative $\Delta^{34}\text{S}_{\text{CAS-py}}$ values coincide with the
38 Alamo impact. Unlike the rapid $\delta^{34}\text{S}_{\text{py}}$ and $\delta^{34}\text{S}_{\text{CAS}}$ oscillations associated with the *punctata* Event, the
39 Upper Kellwasser was a period of relative stability, except for a brief $\delta^{34}\text{S}_{\text{CAS}}$ drop before the event.
40 Paired sulfur isotope data, aided by a simple box model, suggest that the geochemical cycle of sulfur may
41 have been partly responsible for the contrasting biological responses that define these events. High
42 stratigraphic $\delta^{34}\text{S}_{\text{py}}$ and $\delta^{34}\text{S}_{\text{CAS}}$ variability, coupled with strong reservoir effect, demonstrates a relatively
43 small oceanic sulfate pool existed during the *punctata* Event. Further, the Alamo impact likely triggered
44 the rapid oxidation of microbially-produced sulfide within this event. The expansion of sulfidic bottom
45 water thus may have been impeded during the *punctata* Event. In contrast, the lack of a positive shift in
46 $\delta^{34}\text{S}_{\text{CAS}}$ and sizable $\Delta^{34}\text{S}_{\text{CAS-py}}$ values (>15‰) throughout the Upper Kellwasser Event imply higher
47 relative sulfate levels. A larger seawater sulfate reservoir may have promoted the development of sulfidic
48 bottom waters in the eutrophic epicontinental seas, increasing biological stress and potentially
49 contributing to the mass extinction.

50 **1. Introduction**

51 The Late Devonian extinction at the Frasnian-Famennian (F-F) boundary is one of five major
52 biological catastrophes that characterize the Phanerozoic fossil record. This crash in biodiversity has been
53 related to intense biological and environmental change, including (but not limited to): terrestrial
54 afforestation (Algeo *et al.*, 1995), a series of asteroid impacts (McGhee, 2001), global cooling
55 (Joachimski and Buggisch, 2002), and active orogeny due to the accretion of continental blocks
56 (Averbuch *et al.*, 2005). Among them, eutrophication and marine anoxia, triggered by increased
57 continental weathering, nutrient delivery and organic carbon production, are widely thought to contribute
58 to the Late Devonian mass extinction (Murphy *et al.*, 2000; Bond *et al.*, 2004). The evidence for
59 eutrophication and marine anoxia at this time is found in the Lower and Upper Kellwasser Horizons that
60 straddle the F-F boundary, which are each marked by positive carbon isotope excursions in marine
61 carbonate and organic carbon (Fig. 1) (Murphy *et al.*, 2000; Buggisch and Joachimski, 2006). However,
62 the widespread deposition of organic-rich facies and the existence of comparable carbon isotope
63 anomalies prior to the Kellwasser events suggest that multiple episodes of oxygen depletion occurred
64 during the Late Devonian (Buggisch and Joachimski, 2006; Yan *et al.*, 2007). Seawater $^{87}\text{Sr}/^{86}\text{Sr}$ values
65 indeed indicate that an increase in continental weathering flux predates the F-F transition (Fig. 1). The
66 biological consequences of earlier anoxic events were, nevertheless, noticeably different from those of the
67 Kellwasser events. The early to middle Frasnian transition, for example, records a marine hypoxic/anoxic
68 event (Casier *et al.*, 2006; Marynowski *et al.*, 2008) and a large-scale carbon isotope perturbation through
69 the earliest middle Frasnian *punctata* biozone (Fig. 1), but this so-called “*punctata* Event” is not
70 correlated with extinction events (Morrow *et al.*, 2009; Piszczowska and Racki, 2012) except for the
71 regional reef crisis in central Europe (Copper, 2002). While previous work has highlighted the contrasting
72 biological response to the *punctata* and Kellwasser events (John *et al.*, 2008; Piszczowska and Racki,
73 2012), the underlying mechanism/s for these differences remain unknown.

74 Due to its wide range of oxidation states, sulfur is cycled through a variety of environmental and
75 biological reservoirs. Organic carbon availability and marine anoxia influence the geochemical cycle of
76 sulfur through microbial sulfate reduction (MSR), an anaerobic process that couples the oxidation of
77 organic matter to the reduction of sulfate. MSR relies on the supply of organic matter to oxygen-depleted
78 environments, and therefore increased deposition of organic matter can accelerate sulfate reduction in
79 marine sediments (Bernier and Raiswell, 1983). Importantly, the product of sulfate reduction, H₂S, is
80 lethal to most aerobic organisms, and also the buildup of sulfidic bottom water can influence the cycles of
81 other essential elements such as phosphorous and iron, exacerbating biological stress during an oceanic
82 anoxic event (Murray, 1995; Kleeberg, 1997). Since significant isotopic discrimination accompanies
83 MSR (Chambers *et al.*, 1975; Sim *et al.*, 2011a), global changes in H₂S production can be inferred by
84 tracking the sulfur isotope composition of seawater sulfate through time.

85 Here we present the sulfur isotope composition of carbonate-associated sulfate ($\delta^{34}\text{S}_{\text{CAS}}$) and
86 pyrite ($\delta^{34}\text{S}_{\text{py}}$) from Late Devonian carbonate successions in Nevada and western Utah in order to evaluate
87 the nature of sulfur cycling during the *punctata* and Upper Kellwasser events. Distinct sulfur isotope
88 patterns recorded in these events, along with their quantitative interpretation using a simple box model,
89 highlight the importance of marine sulfate concentration as a potential determinant in environmental
90 stress during ocean anoxic events. In addition to conventional ³⁴S/³²S ratios, analyses of minor sulfur
91 isotopes (³³S and ³⁶S) help constrain Late Devonian sulfur cycle dynamics. Finally, proximity of the
92 studied area to the site of the Alamo impact, which has been implicated as a cause of the Late Devonian
93 extinction (McGhee, 2001), provides a unique opportunity to examine what influence, if any, a large
94 asteroid impact had on the sulfur cycle.

95

96 **2. Geologic setting**

97 Devonian shelf deposits in Nevada and western Utah reflect progressive deepening from east to
98 west, representing inner shelf, middle to outer shelf, ramp, slope and oceanic basin environments

99 (Morrow and Sandberg, 2008) (Fig. 2). During the late Givetian to middle Frasnian, limestones of Devil's
100 Gate and Guilmette formations were deposited in the Great Basin, overlying the middle Givetian Fox
101 Mountain Formation (Sandberg *et al.*, 1997). The Guilmette Formation in eastern Nevada and Utah
102 consists of limestone and minor sandstone units deposited in the central part of a carbonate platform,
103 while its deep-water equivalent, the Devil's Gate Limestone in central Nevada represents a platform to
104 slope setting (Sandberg *et al.*, 1989). Throughout the latter Devonian, however, the development of the
105 proto-Antler forebulge in central Nevada altered the depositional regime and reduced the area of
106 carbonate deposition (Morrow and Sandberg, 2008). The backbulge basin developed to the east of the
107 proto-Antler forebulge. Basin facies of the Pilot Shale, including siltstones, thin micrites, and sandy
108 turbidites, filled this intra-shelf basin, covering the former middle to outer shelf carbonate deposits
109 (Sandberg *et al.*, 1989).

110 The Alamo bolide impact interrupted the middle Frasnian sedimentary record of this area. A large
111 body of evidence, including megabreccia, carbonate accretionary lapilli, displaced conodonts, shocked
112 quartz grains, and an iridium anomaly, indicates that a km-scale meteorite impacted the offshore setting
113 west of the carbonate-shelf margin (Warme and Sandberg, 1996; Warme and Kuehner, 1998; Fig. 2).
114 Conodont biostratigraphy constrains the timing of the Alamo event to the earliest middle Frasnian
115 *Palmatolepis punctata* zone at ~382 Ma (Morrow *et al.*, 2009). Although this large impact to a
116 subtropical carbonate shelf likely caused a mega-tsunami and released large amounts of climatically
117 active and potentially lethal volatiles, bioherm mudmounds directly above the Alamo Breccia and
118 taxonomic comparison of pre- and post-breccia stages suggest that the impact had no major effect on the
119 carbonate platform fauna near the impact site (Warme and Kuehner, 1998; Casier *et al.*, 2006).

120 In this study, data are presented from three stratigraphic sections, including Hancock Summit West
121 (HSW), Devil's Gate (DG), and Granite Mountains (GM). We investigated the middle Frasnian interval at
122 HSW and DG sections, while focusing on the F-F boundary at the GM section (Fig. 3). Sedimentology
123 and conodont biostratigraphy of these sections are described by Sandberg *et al.* (1997), Morrow and

124 Sandberg (2003), Casier *et al.* (2006), and Warne *et al.*, (2008). Here, we summarize the key features. At
125 the HSW section, the upper Givetian to middle Frasnian Guilmette Formation is exposed along the crest
126 of “Dropped Mountain” (Warne *et al.*, 2008). As the type section of the Alamo Breccia Member of
127 the Guilmette Formation, the *punctata* biozone contains a 60-m-thick impact breccia that is rich in
128 megaclasts (Warne *et al.*, 2008; Morrow *et al.*, 2009). Most clasts are locally-derived Devonian platform
129 rocks, composed of micrite with scattered stromatoporoids, corals, and brachiopods (Warne and
130 Sandberg, 1996; Morrow *et al.*, 2009). Instead of large clasts, matrix was preferentially sampled as
131 representative of the Alamo Breccia. The DG section is located northwest of Eureka, Nevada, where
132 middle Frasnian rocks within the lower member of the Devil’s Gate Limestone consist of open-marine
133 and carbonate platform deposits (Casier *et al.*, 2006). Contrary to the HSW section, only a 29-cm-thick
134 diamictite bed with granule-size carbonate clasts records the Alamo event in the DG section (Sandberg *et*
135 *al.*, 1997). The F-F boundary interval at the GM section is composed of the lower member of the Pilot
136 Shale, containing turbiditic calcareous and siliceous siltstones, sandstone, and debris-flow limestone
137 (Morrow and Sandberg, 2003).

138

139 **3. Methods**

140 Samples were cut into small pieces to remove weathered surfaces and veins. Fresh rock chips
141 were powdered in a Spex 8530 shatterbox with an alumina ceramic grinding container. Inorganic carbon
142 contents of powdered samples were determined on a UIC carbon coulometer, and only samples with
143 inorganic carbon contents greater than 7%, which amounts to 58% of equivalent CaCO_3 , were used for
144 carbonate-associated sulfate (CAS) extraction. We extracted CAS for sulfur isotope analysis using a
145 method slightly modified after Wotte *et al.* (2012). Depending on the inorganic carbon content, 80-120g
146 of samples were leached twice in 10% NaCl solution under continuous stirring and rinsed in DI water to
147 remove any water-soluble sulfate. The absence of sulfate in the rinse water was tested by adding a BaCl_2
148 solution (200 g/L). These leaching and rinsing steps were repeated until BaSO_4 did not precipitate from

149 the solution. Rinsed samples were soaked in 6N HCl for 3 hours to dissolve CaCO₃ and liberate sulfate
150 from the carbonate matrix. The acidified solution was filtered with a 0.45 μm cellulose nitrate filter, and
151 the insoluble residue was reserved for subsequent pyrite extraction. BaCl₂ solution was added to the
152 filtrate in order to quantitatively precipitate sulfate as BaSO₄, which was then collected on a 0.45 μm
153 cellulose nitrate filter *via* vacuum filtration.

154 Pyrite sulfur (S_{py}) was extracted from insoluble residue and clay-rich samples using the technique
155 of Canfield *et al.* (1986). Samples were treated with a reduced chromium chloride/HCl solution (boiling,
156 2 hr) and H₂S was driven via an N₂ carrier gas into a 3% AgNO₃ - 10% NH₄OH solution, trapped as Ag₂S,
157 and collected by filtration. For ³⁴S/³²S ratio determination, isotope analysis was conducted using a
158 Thermo-electron Delta V continuous-flow isotope ratio mass spectrometer housed at Northwestern
159 University. For each analysis, 0.9 mg of BaSO₄ or Ag₂S was mixed with 2 mg of V₂O₅ and combusted to
160 SO₂ gas. The resulting isotope ratios were reported in the δ³⁴S notation normalized to Vienna Canyon
161 Diablo Troilite (VCDT). Linear scale correction was applied to yield δ³⁴S values of 0.5‰ and 20.3‰ for
162 IAEA SO-5 and NBS-127 (BaSO₄ standards), and 22.7‰, -0.3‰, and -32.3‰ for IAEA S-1, S-2, and S-
163 3 (Ag₂S standards). Standards were inserted within each run of 10 samples. The analytical reproducibility
164 was less than 0.2‰ based on repeat analyses of standard materials.

165 Minor sulfur isotope compositions (³³S and ³⁶S) were determined for samples collected from the
166 HSW section. BaSO₄ precipitates were reduced to H₂S by reacting with a boiling reducing solution
167 (mixture of HI, H₃PO₂, and HCl, Thode *et al.*, 1961) under continuous N₂ purging, and the H₂S produced
168 was precipitated as Ag₂S in an AgNO₃-NH₄OH trap. For the isotope analysis, Ag₂S samples were reacted
169 with an excess of F₂ gas for more than 5 hours at 300 °C and converted to SF₆, which in turn was purified
170 by gas chromatography and transferred into a mass spectrometer. In total, 27 pyrite and 7 CAS samples
171 were analyzed using a Thermo-electron MAT 253 isotope mass spectrometer at Massachusetts Institute of
172 Technology. The measured ³³S/³²S and ³⁶S/³²S ratios were calibrated to the VCDT scale by defining the

173 international standard IAEA S-1 to be -0.055‰ and -1.14‰ for $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$, respectively (Ono *et al.*,
174 2012). The abundance of ^{33}S and ^{36}S was then reported using capital delta notation ($\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$):

$$175 \quad \Delta^{33}\text{S} = 1000 \times \left\{ \ln \left(\frac{\delta^{33}\text{S}}{1000} + 1 \right) - 0.515 \cdot \ln \left(\frac{\delta^{34}\text{S}}{1000} + 1 \right) \right\} \quad (1)$$

$$176 \quad \Delta^{36}\text{S} = 1000 \times \left\{ \ln \left(\frac{\delta^{36}\text{S}}{1000} + 1 \right) - 1.9 \cdot \ln \left(\frac{\delta^{34}\text{S}}{1000} + 1 \right) \right\} \quad (2)$$

177 The analytical reproducibility for $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$, as determined by replicate analyses of a reference
178 material (IAEA S-1), is 0.014‰ and 0.19‰, respectively (Ono *et al.*, 2012).

179 For carbonate carbon and oxygen isotope analyses, samples were reacted with 100% H_3PO_4 under
180 helium atmosphere, and the released CO_2 was measured using a Thermo Gas Bench coupled to a Thermo
181 Delta V continuous-flow isotope ratio mass spectrometer at Northwestern University.

182

183 **4. Results**

184 Stratigraphy and geochemical results of the HSW, DG, and GM sections are shown in Figure 3
185 and Supplementary Table 1. The studied sections lack discernible unconformities and contain all known
186 conodont biozones of the F-F interval (Morrow and Sandberg, 2003; Casier *et al.*, 2006; Morrow *et al.*,
187 2009). Sample ages are estimated by linearly interpolating between biozone boundary ages (Kaufmann,
188 2006) according to their relative positions within the biozone. The HSW and DG sections record a ~3‰
189 positive carbon isotope excursion across the *punctata* biozone, which is consistent with previously
190 reported results from the Great Basin (Morrow *et al.*, 2009) and other areas (Yan *et al.*, 2007;
191 Piszarska and Racki, 2012) (Fig. 4). Similarly, $\delta^{34}\text{S}_{\text{CAS}}$ and $\delta^{34}\text{S}_{\text{py}}$ values increase by ~10‰ and 40‰,
192 respectively (Fig. 4). Given the greater increase in $\delta^{34}\text{S}_{\text{py}}$, sulfur isotope offsets between CAS and pyrite
193 ($\Delta^{34}\text{S}_{\text{CAS-py}} = \delta^{34}\text{S}_{\text{CAS}} - \delta^{34}\text{S}_{\text{py}}$) decrease from 40‰ to less than 10‰ and persist at relatively low values
194 throughout the *punctata* Event (Fig. 4). In the middle of the *punctata* biozone, several of $\delta^{34}\text{S}_{\text{CAS}}$ values
195 are extremely low, down to 13‰, resulting in negative $\Delta^{34}\text{S}_{\text{CAS-py}}$ values. This sharp negative $\delta^{34}\text{S}_{\text{CAS}}$
196 excursion coincides with the Alamo impact event (Sandberg *et al.*, 1997; Morrow *et al.*, 2009). Parallel to

197 the decline in $\delta^{13}\text{C}_{\text{carb}}$ at the end of the *punctata* Event, $\delta^{34}\text{S}_{\text{CAS}}$ and $\delta^{34}\text{S}_{\text{py}}$ values shift back to $\sim 30\text{‰}$ and
198 10‰ , respectively, thereby increasing $\Delta^{34}\text{S}_{\text{CAS-py}}$ values up to 20‰ .

199 Sulfur isotope variations throughout the F-F boundary are relatively small in the studied section
200 (GM), compared to the fluctuations in $\delta^{34}\text{S}_{\text{CAS}}$ and $\delta^{34}\text{S}_{\text{py}}$ during the *punctata* Event (Fig. 3). The GM
201 section does not exhibit a positive $\delta^{34}\text{S}_{\text{CAS}}$ shift that corresponds to the Upper Kellwasser positive $\delta^{13}\text{C}$
202 excursion at the F-F boundary. Instead, the late Frasnian *linguiformis* zone is characterized by an $\sim 5\text{‰}$
203 decline in $\delta^{34}\text{S}_{\text{CAS}}$ (Fig. 5). This comparatively stable seawater sulfate isotope composition throughout the
204 F-F boundary is similar to those reported from Belgium and Poland (John *et al.*, 2010) (Fig. 5). In
205 contrast to the negative shift in $\delta^{34}\text{S}_{\text{CAS}}$, $\delta^{34}\text{S}_{\text{py}}$ increases by 10‰ through the *linguiformis* to early
206 *triangularis* biozone, leading to a moderate decrease in $\Delta^{34}\text{S}_{\text{CAS-py}}$ from 30 to 15‰ .

207 The $\Delta^{33}\text{S}$ of CAS through the HSW section exhibits positive values ranging from 0.029 to 0.074,
208 except for two negative values from the Alamo Breccia (Fig. 6). Pyrites yield a wide range of $\Delta^{33}\text{S}$ values
209 from -0.043 to 0.044 .

210

211 **5. Discussion**

212 **5.1. Preservation of primary sulfur isotope signatures**

213 It is important to determine if the $\delta^{34}\text{S}_{\text{CAS}}$ values reflect primary seawater signatures or post-burial
214 alteration processes. A positive correlation between $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ can indicate the influence of
215 meteoric fluids, which are typically ^{13}C - and ^{18}O -depleted relative to seawater. A cross-plot of $\delta^{13}\text{C}_{\text{carb}}$ and
216 $\delta^{18}\text{O}_{\text{carb}}$ for the HSW and DG sections lacks this trend (Fig. 7A). In contrast, a strong positive correlation
217 ($R^2 = 0.84$) is observed in the GM section (Fig. 7A), where ^{13}C - and ^{18}O -depleted samples also yield low
218 CAS contents (Fig. 7B), suggesting that it has experienced meteoric diagenesis and CAS was removed
219 during this process. The lack of correlation between $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{34}\text{S}_{\text{CAS}}$, however, indicates little impact
220 on the isotope composition of CAS (Fig. 7C). While several extremely low $\delta^{18}\text{O}_{\text{carb}}$ values (down to -16‰)
221 at the DG section are likely the result of diagenetic alteration at elevated temperatures, they are not

222 associated with correspondingly low $\delta^{13}\text{C}_{\text{carb}}$ or $\delta^{34}\text{S}_{\text{CAS}}$ values. Moreover, both carbon and sulfur isotope
223 trends at the DG section are consistent with HSW results where $\delta^{18}\text{O}_{\text{carb}}$ plot within the typical range for
224 Frasnian limestones (Morrow *et al.*, 2009). Thus, geochemical evidence suggests that a subset of $\delta^{18}\text{O}_{\text{carb}}$
225 were likely affected by post-burial alteration but that overall, $\delta^{34}\text{S}_{\text{CAS}}$ values reflect primary marine
226 signatures.

227 It is also important to rule out possible incorporation of contaminant sulfate as CAS. Pyrite
228 oxidation can artificially lower $\delta^{34}\text{S}_{\text{CAS}}$ values (Marengo *et al.*, 2008), which is more likely when pyrite
229 concentrations are high and $\delta^{34}\text{S}_{\text{py}}$ values ^{34}S -depleted. To limit contamination risks, we screened samples
230 for carbonate (> 58%) and pyrite ($\text{S}_{\text{py}} < 250$ ppm) content. In all studied sections, neither S_{py} content nor
231 $\delta^{34}\text{S}_{\text{py}}$ is correlated significantly with $\delta^{34}\text{S}_{\text{CAS}}$ ($R^2 < 0.1$) (Figs. 7D and 7E), indicating no obvious
232 influence from pyrite oxidation. A water leaching procedure was utilized to minimize contamination by
233 secondary atmospheric sulfate (Peng *et al.* 2014). Finally, similar sulfur isotope trends at two different
234 localities support preservation of primary signals (Figs. 3 and 4).

235

236 **5.2. Controls on sulfur cycling during the *punctata* Event**

237 The onset of the *punctata* Event is characterized by positive $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{34}\text{S}_{\text{CAS}}$ shifts in both
238 studied sections (Fig. 4). The $\delta^{13}\text{C}$ excursion has been ascribed to an increase in the preferential removal
239 of ^{12}C resulting from enhanced primary productivity and organic carbon (C_{org}) burial. Increased C_{org} burial
240 during this period has been linked to elevated rates of nutrient delivery from the continents to the ocean
241 due to terrestrial afforestation and orogenic activity (John *et al.*, 2008). Phanerozoic marine sediments
242 often show a positive correlation between C_{org} and pyrite burial as a result of sulfate reduction (Raiswell
243 and Berner, 1986). If the residence time of seawater sulfate is low (relative to modern levels), the
244 coupling of these two burial fluxes can result in sympathetic shifts in $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{34}\text{S}_{\text{CAS}}$, because
245 microbes preferentially remove ^{32}S during the production of sulfide. Therefore, assuming sulfate and
246 reactive iron are not limiting with respect to pyrite formation (Berner, 1984), the coupled carbon and

247 sulfur isotope trends indicate that the supply of organic matter to marine sediments primarily controlled
248 the burial of pyrite through the *punctata* Event.

249 A rapid decrease in $\Delta^{34}\text{S}_{\text{CAS-py}}$ values at the beginning of the *punctata* Event puts an additional
250 constraint on the middle Frasnian sulfur cycle. CAS is incorporated into CaCO_3 as a structural
251 substitution of the carbonate ion and ideally represents the $\delta^{34}\text{S}$ of water column sulfate (Lyons, 2004).
252 Conversely, pyrite can form in the water column and/or in sediment porewaters. In the water column or
253 near the sediment surface, where seawater acts as an infinite sulfate reservoir for MSR, $\Delta^{34}\text{S}_{\text{CAS-py}}$ values
254 are large and reflect the magnitude of microbial sulfur isotope fractionation. However, porewater
255 transport of sulfate to sediments deeper below the sediment-water interface is often insufficient to
256 compensate for loss due to MSR and pyrite burial. Thus, pyrite formed in deeper sediments may exhibit
257 closed system effects, resulting in relatively small $\Delta^{34}\text{S}_{\text{CAS-py}}$ values. The degree to which closed system
258 behavior exists depends upon organic matter and reactive iron availability. Quantitative reduction and
259 subsequent precipitation of pyrite would produce near zero $\Delta^{34}\text{S}_{\text{CAS-py}}$ values. As a result, the reduction of
260 $\Delta^{34}\text{S}_{\text{CAS-py}}$ values is likely more pronounced at low sulfate levels (Gomes and Hurtgen, 2013).
261 Alternatively, because the magnitude of sulfur isotope fractionation during MSR tends to be smaller when
262 labile organic compounds support fast growth rates and at the high supply rate of the organic electron donor
263 (Chambers *et al.*, 1975; Sim *et al.*, 2011a, 2011b), small $\Delta^{34}\text{S}$ values during the *punctata* Event may
264 reflect the change in the nature of organic material available in the sulfate reduction zone. Although both
265 hypotheses accord with the increased C_{org} and pyrite burial that characterize the early to middle Frasnian
266 boundary, the argument for low sulfate levels becomes stronger when $\Delta^{33}\text{S}$ data are considered.

267 Throughout the late Givetian to middle Frasnian, $\Delta^{33}\text{S}$ values of pyrite are more negative than
268 those of CAS (Fig. 6), except for two negative $\Delta^{33}\text{S}_{\text{CAS}}$ values from the Alamo Breccia (discussed in
269 section 5.3). In contrast, laboratory culture studies have shown that MSR generates H_2S with only more
270 positive $\Delta^{33}\text{S}$ values relative to the reactant sulfate (Johnston *et al.*, 2007; Sim *et al.*, 2011a, 2011b).
271 Johnston *et al.* (2005) reported that sulfide produced by microbial sulfur disproportionation yields $\Delta^{33}\text{S}$

272 values more negative than those of sulfate, but both products (sulfate and sulfide) are enriched in ^{33}S
 273 compared to the reactant elemental sulfur. It is thus difficult to attribute negative $\Delta^{33}\text{S}$ values of pyrite
 274 solely to microbial processes (Shen *et al.*, 2011). Instead, a reservoir effect in a low-sulfate ocean may
 275 explain these contradictory observations. It is important to note that previous culture studies were carried
 276 out in the presence of excess sulfate (Johnston *et al.*, 2007; Sim *et al.*, 2011a, 2011b), but if microbes
 277 reduce the entire sulfate reservoir, the resulting sulfide should have $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values identical to the
 278 initial sulfate. In this study, interestingly, pyrite $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values are aligned on one mixing line that
 279 passes through the isotopic composition of CAS. Since this line also passes through the range of isotope
 280 compositions typically attributed to MSR (Fig. 6), the observed trend most likely reflects the mixing
 281 between sulfide with negative $\delta^{34}\text{S}$ values and positive $\Delta^{33}\text{S}$ values, produced by sulfate reduction in a
 282 relatively open system, and sulfide isotopically similar to seawater sulfate, produced by quantitative
 283 sulfate reduction. If the enhanced burial of C_{org} decreased the magnitude of microbial sulfur isotope
 284 fractionation by more than 20‰ at the beginning of the *punctata* Event, the mixing line should also
 285 change as the open system end-member leaps toward more positive $\delta^{34}\text{S}$ values, but our data do not
 286 support this hypothesis. Instead, a sulfur isotope shift in pyrite toward CAS values on the same mixing
 287 line demonstrates the increasing contribution of quantitative sulfate reduction during the *punctata* Event
 288 (Fig. 6). This is consistent with the reservoir effect in a low-sulfate ocean where increased organic matter
 289 availability allowed sulfate reduction to proceed to completion.

290 To place quantitative constraints on the sulfur cycle during the *punctata* Event, we construct a
 291 geochemical box model that tracks the temporal evolution of the mass and isotopic composition of marine
 292 sulfate (Kurtz *et al.*, 2003; Hurtgen *et al.*, 2009; Gill *et al.*, 2011):

$$\frac{d}{dt} M_s = F_w - (F_{\text{py}} + F_{\text{evap}}) \quad (3)$$

$$\frac{d}{dt} \delta^{34} S_{\text{sulfate}} = \frac{F_w(\delta_w^{34} - \delta^{34} S_{\text{sulfate}}) - F_{\text{py}}\Delta^{34}\text{S}}{M_s} \quad (4)$$

295 where M_s represents the mass of sulfate in the ocean reservoir, F_w is the input flux to the ocean, F_{py} is the
296 burial flux of pyrite, F_{evap} is the evaporate burial flux, $\delta^{34}S_{sulfate}$ is the isotope composition of marine
297 sulfate, δ_w is the sulfur isotope composition of sulfate input, and $\Delta^{34}S$ is the average isotope fractionation
298 associated with pyrite deposition. We combine both continental weathering and magmatic processes as a
299 single input flux, because their isotopic compositions are comparable (Kurtz *et al.*, 2003; Gill *et al.*, 2011)
300 and prescribe a $\Delta^{34}S$ value of -30‰, which approximates the Frasnian baseline in the studied sections
301 (dashed line in Fig. 4). Initial conditions used in this model were summarized in Table 1.

302 In our model runs, we explore three different initial sulfate concentrations (1, 3, and 15 mM).
303 Previous estimates for Middle Devonian sulfate concentrations, based on the chemical composition of
304 fluid inclusions encased in halite, range from 3 to 15 mM (Horita *et al.*, 2002). However, recent sulfur
305 isotope studies suggest sulfate concentrations as low as 1 mM may have existed for portions of the
306 Paleozoic (Hurtgen *et al.*, 2009; Luo *et al.*, 2010). For sulfate concentration, we estimate the time-
307 integrated amount of pyrite burial required to replicate the *punctata* Event positive sulfur isotope
308 excursion (Fig. 8). At the initial concentration of 1 mM, a 1.6-fold increase in pyrite burial for 0.5 million
309 years generates the observed isotope excursion. If we assume the *punctata* Event represents a 50%
310 increase in C_{org} burial (Pisarzowska and Racki, 2012), then our model results indicate a near-constant S/C
311 burial ratio in a low sulfate ocean (1 mM). By contrast, a larger marine sulfate reservoir demands a
312 greater increase in pyrite burial to generate the same sulfur isotope excursion, leading to a significant
313 increase in the S/C burial ratio. Although sediments deposited under euxinic conditions often exhibit
314 high S/C ratios (Bernier, 1984), previous work indicates shallow-water euxinia was limited through the
315 *punctata* Event (Pisarzowska and Racki, 2012). The observed decrease in $\Delta^{34}S_{CAS-py}$ during the *punctata*
316 Event also suggests that burial of ^{34}S -depleted syngenetic pyrite under euxinic conditions was not
317 important in our study sites. Sulfate concentrations greater than 3 mM require more than 2 million years
318 for $\delta^{34}S_{sulfate}$ to return to pre-event values. Such a long recovery time is not compatible with our
319 observations. These simulations illustrate that if the concentration of sulfate was sufficiently low (1 mM),

320 the positive $\delta^{34}\text{S}_{\text{sulfate}}$ shift at the onset of the *punctata* Event is replicated by transiently increasing the rate
321 of pyrite burial by a factor of 1.6. This estimate is lower than the 3 to 15 mM range suggested by Horita *et*
322 *al.* (2002) and may reflect rapid seawater sulfate concentration fluctuations during the Devonian. For
323 example, deposition of the lower Givetian Prairie evaporites used in Horita *et al.* (2002) predates the
324 *punctata* Event by about 5 million years. Lighter $\delta^{34}\text{S}$ values in the Prairie anhydrite (20‰; Claypool,
325 1980) suggest that enhanced pyrite burial during the intervening time may have lowered sulfate levels.

326

327 **5.3. Influence of the Alamo impact on sulfur isotope records**

328 The positive $\delta^{34}\text{S}_{\text{CAS}}$ excursion that marks the *punctata* Event is interrupted by a short (<200 kyr)
329 but large (>20‰) negative excursion just above the horizon ascribed to the Alamo impact (Fig. 4). The
330 negative excursion is associated with deposition of a massive impact breccia at the HSW section and
331 within normal marine facies at the DG section. Therefore, it does not appear that reworking of older
332 sediments was responsible for the sulfur isotope decline. Instead, given the proximity to the impact site,
333 its short duration, and large amplitude, this event appears to record the local injection of ^{34}S -depleted
334 sulfate by the Alamo impact and the subsequent dilution of the sulfur isotope anomaly by mixing with
335 open ocean sulfate. A large asteroid impact onto the edge of a tropical carbonate shelf would have
336 vaporized and oxidized reduced sulfur in sediment and aqueous phases. Although the base of the Alamo
337 Breccia cuts down into the Middle Devonian strata near the impact center, the impact disintegrated and
338 reworked mostly the carbonate platform sediments deposited within the *punctata* zone (Warme and
339 Kuehner, 1998). The sulfur isotope composition of pyrite buried in the 0.5 million years prior to the
340 impact ranges from 0 to 30‰ (Fig. 4). Therefore, given that sulfate levels appear to have been relatively
341 low through the *punctata* Event, it seems plausible that the oxidation of sedimentary sulfide was
342 responsible for the short-lived $\delta^{34}\text{S}_{\text{CAS}}$ excursion. However, near instantaneous oxidation via the Alamo
343 impact does not explain the negative $\Delta^{34}\text{S}_{\text{CAS-py}}$ values recorded during this event (Fig. 4). Similar inverse
344 isotope offsets have been reported from Proterozoic and early Phanerozoic limestones (Shen *et al.*, 2008;

345 Ries *et al.*, 2009; Gill *et al.*, 2011; Chen *et al.*, 2013). Although not fully understood, most interpretations
346 of “super-heavy pyrite” fall into one of two categories: 1) sulfate reduction with a negligible isotope
347 effect followed by preferential oxidation of H³²S (Ries *et al.*, 2009), and 2) CAS and pyrite derived from
348 isotopically distinct sulfur reservoirs due to chemical stratification (Shen *et al.*, 2008). It is not obvious
349 that a large asteroid impact would fall under either of these scenarios. Here, we speculate that biogenic
350 gas bubbles released during the impact, such as CO₂ and CH₄, may have been responsible for the
351 observed inverse isotope offsets. Increased productivity during the *punctata* Event and subsequent
352 sediment destabilization via the impact may have facilitated an increase in bubble formation and
353 ebullition in sediments. Importantly, gas bubbles can strip volatile sulfide but not sulfate from porewaters,
354 and biogenic sulfide is isotopically lighter than coexisting sulfate. In the interstitial water, as MSR
355 proceeds to completion, the δ³⁴S of accumulated reduced sulfur approaches the seawater sulfate value.
356 However, if sulfide preferentially escapes from the porewater during the early stage of the isotopic
357 evolution, pyrite precipitated later may have a heavier isotope composition than seawater sulfate. In
358 modern estuarine sediments, the effect of sulfide stripping appears insignificant (Chanton and Martens,
359 1987), but perhaps, stripping of sulfide could be more effective in eutrophic carbonate depositional
360 systems.

361 The Alamo impact influenced the distribution of minor sulfur isotopes in sedimentary sulfate as
362 well. Anomalous ³³S and ³⁶S abundances in Archean sediments (deviated from the mass-dependent
363 fractionation line) have been widely accepted as one of the strongest lines of evidence for the oxygen-
364 poor atmosphere on early Earth, because mass-independent signals produced by UV-photolysis of SO₂
365 would disappear rapidly due to mixing with different sulfur pools in the oxygenated atmosphere
366 (Farquhar *et al.*, 2000). It has been shown that mass-independent fractionation can also be produced in an
367 oxic atmosphere when large stratospheric volcanic eruptions bring SO₂ to the stratosphere where SO₂
368 photolysis below 220 nm is possible (Savarino *et al.*, 2003, Baroni *et al.*, 2007). Recently, Glikson (2010)
369 proposed a possible correlation between asteroid impacts and mass-independent fractionation of sulfur

370 isotopes, based on the fact that a large impact not only releases a significant amount of SO₂ to the
371 atmosphere but also facilitates ozone depletion, increasing UV radiation. In this study, CAS obtained
372 from the impact bed are characterized by negative $\Delta^{33}\text{S}$ values down to -0.030‰, while others have
373 positive $\Delta^{33}\text{S}$ values with a mean of 0.050 ± 0.019 ‰. Interestingly, K-T impact samples also show $\Delta^{33}\text{S}$
374 values of -0.08‰ (Koeberl and Thiemens, 2008). These anomalies are much smaller than those of sulfate
375 aerosols deposited in snow during the stratospheric eruption, which deviate from the normal mass
376 fractionation by up to 1‰ (Savarino *et al.*, 2003; Baroni *et al.*, 2007). Since the measured $\Delta^{33}\text{S}$ values are
377 within the range produced by mass-dependent microbial or geochemical processes (Johnston *et al.*, 2005;
378 Sim *et al.*, 2011a; Ono *et al.*, 2012), further studies on other impact-related deposits are needed to
379 unambiguously demonstrate the origin of negative $\Delta^{33}\text{S}$ values.

380

381 **5.4. Comparison between the *punctata* and Upper Kellwasser events**

382 In contrast to the *punctata* Event, the Upper Kellwasser Event is associated with a negative
383 $\delta^{34}\text{S}_{\text{CAS}}$ shift at the GM section, which is consistent with correlative sections in Europe and China (John *et*
384 *al.*, 2010; Chen *et al.*, 2013) (Fig. 5). The variable sulfur isotope records from different localities suggests
385 a spatially heterogeneous and small sulfate pool existed during this time (relative to the modern ocean)
386 and/or that deposition of the Fuhe section occurred in a setting that was partially restricted from the open
387 ocean (Chen *et al.*, 2013). Provided that the positive $\delta^{13}\text{C}$ excursion reflects increased organic carbon
388 burial during the Upper Kellwasser event, the absence of a sympathetic $\delta^{34}\text{S}_{\text{CAS}}$ shift may indicate that
389 increased delivery of ³⁴S-depleted sulfate to the ocean overwhelmed the impact of enhanced pyrite burial.
390 Indeed, five globally-distributed records show negative $\delta^{34}\text{S}_{\text{CAS}}$ shifts associated with the base of the
391 *linguiformis* conodont zone, and John *et al.* (2010) proposed that this interval corresponds to a transient
392 increase in continental weathering. Additionally, active trap magmatism and rifting in the Russian and
393 Siberian platforms in the Late Devonian—including the Viluy, Pripyat-Dnieper-Donets, and Kola
394 provinces (Kravchinsky, 2012; Ricci *et al.*, 2013)—may have supplied a large amount of ³⁴S-depleted

395 sulfur to the ocean within a relatively short time frame. Using the model and initial conditions discussed
396 above (Table 1), we explore the sulfur flux necessary to generate the observed $\delta^{34}\text{S}_{\text{CAS}}$ decrease. We
397 assume the $\delta^{34}\text{S}$ of volcanic sulfur inputs were 8 ‰, identical to the average riverine inputs. Our model
398 shows that a 5‰ negative shift over half a million years requires a 2-, 3-, and 11-fold increase in the
399 sulfate input to the ocean at initial sulfate concentrations of 1, 3, and 15 mM, respectively (Fig. 9). As a
400 result, the size of marine sulfate reservoir increases by 35 to 40% (Fig. 9). Although both continental
401 weathering and volcanic processes are combined into a single flux in our model, it seems unreasonable
402 that sulfate inputs increased by >10 times on a global scale. For example, massive end-Permian Siberian
403 volcanism was estimated to emit 1.1×10^{18} moles SO_2 (Tang *et al.*, 2013), which approaches 150% of the
404 amount of sulfate delivered to the ocean for half a million years (Table 1). Thus, it is more likely that
405 sulfate concentrations were at or below ~3mM, but higher relative to *punctata* Event levels. The increase
406 in seawater sulfate concentrations also accords with sizable $\Delta^{34}\text{S}_{\text{CAS-py}}$ values (>15‰) throughout the
407 Upper Kellwasser Event.

408 Here, we propose that the contrasting biological responses that characterize the *punctata* and
409 Upper Kellwasser events may have in part been linked to differences in marine sulfate concentrations.
410 Rates of MSR are typically limited by electron donors in sulfate replete oceans. However, sulfate can
411 limit MSR when concentrations are less than 10% of contemporary seawater values (Boudreau and
412 Westrich, 1984; Wortmann and Paytan, 2012). Our simulation suggests that Late Devonian seawater
413 sulfate concentrations were as low as 1 mM during the *punctata* Event. Importantly, a relatively small
414 oceanic sulfate pool would have impeded the development of sulfidic bottom water during this time
415 interval. By contrast, an increase in seawater sulfate concentration, likely due to massive volcanism,
416 would have increased MSR and promoted the development of sulfidic bottom water during the Upper
417 Kellwasser Event. An accumulation of sulfide could have impacted marine ecosystems in several ways.
418 The presence of isorenieratane in Frasnian black shales suggests that H_2S diffused into the water column
419 and poisoned both benthic and planktonic organisms, at least in some regions (Joachimski *et al.*, 2001). In

420 addition to toxicity, the buildup of sulfidic bottom water could have altered the cycles of other essential
421 elements, affecting organisms even in the surface water directly aerated by oxygen diffusion from the
422 atmosphere. Dissolved sulfide scavenges iron by precipitating insoluble iron sulfide compounds, reducing
423 the adsorption of phosphorus to iron oxyhydroxide (Murray, 1995; Kleeberg, 1997). Given that
424 phosphorus is an important limiting nutrient, enhanced release of phosphorus from sediments would have
425 exacerbated eutrophication of the overlying water. Indeed, a dramatic increase in C/P ratios of organic
426 matter buried during this time interval shows the enhanced efficiency of phosphorus recycling (Murphy *et*
427 *al.*, 2000). Paleocological evidence for this hypothesis may come from the crisis of shallow-water faunas.
428 Most notably, the great Devonian reef ecosystem was devastated and did not recover their diversity
429 afterwards (Copper, 2002). Deleterious effects of excess phosphorus on reef-building organisms have
430 been recognized for modern reef systems, including overfeeding stress, competition for spaces, and
431 orthophosphate poisoning of calcium carbonate crystal formation (Hallock and Schlager, 1986). Thus, the
432 anomalous phosphorus cycling in the late Devonian ocean may have posed a significant threat to the reef
433 ecosystem and triggered its collapse. The influence of increasing sulfate levels on phosphorus recycling is
434 also consistent with Godd ris and Joachimski (2004) who proposed the requirement of additional (but
435 unspecified) phosphorus flux to explain the sharp increase in $\delta^{13}\text{C}$ values across the Frasnian-Famennian
436 boundary. However, we are not necessarily suggesting that the development of sulfidic bottom water,
437 followed by anomalous nutrient cycling, triggered the catastrophe alone. Instead, it most likely acted as
438 one of perhaps several contributing factors.

439

440 **6. Conclusions**

441 This study presents paired sulfur isotope records during two key intervals of the Late Devonian
442 and provides new insights into the possible role seawater sulfate played in contributing to the F-F mass
443 extinction event. The mid-Frasnian *punctata* Event is characterized by coupled positive carbon and sulfur
444 isotope excursions that likely reflect the enhanced burial of both organic carbon and pyrite. Small and

445 even negative $\Delta^{34}\text{S}_{\text{CAS-py}}$ values are recorded during this event. Multiple sulfur isotope data suggests that
446 the increase in pyrite burial was associated with closed system sulfate reduction. In contrast, the Upper
447 Kellwasser Event, which is contemporaneous with the Frasnian-Famennian mass extinction, shows
448 decoupled carbon and sulfur isotope records and likely reflects intensified continental weathering and
449 active volcanism in the Russian and Siberian platforms that supplied ^{34}S -depleted sulfate into the ocean.
450 A geochemical box model illustrates that sulfate concentrations as low as 1 mM are required to account
451 for the positive $\delta^{34}\text{S}_{\text{CAS}}$ excursion during the *punctata* Event, while sulfate concentrations likely increased
452 before the Upper Kellwasser Event. It was unlikely a direct threat to the Devonian marine biota, but may
453 have set the stage for the subsequent development of toxic sulfidic bottom water, leading to contrasting
454 biological responses to increased C_{org} production/burial for the *punctata* and Upper Kellwasser events.

455

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461

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631

632 **Figure Captions**

633 **Figure 1.** Seawater $\delta^{13}\text{C}_{\text{carb}}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ curves for the Devonian period, modified after Becker *et al.*
634 (2012) and John *et al.* (2008). Time scale is after Kaufmann (2006), and the numerical age of Alamo
635 impact is after Morrow *et al.* (2009).

636
637 **Figure 2.** Paleogeographic reconstruction of the Late Devonian. Depositional settings of the studied
638 sections during middle Frasnian *punctata* Zone and the possible Alamo impact site (Left): DG, Devil's
639 Gate; GM, Granite Mountains; HSW, Hancock Summit West. Late Devonian paleogeography showing
640 the locations of this and previous Late Devonian sulfur isotope studies (Right). Black, gray, and white
641 areas indicate continents, shallow marine environments, and deep sea basins, respectively. Modified after
642 Morrow *et al.* (2009) and Blakey (2011).

643
644 **Figure 3.** Concentrations and isotopic compositions of inorganic carbon, CAS, and pyrite sulfur for (A)
645 Granite Mountains sections, (B) Hancock Summit West, and (C) Devil's Gate sections. A thin impact
646 deposit in the Devils Gate section is marked by a grey wedge. Abbreviations: *ling.*, *linguiformis*; *triang.*,
647 *triangularis*; *disp.*, *disparilis*; *falsi.*, *falsiovalis*; *trans.*, *transitans*.

648
649 **Figure 4.** Composite sulfur and carbon isotope records through the *punctata* Event from Hancock
650 Summit West (circle) and Devil's Gate (diamond) sections. Data from the Alamo impact breccia are not
651 included here (see Supplementary Table 1), because pre-impact sediments may have contributed to the
652 measured isotope ratios. Thick solid lines show the moving averages over three consecutive isotope
653 values, and vertical broken lines represent the Frasnian baseline. A red horizontal line marks the timing of
654 Alamo impact, and a hatched box indicates the duration of the *punctata* Event. In the last panel, a thin
655 solid line and surrounding green-shaded area represents the mean and standard deviation of published
656 $\delta^{13}\text{C}_{\text{carb}}$ data through the *punctata* Event (Morrow *et al.*, 2009, and reference therein).

657

658 **Figure 5.** Sulfur and carbon isotope records across the Frasnian-Famennian boundary. Sulfur isotope
659 data for Hony and Psie Gorki sections are from John *et al.* (2010), carbon isotope data for Hony section
660 are from Kaiho *et al.* (2013), and data for Kowala and Fuhe sections are from Chen *et al.* (2013). The
661 shaded area indicates the *linguiformis* conodont biozone, and the Upper Kellwasser positive $\delta^{13}\text{C}$
662 excursion begins in the uppermost part of this biozone. Abbreviations: *L. rhenana*, Late *rhenana*; *ling.*,
663 *linguiformis*; E.-M. *triang.*, Early to middle *triangularis*.

664

665 **Figure 6.** Variation of $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values for CAS (circle) and pyrite (diamond) through the *punctata*
666 Event at the HSW section. Open symbols indicate the Alamo Breccia, and solid symbols indicate
667 undisturbed sedimentary rocks. All pyrite data are deviated from the trend constrained by previous
668 laboratory culture studies (open arrow) but aligned along a mixing line indicating the contribution of
669 quantitative sulfate reduction. Note that mixing is non-linear in the $\Delta^{33}\text{S}$ vs. $\delta^{34}\text{S}$ plot.

670

671 **Figure 7.** Cross plots for the evaluation of possible diagenetic alteration and pyrite oxidation during the
672 extraction of CAS. (A) $\delta^{13}\text{C}_{\text{carb}}$ vs. $\delta^{18}\text{O}_{\text{carb}}$. (B) CAS vs. $\delta^{18}\text{O}_{\text{carb}}$. (C) $\delta^{34}\text{S}_{\text{CAS}}$ vs. $\delta^{18}\text{O}_{\text{carb}}$. (D) $\delta^{34}\text{S}_{\text{CAS}}$ vs.
673 S_{py} . (E) $\delta^{34}\text{S}_{\text{CAS}}$ vs. $\delta^{34}\text{S}_{\text{py}}$.

674

675 **Figure 8.** Modeled isotope composition and concentration of seawater sulfate through the *punctata* Event.
676 Under varying initial sulfate concentrations, the rate of pyrite burial is increased for 0.5 million years to
677 generate a positive 5‰ $\delta^{34}\text{S}_{\text{sulfate}}$ shift. At the sulfate concentration of 1 mM, the positive $\delta^{34}\text{S}_{\text{sulfate}}$ shift at
678 the onset of the *punctata* Event can be replicated by increasing the rate of pyrite burial by a factor of 1.6.

679

680 **Figure 9.** Modeled isotope composition and concentration of seawater sulfate before the onset of Upper
681 Kellwasser Event. To generate a negative 5‰ $\delta^{34}\text{S}_{\text{sulfate}}$ shift in 0.5 million years, a 2- to 11-fold increase

682 in weathering flux is required depending on initial sulfate concentrations. The sulfate input increases the
683 size of the marine sulfate pool by 40% and 35% at the initial sulfate concentration of 1 and 15 mM,
684 respectively.

Supplementary Table 1. Sulfur, carbon, and oxygen isotopic data from the Great Basin, USA

Height (m)	Conodont zone	Calibrated age (Ma)	TIC (%)	CAS (ppm)	S _{py} (ppm)	δ ³⁴ S _{CAS}	δ ³³ S _{CAS}	δ ³⁶ S _{CAS}	δ ³⁴ S _{py}	δ ³³ S _{py}	δ ³⁶ S _{py}
<i>Hancock Summit West</i>											
214.0	<i>Palmatolepis hassi</i>	381.50	7.7	185	43	31.5	16.1	60.5	10.9	5.6	20.6
200.0	<i>Palmatolepis punctata</i>	381.64	7.0	33	7	29.9			8.6	4.4	16.6
185.0	<i>Palmatolepis punctata</i>	381.80	11.1	175	58	33.2			3.1	1.6	5.7
182.0 ⁺	<i>Palmatolepis punctata</i>	381.83	10.8	264	61	29.7	15.1	57.2	4.1	2.1	7.5
180.0 ⁺	<i>Palmatolepis punctata</i>	381.85	10.3	150	11	31.5			23.6	12.1	45.1
178.0 ⁺	<i>Palmatolepis punctata</i>	381.87	11.5	146	35	28.1			11.7	6.0	22.4
177.0 ⁺	<i>Palmatolepis punctata</i>	381.89	11.6	278	26	20.6			15.2	7.8	29.0
173.0 ⁺	<i>Palmatolepis punctata</i>	381.92	11.7	712	12	14.3	7.3	27.5	20.5	10.5	39.4
169.0 ⁺	<i>Palmatolepis punctata</i>	381.97	11.6	215	28	21.6			16.0	8.2	30.6
163.0	<i>Palmatolepis punctata</i>	382.02	11.6	125	40	30.5			19.9	10.2	38.3
156.0	<i>Palmatolepis punctata</i>	382.09	11.8	295	61	31.7	16.3	61.1	27.9	14.3	53.5
154.0	<i>Palmatolepis punctata</i>	382.12	11.9	134	51	34.4			28.8	14.8	55.3
149.0	<i>Palmatolepis punctata</i>	382.17	11.8	491	44	35.4	18.1	68.1	30.1	15.4	57.8
147.0	<i>Palmatolepis punctata</i>	382.19	11.8	262	103	32.4			34.0	17.4	65.5
143.0 ⁺	<i>Palmatolepis punctata</i>	382.23	11.4	250	34	16.6			4.5	2.3	8.8
141.0	<i>Palmatolepis punctata</i>	382.25	11.3	102	37	32.2			16.6	8.5	31.5
138.0	<i>Palmatolepis punctata</i>	382.28	11.8	214	58	28.5			27.7	14.2	52.8
134.0	<i>Palmatolepis transitans</i>	382.32	11.2	266	24	32.9	16.9	63.3	-1.7	-0.9	-3.9
129.0	<i>Palmatolepis transitans</i>	382.37	11.8	148	42	30.2			19.7	10.1	37.4
102.0	<i>Palmatolepis transitans</i>	382.63	12.3	63	71	27.0			-7.2	-3.7	-14.4
81.0	<i>Mesotaxis falsovalis</i>	382.87	11.7	287	37	30.3			14.7	7.5	27.8
46.0	<i>Mesotaxis falsovalis</i>	383.69	11.5	934	145	27.0	13.9	51.9	-10.8	-5.6	-21.0
2.0	<i>Klapperina disparilis</i>	384.73	12.9	8	35	30.1			-12.2	-6.3	-23.6
<i>Devils Gate</i>											
71.3	<i>Palmatolepis punctata</i>	381.82	11.5	88	61	27.2			4.7		
69.2	<i>Palmatolepis punctata</i>	381.83	11.2	191	158	27.9			5.6		
67.1	<i>Palmatolepis punctata</i>	381.85	11.8	38	35	34.7			25.9		
65.0	<i>Palmatolepis punctata</i>	381.86	11.7	60	59	36.7			22.3		
62.9	<i>Palmatolepis punctata</i>	381.88	11.8	67	105	39.8			30.1		
61.6	<i>Palmatolepis punctata</i>	381.88	11.8		82				15.4		
60.2	<i>Palmatolepis punctata</i>	381.89	11.9	44	35	35.7			30.0		
58.9	<i>Palmatolepis punctata</i>	381.90	11.9	70	18	23.8			28.2		
57.7	<i>Palmatolepis punctata</i>	381.91	11.9	61	21	31.6			30.3		
56.6	<i>Palmatolepis punctata</i>	381.92	11.9	119	60	32.0			31.8		
55.4	<i>Palmatolepis punctata</i>	381.92	11.8	101	12	36.2			29.9		
54.9	<i>Palmatolepis punctata</i>	381.93	11.9	40	14	34.8			35.1		
53.9	<i>Palmatolepis punctata</i>	381.93	11.9	20	5	31.7			30.5		
52.9	<i>Palmatolepis punctata</i>	381.94	11.6	18	152	33.5			14.8		
51.9	<i>Palmatolepis punctata</i>	381.95	11.9	7		27.9			21.4		
51.0	<i>Palmatolepis punctata</i>	381.95	11.9	113	15	24.1			29.8		
50.5	<i>Palmatolepis punctata</i>	381.96	11.8	21	23	26.3			16.6		
50.0	<i>Palmatolepis punctata</i>	381.96	11.9		15				24.0		
49.6	<i>Palmatolepis punctata</i>	381.96	11.9	122	9	12.6			23.4		
49.0	<i>Palmatolepis punctata</i>	381.97	11.9	72	17	18.1			22.3		
48.6	<i>Palmatolepis punctata</i>	381.97	11.9	107	14	22.8			30.7		
46.3	<i>Palmatolepis punctata</i>	381.98	11.0	74	30	26.2			5.0		
43.9	<i>Palmatolepis punctata</i>	382.00	11.9		15				16.1		
40.0	unzoned	382.04	11.9		10				18.7		
37.6	unzoned	382.06	11.9	1	20	31.7			22.3		
31.9	unzoned	382.11	11.6	63	37	31.8			22.4		
26.3	unzoned	382.16	11.8	62	13	32.4			21.6		
17.1	unzoned	382.24	12.2	5	15	29.8			9.3		
16.6	unzoned	382.25	11.9	1	21	28.5			14.3		
11.6	unzoned	382.29	11.3	22	20	29.8			-0.7		
8.4	unzoned	382.32	11.6	12	29	26.1			1.2		
6.3	unzoned	382.34	11.9	135	35	28.7			19.8		
4.2	unzoned	382.36	11.8	5	25	23.5			15.5		
2.1	unzoned	382.38	11.7	41	77	23.9			9.5		
0.0	unzoned	382.40	12.1	176	44	29.7			-6.7		
<i>Granite Mountain</i>											
23.8	late <i>Palmatolepis triangularis</i>	374.58	6.6		175				11.5		
22.8	late <i>Palmatolepis triangularis</i>	374.78	5.5		102				7.5		
20.3	early to middle <i>Palmatolepis triangularis</i>	375.30	8.2	332	208	24.5			8.5		
19.5	early to middle <i>Palmatolepis triangularis</i>	375.44	8.3	428	131	24.9			9.9		
19.0	early to middle <i>Palmatolepis triangularis</i>	375.55	7.5	388	150	24.6			9.1		
18.5	early to middle <i>Palmatolepis triangularis</i>	375.65	5.7		250				11.7		
18.0	early to middle <i>Palmatolepis triangularis</i>	375.75	7.0	371	114	24.9			7.0		
17.5	early to middle <i>Palmatolepis triangularis</i>	375.86	7.3	433	139	24.8			6.9		
17.0	early to middle <i>Palmatolepis triangularis</i>	375.95	6.8		28				11.6		
16.2	<i>Palmatolepis linguiformis</i>	376.09	8.4	169	53	22.9			0.1		
15.4	<i>Palmatolepis linguiformis</i>	376.16	9.0	271	43	26.2			-0.3		
14.9	<i>Palmatolepis linguiformis</i>	376.21	10.3	122	14	26.0			-4.5		

14.4	<i>Palmatolepis linguiformis</i>	376.26	10.4	149	4	25.5	-5.1
12.1	<i>Palmatolepis linguiformis</i>	376.49	10.8	215	108	29.6	5.2
10.1	late <i>Palmatolepis rhenana</i>	376.65	4.0		90		-10.7
9.1	late <i>Palmatolepis rhenana</i>	376.73	8.3	255	100	28.1	-2.1
8.1	late <i>Palmatolepis rhenana</i>	376.81	7.1	304	136	28.1	0.0
7.4	late <i>Palmatolepis rhenana</i>	376.86	6.8		129		1.4
6.6	late <i>Palmatolepis rhenana</i>	376.92	6.9		127		4.0
4.9	late <i>Palmatolepis rhenana</i>	377.05	8.3	332	144	28.4	-2.0
2.8	late <i>Palmatolepis rhenana</i>	377.22	8.5	235	152	27.9	3.1
0.0	late <i>Palmatolepis rhenana</i>	377.43	6.7		62		0.7

^a, Alamo impact breccia samples

$\Delta^{34}\text{S}_{\text{CAS-py}}$	$\Delta^{33}\text{S}_{\text{CAS}}$	$\Delta^{36}\text{S}_{\text{CAS}}$	$\Delta^{32}\text{S}_{\text{py}}$	$\Delta^{30}\text{S}_{\text{py}}$	$\delta^{13}\text{C}_{\text{carb}}$	$\delta^{18}\text{O}_{\text{carb}}$
20.6	0.052	-0.192	-0.008	-0.172	0.6	-4.6
21.3			-0.043	0.076	0.5	-6.7
30.1			0.005	-0.239	-0.2	-4.5
25.6	-0.029	0.080	0.008	-0.176	-0.1	-4.9
7.9			0.033	-0.224	-0.8	-5.6
16.4			0.002	-0.040	0.0	-4.3
5.4			0.001	-0.036	0.5	-5.9
-6.2	-0.025	0.141	0.002	0.054	-1.5	-8.2
5.6			0.006	0.004	0.3	-5.0
10.6			-0.020	0.123	2.3	-4.9
3.9	0.032	-0.066	0.015	-0.102	0.3	-4.9
5.6			0.040	-0.159	0.8	-4.7
5.3	0.029	-0.110	0.037	-0.105	1.2	-5.0
-1.6			0.041	-0.111	0.6	-5.3
12.0			-0.012	0.154	-0.9	-6.5
15.6			-0.024	-0.308	-2.8	-6.6
0.8			0.008	-0.409	-0.3	-5.2
34.7	0.057	-0.156	-0.010	-0.606	-0.7	-3.7
10.5			-0.019	-0.338	-0.5	-4.6
34.1			0.036	-0.833	-0.5	-5.1
15.6			-0.001	-0.366	-0.7	-4.9
37.8	0.074	-0.124	0.020	-0.578	-1.5	-1.6
42.4			0.044	-0.555	-0.7	-8.4
22.6					1.5	-15.6
22.3					-0.2	-10.0
8.8					0.9	-10.8
14.4					0.9	-9.8
9.7					0.6	-11.8
					1.5	-14.2
5.7					1.1	-11.4
-4.4					1.9	-10.5
1.2					2.1	-8.7
0.2					1.7	-10.4
6.3					1.5	-11.2
-0.3					2.0	-9.0
1.2					1.0	-10.5
18.7					0.8	-10.4
6.5					2.3	-10.3
-5.7					1.1	-11.7
9.6					1.3	-13.3
					1.6	-14.8
-10.7					1.4	-11.5
-4.2					1.7	-11.3
-7.9					1.6	-10.1
21.1					-2.4	-12.4
					0.9	-8.7
					1.1	-9.5
9.3					0.2	-12.1
9.4					0.3	-8.4
10.8					1.4	-9.4
20.5					0.9	-6.6
14.3					0.4	-7.4
30.5					-0.1	-6.8
24.9					-0.6	-5.9
8.9					-0.3	-9.0
8.0					-0.7	-9.2
14.4					-1.5	-6.6
36.3					-0.4	-3.6
15.9					-1.3	-5.3
15.0					-0.9	-5.3
15.6					-0.7	-5.0
17.9					-0.5	-4.7
17.9					-0.6	-4.6
					-0.5	-4.9
22.9					-2.1	-7.9
26.5					-1.8	-6.7
30.5					-2.3	-7.1

30.6	-2.3	-7.8
24.4	-2.2	-6.1
30.2	-1.5	-6.1
28.0	-0.6	-5.0
	-1.3	-6.2
	-0.1	-4.8
30.3	-0.9	-5.1
24.7	-0.2	-5.0
	-0.4	-4.6

Table 1. Parameters and constants used in the model

Parameter	Value	References
Volume of Devonian Ocean	$1.5 \times 10^9 \text{ km}^3$	Wallmann (2001)
Seawater sulfate concentration	1 to 15 mM	Horita <i>et al.</i> (2002), Hurtgen <i>et al.</i> (2009), Luo <i>et al.</i> (2010)
continental/atmospheric sulfate input	$1.5 \times 10^{12} \text{ mole/yr}$	Gill <i>et al.</i> (2011)
Pyrite burial	$1.0 \times 10^{12} \text{ mole/yr}$	Gill <i>et al.</i> (2011)
Gypsum burial	$0.5 \times 10^{12} \text{ mole/yr}$	Gill <i>et al.</i> (2011)
Sulfur isotope composition of the riverine input	8 ‰	Gill <i>et al.</i> (2011)
Sulfur isotope fractionation during microbial sulfate reduction	-30‰	This study