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1 MODEL BASED PALEOZOIC ATMOSPHERIC OXYGEN ESTIMATES: A REVISIT TO  
2 GEOCARBSULF

3  
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14 **Keywords:** Atmospheric O<sub>2</sub>; GEOCARBSULF; Paleozoic; Carbonate isotope; Plant evolution

27  
28 **Abstract. Geological redox proxies increasingly point toward low atmospheric oxygen**  
29 **concentrations during the early Paleozoic Era, and a protracted rise towards present-day levels.**  
30 **However, these proxies currently provide qualitative estimates of atmospheric O<sub>2</sub> levels. Global**  
31 **biogeochemical models, in contrast, are commonly employed to generate quantitative estimates for**  
32 **atmospheric O<sub>2</sub> levels through Earth's history. Estimates for Paleozoic pO<sub>2</sub> generated by**  
33 **GEOCARBSULF, one of the most widely implemented carbon and sulfur cycle models, have**  
34 **historically suggested high atmospheric O<sub>2</sub> level throughout the Paleozoic, in direct contradiction to**  
35 **competing models. In this study, we evaluate if GEOCARBSULF can predict relatively low**  
36 **Paleozoic O<sub>2</sub> levels. We first updated GEOCARBSULF by adopting the recent complication of the**  
37 **δ<sup>13</sup>C value of marine buried carbonate and replacing the old formulation of sulfur isotope**  
38 **fractionation factor with the empirical sulfur isotope records. Afterwards, we constructed various**  
39 **O<sub>2</sub> evolution scenarios (with low O<sub>2</sub> levels in the early Paleozoic) and examined if GEOCARBSULF**  
40 **could reproduce these scenarios by varying the weathering/degassing fluxes of carbon and sulfur,**  
41 **or carbonate δ<sup>13</sup>C. We show that GEOCARBSULF can, in fact, maintain low-O<sub>2</sub> (even 1–5% atm)**  
42 **levels through the early Paleozoic by only varying the carbonate δ<sup>13</sup>C within 2SD bounds permitted**  
43 **by the geological record. In addition, it can generate a middle–late Paleozoic rise in O<sub>2</sub>**  
44 **concentration, coincident with the diversification of land plants. However, given the complexity of**  
45 **the carbonate δ<sup>13</sup>C record, we also argue that GEOCARBSULF cannot be used to track**  
46 **atmospheric O<sub>2</sub> levels until we have a better record of Paleozoic marine carbonate carbon isotope**  
47 **evolution.**

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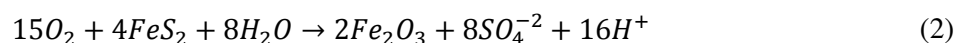
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## INTRODUCTION

55       The protracted rise of atmospheric oxygen is one of the most obvious ways in which life has  
56 reshaped our planet. However, almost all aspects of the history of atmospheric oxygen have been  
57 fervently debated over the past few decades. For instance, there is still persistent debate about the role—if  
58 any—that land plants played in driving the rise of atmospheric oxygen over the Paleozoic (Bergman and  
59 others, 2004; Berner, 1987; Berner, 2001a; Berner, 2006b; Berner and Canfield, 1989; Lenton and others,  
60 2016; Wallace and others, 2017). A series of geochemical redox proxies have been used to estimate the  
61 atmospheric O<sub>2</sub> levels qualitatively. Statistical analysis of iron speciation (Sperling and others, 2015)  
62 indicates widespread anoxic marine subsurface waters in the Cambrian. Cerium anomalies in well  
63 preserved marine cements and other marine precipitates confirmed that ocean anoxia was prevalent not  
64 only in the Cambrian but also through the Ordovician to Early Devonian (Wallace and others, 2017). The  
65 cerium anomaly record also argues for a continuous rise of surface O<sub>2</sub> levels through the Devonian, which  
66 has also been suggested using Mo isotope data (Dahl and others, 2010).

67       Although there are consistent advances in using geochemical paleo-redox proxies to predict O<sub>2</sub>  
68 levels qualitatively, quantitative estimates of atmospheric oxygen for the Phanerozoic still come from  
69 global biogeochemical models. Over geologic time scales (>1 million years), atmospheric O<sub>2</sub> levels are  
70 controlled by the carbon (C) and sulfur (S) sedimentary redox cycles (Berner, 1987). Oxidative  
71 weathering of organic carbon and pyrite (and oxidation of reduced gases) will consume O<sub>2</sub> while  
72 sediment burial of organic carbon and pyrite will release O<sub>2</sub>.

73       The representative reactions for O<sub>2</sub> uptake are:



74       The representative reactions for O<sub>2</sub> release are just the reverse of the reactions above. Based on  
75 these reactions, changes in atmospheric O<sub>2</sub> with time can be formulated as (Berner, 2004):

$$\frac{d[O_2]}{dt} = F_{bg} - F_{wg} - F_{mg} + \left(\frac{15}{8}\right)(F_{bp} - F_{wp} - F_{mp}) \quad (3)$$

76           Where  $F_{bg}$  and  $F_{bp}$  are the rate of burial of organic carbon and of pyrite sulfur in sediments  
 77 respectively,  $F_{wg}$  and  $F_{wp}$  are the rate of oxidative weathering of organic carbon and of pyrite sulfur  
 78 respectively, and  $F_{mg}$  and  $F_{mp}$  are the rate of oxidation of reduced carbon-containing gases and of reduced  
 79 sulfur-containing gases released via diagenesis, metamorphism, and volcanism respectively. The  
 80 embedded ratio refers to the stoichiometry of the reaction related to pyrite formation and oxidation.

81           Various numeric models have been built to estimate atmospheric  $O_2$  levels over the Phanerozoic,  
 82 and these models differ in how they calculate the weathering and burial fluxes of organic carbon and  
 83 pyrite (Arvidson and others, 2013; Bergman and others, 2004; Berner, 2001b; Berner, 2006b; Berner and  
 84 Canfield, 1989; Falkowski and others, 2005; Hansen and Wallmann, 2003; Lenton and others, 2016;  
 85 Mills and others, 2014; Mills and others, 2016). The two mostly commonly utilized models for the  
 86 Phanerozoic are GEOCARBSULF (Berner, 2006b; Berner, 2009) and COPSE (Bergman and others,  
 87 2004; Lenton and others, 2016; Mills and others, 2014). These models produce fundamentally different  
 88 predictions for atmospheric oxygen levels over the Paleozoic. Specifically, GEOCARBSULF predicts  
 89 near modern  $pO_2$  throughout the Paleozoic (fig. 1), which implies that land plants were not essential to  
 90 drive Earth to the high oxygen state characteristic of the modern world. COPSE, on the other hand,  
 91 predicts low atmospheric oxygen throughout the early Paleozoic, and a rise towards modern levels during  
 92 the middle-late Paleozoic coincident with the evolution of land plants (fig. 1).

93           These differences between models arise from the methods used to calculate  $O_2$  fluxes: in the  
 94 GEOCARBSULF model, carbon and sulfur burial rates are inverted from isotope mass balance, whereas  
 95 the COPSE model calculates their burial rates based on assumed primary productivity and nutrient  
 96 recycling. Primary productivity and nutrient recycling are difficult to estimate for Earth's past, especially  
 97 when considering the Paleozoic where geologic data are sparse. In COPSE (Bergman and others, 2004),  
 98 an increase of carbon burial on land in the Carboniferous was driven by doubling the C:P burial ratio of  
 99 land organic matter to represent the effects of enhanced preservation in swamps and mires. This model

100 condition contributes to a mid-Paleozoic O<sub>2</sub> rise. Similarly, the assumption of a high C:P ratio and high  
101 land primary productivity starting from ~470 Ma leads to the rapid rise of O<sub>2</sub> in the early Paleozoic in the  
102 more recent version of COPSE (Lenton and others, 2016). Therefore, the COPSE model is parameterized  
103 in such a way as to directly drive a rise in atmospheric oxygen levels with the emergence of land plants,  
104 and thus does not provide truly independent support for the link between land plant evolution and global  
105 oxygenation.

106 Here we revisit GEOCARBSULF to explore if this model can be consistent with land plants  
107 reshaping our atmosphere. Specifically, we test whether atmospheric O<sub>2</sub> can be maintained at relatively  
108 low levels in the early Paleozoic, and if O<sub>2</sub> can rise over the latter half of the Paleozoic in  
109 GEOCARBSULF. We address this question by investigating the sources and sinks of O<sub>2</sub>, as shown in  
110 equation (3). First, we conducted sensitivity analyses on the weathering and degassing of carbon and  
111 sulfur reservoir, which directly influences the O<sub>2</sub> sinks and also determines the O<sub>2</sub> sources indirectly  
112 through their control on the burial rate of organic carbon and pyrite. Second, we investigated the effect on  
113 O<sub>2</sub> levels of a single term — the  $\delta^{13}\text{C}$  value of buried carbonate through time, which directly reflects the  
114 burial of organic carbon and in turn regulates the rates of O<sub>2</sub> release. In addition, we used a more  
115 reasonable value of the initial sulfate proportion in the crust and performed sensitivity analyses on  $\delta^{13}\text{C}$   
116 value of buried carbonate using this updated value. Building from this work we argue that  
117 GEOCARBSULF can produce low Paleozoic O<sub>2</sub> level by only varying the  $\delta^{13}\text{C}$  values within  
118 uncertainties of the geological record. In other words, variation of  $\delta^{13}\text{C}$  values of carbonate plays a big  
119 role in controlling the model output. Therefore, unless we have a better constrained and more robust  
120 carbonate carbon isotope record, GEOCARBSULF is not capable of pinpointing atmospheric O<sub>2</sub>  
121 evolution through Paleozoic.

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## 123 A BRIEF INTRODUCTION TO GEOCARBSULF

124 GEOCARBSULF was constructed upon a series of seminal studies on global carbon and sulfur  
125 cycling. The numerical models for reconstructing the mass of oxidized and reduced carbon and sulfur

126 through the Phanerozoic build heavily upon the work of Garrels and Lerman (1981; 1984), which outlined  
127 the central tenets in global isotope mass balance modeling. Berner (1987) made a major modification  
128 when he put forward the idea of “rapid recycling” to provide strong negative feedback on O<sub>2</sub> fluctuations  
129 and predicted atmospheric O<sub>2</sub> evolution through the Phanerozoic. In rapid recycling, the mass of each  
130 sedimentary reservoir is divided into young (rapidly weathering) and old (slowly weathering)  
131 components. All newly buried carbon and sulfur go to the young reservoirs. In this way, whenever there is  
132 a rapid burial of organic carbon or pyrite (leading to rapid O<sub>2</sub> release), there will be a subsequent rapid  
133 weathering of those young organic carbon or pyrite (leading to rapid O<sub>2</sub> consumption), which will  
134 mitigate the fluctuation of O<sub>2</sub>. To provide a stronger negative feedback, Berner and others (2000) and  
135 Berner (2001b) also incorporated O<sub>2</sub>-dependent carbon and sulfur isotope fractionation into the model. In  
136 2006, Berner combined GEOCARB III (a classic model to reconstruct the CO<sub>2</sub> levels in the past and  
137 largely developed by Berner) and the O<sub>2</sub> model into a single model called GEOCARBSULF, which could  
138 simultaneously calculate the evolution of CO<sub>2</sub> and O<sub>2</sub> through the Phanerozoic (Berner, 2006b). In the  
139 following years, GEOCARBSULF was continuously updated and refined (for example, inclusion of the  
140 weathering of volcanic rocks and reconsideration of the fractionation of carbon isotopes) (Berner, 2006a;  
141 Berner, 2009) and the most recent version is described by Royer and others (2014).

142 An overview of the geochemical cycles of carbon, sulfur and oxygen in GEOCARBSULF is  
143 presented in figure 2. The full equations and parameters of GEOCARBSULF are described in detail in the  
144 Appendix. Below we list the key equations (with parameters defined in figure 2 and the Appendix) in  
145 GEOCARBSULF that are used to calculate the fluxes related to O<sub>2</sub> evolution.

$$F_{wgy} = f_A \cdot f_R \cdot k_{wgy} \cdot G_y(t) \quad (4)$$

$$F_{wga} = f_R \cdot F_{wga-0} \quad (5)$$

$$F_{wcy} = f_A \cdot f_D \cdot f_L \cdot f_E \cdot f_{Bb\_ca} \cdot k_{wcy} \cdot C_y(t) \quad (6)$$

$$F_{wca} = f_A \cdot f_D \cdot f_L \cdot f_E \cdot f_{Bb\_ca} \cdot F_{wca-0} \quad (7)$$

$$F_{wpy} = f_A \cdot f_R \cdot k_{wpy} \cdot P_y(t) \quad (8)$$

$$F_{wpa} = f_R \cdot F_{wpa-0} \quad (9)$$

$$F_{wsy} = f_A \cdot f_D \cdot k_{wsy} \cdot S_y(t) \quad (10)$$

$$F_{wsa} = f_A \cdot f_D \cdot F_{wsa-0} \quad (11)$$

$$F_{mg} = f_{SR} \cdot F_{mg-0} \quad (12)$$

$$F_{mc} = f_{SR} \cdot f_C \cdot F_{mc-0} \quad (13)$$

$$F_{mp} = f_{SR} \cdot F_{mp-0} \quad (14)$$

$$F_{ms} = f_{SR} \cdot F_{ms-0} \quad (15)$$

$$F_{bg} = \frac{1}{\Delta^{13}C} \times [(\delta^{13}C - dlcy) \cdot F_{wcy} + (\delta^{13}C - dlca) \cdot F_{wca} + (\delta^{13}C - dlgy) \cdot F_{wgy} + (\delta^{13}C - dlga) \cdot F_{wga} + (\delta^{13}C - dlca) \cdot F_{mc} + (\delta^{13}C - dlga) \cdot F_{mg}] \quad (16)$$

$$F_{bp} = \frac{1}{\Delta^{34}S} \times [(\delta^{34}S - dlcy) \cdot F_{wcy} + (\delta^{34}S - dlca) \cdot F_{wca} + (\delta^{34}S - dlpy) \cdot F_{wpy} + (\delta^{34}S - dlpa) \cdot F_{wpa} + (\delta^{34}S - dlca) \cdot F_{ms} + (\delta^{34}S - dlpa) \cdot F_{mp}] \quad (17)$$

$$\frac{d[O_2]}{dt} = F_{bg} - F_{wgy} - F_{wga} - F_{mg} + \left(\frac{15}{8}\right) (F_{bp} - F_{wpy} - F_{wpa} - F_{mp}) \quad (18)$$

146 Using the “rapid recycling” concept, the weatherable shell is divided into a young reservoir ( $F_{wgy}$ ,  
147  $F_{wcy}$ ,  $F_{wpy}$ ,  $F_{wsy}$ ) and an old reservoir ( $F_{wga}$ ,  $F_{wca}$ ,  $F_{wpa}$ ,  $F_{wsa}$ ). The isotope mass balance technique is given in  
148 equations (16) and (17). In addition to the terms defined above (and in the caption of figure 2),  $f_A$  is land  
149 area at time (t) relative to the present-day;  $f_D$  is global river runoff at time (t) relative to the present-day in  
150 the absence of changing  $CO_2$  and solar luminosity;  $f_L$  is land area covered by carbonates at time (t)  
151 relative to the present-day;  $f_R$  is effect of relief on chemical weathering at time (t) relative to the present-  
152 day;  $f_{SR}$  is seafloor creation rate at time (t) relative to the present-day;  $f_E$  is effect of plants on weathering  
153 rate at time (t) relative to the present-day;  $f_{BB}$  is effect of  $CO_2$  on plant-assisted weathering for carbonates  
154 at time (t) relative to the present-day;  $k_{wgy}$  is rate of mass dependence for young organic carbon

155 weathering;  $k_{wcy}$  is rate of mass dependence for young carbonate weathering;  $k_{wpy}$  is rate of mass  
156 dependence for young pyrite sulfur weathering;  $k_{wsy}$  is rate of mass dependence for young sulfate sulfur  
157 weathering;  $F_{wga\_0}$  is carbon flux from weathering of old sedimentary organic matter at present-day;  
158  $F_{wca\_0}$  is carbon flux from weathering of old carbonates at present-day;  $F_{wpa\_0}$  is sulfur flux from  
159 weathering of old pyrite at present-day;  $F_{wsa\_0}$  is sulfur flux from weathering of old sulfate at present-day;  
160  $F_{mg\_0}$  is carbon degassing flux of organic carbon at present-day;  $F_{mc\_0}$  is carbon degassing flux of  
161 carbonates at present-day;  $F_{mp\_0}$  is sulfur degassing flux of pyrite at present-day;  $F_{ms\_0}$  is sulfur  
162 degassing flux of sulfate at present-day;  $\Delta^{13}C$  is the carbon isotope fractionation between carbonate and  
163 organic carbon;  $\delta^{13}C$  is the isotope value of carbonate carbon;  $dlgy$ ,  $dlga$ ,  $dlyc$  and  $dlca$  are the  $\delta^{13}C$  value  
164 of young organic carbon, old organic carbon, young carbonate carbon and old carbonate carbon  
165 respectively;  $\Delta^{34}S$  is the carbon isotope fractionation between gypsum and pyrite;  $\delta^{34}S$  is the isotope value  
166 of gypsum sulfur;  $dlyp$ ,  $dlpa$ ,  $dlsy$  and  $dlsa$  are the  $\delta^{34}S$  value of young pyrite sulfur, old pyrite sulfur,  
167 young gypsum sulfur and old gypsum sulfur respectively.

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#### MODIFICATION TO GEOCARBSULF

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We modified the GEOCARBSULF version presented by Royer and others (2014), which is largely identical to the initial versions of GEOCARBSULF (Berner, 2006b; Berner, 2009). In GEOCARBSULF, the carbon and sulfur isotope fractionation ( $\Delta^{13}C$  and  $\Delta^{34}S$ ) is dependent on the  $O_2$  levels, which could provide a negative feedback to the  $O_2$  fluctuation and help avoid unrealistic atmospheric  $O_2$  levels throughout the Phanerozoic. Their relationship can be formulated as follows:

$$\Delta^{13}C = \Delta^{13}C_0 + [J \cdot (RO_2 - 1)] \quad (19)$$

$$\Delta^{34}S = \Delta^{34}S_0 \times RO_2^n \quad (20)$$

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Where  $\Delta^{13}C_0$  represents the carbon isotopic fractionation between carbonate and organic matter at present-day;  $J$  is an adjustable curve fit parameter;  $RO_2$  is the mass of oxygen in the atmosphere in the past relative to the present day;  $\Delta^{34}S_0$  represents the sulfur isotopic fractionation between gypsum and pyrite at present-day;  $n$  is an adjustable fit parameter. Unlike the relationship between  $O_2$  and the carbon

179 isotope fractionation factor ( $\Delta^{13}\text{C}$ ), which is based on lab experiments (Beerling and others, 2002; Berner  
180 and others, 2000), the  $\text{O}_2$  dependency of  $\Delta^{34}\text{S}$  is not well constrained and the relationship used in  
181 GEOCARBSULF is likely overly simplified. Because the majority of pyrite formed through sulfate  
182 reduction will be reoxidized (and potentially processed by bacterial disproportionation), which could  
183 possibly produce bigger sulfur isotope fractionations (for example, Berner, 2001a; Canfield, 2001;  
184 Johnston, 2011), it is very difficult to constrain the sulfur isotope fractionation system only by  
185 experimental approach. Making things more complex, recent experimental studies (Sim and others, 2011)  
186 have shown that large sulfur isotope fractionations can be also obtained from sulfate reduction alone  
187 without the need for disproportionation.

188 To quantify  $\Delta^{34}\text{S}$  through time, Wu and others (2010) adopted two methods: an arithmetic  
189 difference method ( $\Delta^{34}\text{S} = \delta^{34}\text{S}_{\text{sw}} - \delta^{34}\text{S}_{\text{py}}$ ) which is totally based on geological empirical records, and an  
190 independent method that calls upon  $\Delta^{33}\text{S}$  and sulfur cycle models. These two methods yield similar results  
191 (particularly before the Permian) and proves the robustness of using the empirical records to determine  
192  $\Delta^{34}\text{S}$ . Although those geological records can only represent a small fraction of what was deposited, they  
193 do construct the current best available  $\Delta^{34}\text{S}$  curve. Therefore, in our revised model calculations, we used  
194 an empirically based record of  $\Delta^{34}\text{S}$  (and assign 4‰ as the 2SD), which eliminates the strong  $\text{O}_2$  feedback  
195 in the sulfur cycle. We also updated GEOCARBSULF by replacing the old  $\delta^{13}\text{C}$  curve with the new 10  
196 million years average curve (Grossman and others, 2008; Saltzman and Thomas, 2012; Veizer and others,  
197 1999). Similar to Royer and others (2014), we used a Monte Carlo approach (10000 resampling) to  
198 quantify the errors of the model outputs. During each resample, GEOCARBSULF can fail at a specific  
199 time step for several reasons: 1) Any carbon or sulfur flux goes negative; 2) Calculated  $\text{CO}_2$  is less than  
200 150 ppm or bigger than 50000 ppm; 3) Calculated  $\text{CO}_2$  or  $\text{O}_2$  at 0 Ma deviate from their measured values  
201 ( $\text{CO}_2$  is not in the 200–300 ppm range and  $\text{O}_2$  is not in the 19–23% range) (Royer and others, 2014).  
202 Following the above two updates, we ran GEOCARBSULF with a starting atmospheric  $\text{O}_2$  level of 1%  
203 and 5% respectively at 570 Ma. We also run GEOCARBSULF with updated  $\delta^{13}\text{C}$  curve but keeping the  
204 old  $\Delta^{34}\text{S}$  formulation. Compared with the model run using the old  $\Delta^{34}\text{S}$  formulation (fig. 3A), using

205 updated  $\Delta^{34}\text{S}$  did not help lower  $\text{O}_2$  level in the early Paleozoic (fig. 3B), but does serve to remove  
206 unrealistic negative feedback.

207         In addition to the updates related to the carbon and sulfur isotope system, essential to our new  
208 method (sensitivity tests) is that it allows us to input the desired model output (that is,  $\text{O}_2$  evolution) and  
209 observe the underlying parameter changes required for the model to generate such an output. This is a  
210 modification of the traditional use of GEOCARBSULF where one predicts  $\text{O}_2$  evolution from carbon and  
211 sulfur fluxes and isotope records. One set of underlying parameters that could be explored using this new  
212 method is the weathering and degassing fluxes of carbonates, organic carbon, sulfate and pyrite, which  
213 could affect the  $\text{O}_2$  sink, as well as the  $\text{O}_2$  source via isotope mass balance (equations 16 and 17). There  
214 are large uncertainties for these parameters in the current version of GEOCARBSULF. For example, the  
215 total land area that experienced extensive weathering, and the global runoff through time, are not well  
216 constrained (Royer and others, 2014). In addition, the oxygen dependency of the weathering rate of  
217 organic carbon and pyrite is debated (for example, Bolton and others, 2006; Lasaga and Ohmoto, 2002).  
218 The volcanic degassing rate, directly linked to degassing fluxes of carbon and sulfur, is likewise under  
219 continuous revision (for example, Berner, 2004; McKenzie and others, 2016; Van Der Meer and others,  
220 2014). Another underlying parameter that has large uncertainties is the  $\delta^{13}\text{C}$  of marine dissolved inorganic  
221 carbon (DIC), which is derived from buried carbonate and influences the calculated organic carbon burial  
222 rate — a key  $\text{O}_2$  source. The record of burial carbonate  $\delta^{13}\text{C}$  before the Mid-Jurassic is predominantly  
223 from measurements of platform carbonates, which exhibit greater spatial heterogeneity in  $\delta^{13}\text{C}$  values  
224 than those from the Mid-Jurassic to Cenozoic measurements of pelagic carbonates (Panchuk and others,  
225 2006; Saltzman and Thomas, 2012). Lastly, the initial reservoir sizes of sulfate and pyrite in the crust,  
226 which will shape Paleozoic redox conditions, are poorly constrained.

227         Here, we use the new method to test if GEOCARBSULF can maintain a low atmospheric  $\text{O}_2$   
228 level in the early Paleozoic given available empirical constraints. To do this, we first constructed four  
229 example  $p\text{O}_2$  evolution scenarios through the Paleozoic (fig. 4), which are based on paleo-proxy records  
230 and previous model studies (fig. 1) and will be used as an input to our new methods in the following

231 sections. We used scenarios that cover a wide spectrum of delayed O<sub>2</sub> evolution patterns and thus can be  
 232 used to test the potential for predicting these oxygenation histories using GEOCARBSULF.

233

234 SENSITIVITY TESTS OF THE WEATHERING AND DEGASSING FLUXES OF CARBON  
 235 AND SULFUR ON O<sub>2</sub> LEVELS

236 We applied our new method to investigate the sensitivity of O<sub>2</sub> levels to the weathering and  
 237 degassing fluxes of different rock reservoirs, namely carbonate weathering (F<sub>wcy</sub> and F<sub>wca</sub>), organic carbon  
 238 weathering (F<sub>wgy</sub> and F<sub>wga</sub>), carbonate degassing (F<sub>mc</sub>), organic carbon degassing (F<sub>mg</sub>), sulfate weathering  
 239 (F<sub>wsy</sub> and F<sub>wsa</sub>), sulfate degassing (F<sub>ms</sub>), pyrite weathering (F<sub>wpy</sub> and F<sub>wpa</sub>), pyrite degassing (F<sub>mp</sub>). We used  
 240 a general-purpose optimization routine (L-BFGS-B in R language) to solve all the weathering and  
 241 degassing fluxes of carbon and sulfur. Specifically, we multiply these fluxes each by a scaling factor,  
 242 aiming to evaluate the relative importance of these fluxes in controlling pO<sub>2</sub>. The modified equations are  
 243 as follows (\_S means scaling):

$$F_{wgy-S} = S_{wg} \cdot f_A \cdot f_R \cdot k_{wgy} \cdot G_y(t) \quad (21)$$

$$F_{wga-S} = S_{wg} \cdot f_R \cdot F_{wga-0} \quad (22)$$

$$F_{wcy-S} = S_{wc} \cdot f_A \cdot f_D \cdot f_L \cdot f_E \cdot f_{Bb\_ca} \cdot k_{wcy} \cdot C_y(t) \quad (23)$$

$$F_{wca-S} = S_{wc} \cdot f_A \cdot f_D \cdot f_L \cdot f_E \cdot f_{Bb\_ca} \cdot F_{wca-0} \quad (24)$$

$$F_{wpy-S} = S_{wp} \cdot f_A \cdot f_R \cdot k_{wpy} \cdot P_y(t) \quad (25)$$

$$F_{wpa-S} = S_{wp} \cdot f_R \cdot F_{wpa-0} \quad (26)$$

$$F_{wsy-S} = S_{ws} \cdot f_A \cdot f_D \cdot k_{wsy} \cdot S_y(t) \quad (27)$$

$$F_{wsa-S} = S_{ws} \cdot f_A \cdot f_D \cdot F_{wsa-0} \quad (28)$$

$$F_{mg-S} = S_{mg} \cdot f_{SR} \cdot F_{mg-0} \quad (29)$$

$$F_{mc-S} = S_{mc} \cdot f_{SR} \cdot f_C \cdot F_{mc-0} \quad (30)$$

$$F_{mp-S} = S_{mp} \cdot f_{SR} \cdot F_{mp-0} \quad (31)$$

$$F_{ms\_S} = S_{ms} \cdot f_{SR} \cdot F_{ms\_0} \quad (32)$$

$$F_{bg\_S} = \frac{1}{\Delta^{13}C} \times [(\delta^{13}C - dlcy) \cdot F_{wcy\_S} + (\delta^{13}C - dlca) * F_{wca\_S} + (\delta^{13}C - dlgy) * F_{wgy\_S} + (\delta^{13}C - dlga) * F_{wga\_S} + (\delta^{13}C - dlca) * F_{mc\_S} + (\delta^{13}C - dlga) * F_{mg\_S}] \quad (33)$$

$$F_{bp\_S} = \frac{1}{\Delta^{34}S} \times [(\delta^{34}S - dlsy) \cdot F_{wsy\_S} + (\delta^{34}S - dlpa) * F_{wpa\_S} + (\delta^{34}S - dlpy) * F_{wpy\_S} + (\delta^{34}S - dlpa) * F_{mp\_S} + (\delta^{34}S - dlpa) * F_{mp\_S}] \quad (34)$$

$$\frac{d[O_2]}{dt} = F_{bg\_S} - F_{wgy\_S} - F_{wga\_S} - F_{mg\_S} + \left(\frac{15}{8}\right) (F_{bp\_S} - F_{wpy\_S} - F_{wpa\_S} - F_{mp\_S}) \quad (35)$$

244           The method searches for the optimized value for each scaling factor (as close as to 1, meaning the  
 245 new flux is as close as to the original flux) needed to match a predicted O<sub>2</sub> at each time step. Specifically,  
 246 using equation (21) to (35), we could solve F<sub>ms\_S</sub> in terms of F<sub>wgy\_S</sub>, F<sub>wga\_S</sub>, F<sub>wcy\_S</sub>, F<sub>wca\_S</sub>, F<sub>wpy\_S</sub>,  
 247 F<sub>wpa\_S</sub>, F<sub>wsy\_S</sub>, F<sub>wsa\_S</sub>, F<sub>ng\_S</sub>, F<sub>mc\_S</sub>, F<sub>mp\_S</sub> and d[O<sub>2</sub>]/dt. Afterwards, we could use L-BFGS-B to  
 248 minimize the following expression:  
 249

$$\begin{aligned} & \left| \frac{F_{wgy\_S} + F_{wga\_S} - F_{wgy} - F_{wga}}{F_{wgy} + F_{wga}} \right| + \left| \frac{F_{wcy\_S} + F_{wca\_S} - F_{wcy} - F_{wca}}{F_{wcy} + F_{wca}} \right| \\ & + \left| \frac{F_{wpy\_S} + F_{wpa\_S} - F_{wpy} - F_{wpa}}{F_{wpy} + F_{wpa}} \right| \\ & + \left| \frac{F_{wsy\_S} + F_{wsa\_S} - F_{wsy} - F_{wsa}}{F_{wsy} + F_{wsa}} \right| + \left| \frac{F_{mg\_S} - F_{mg}}{F_{mg}} \right| \\ & + \left| \frac{F_{mc\_S} - F_{mc}}{F_{mc}} \right| + \left| \frac{F_{mp\_S} - F_{mp}}{F_{mp}} \right| + \left| \frac{F_{ms\_S} - F_{ms}}{F_{ms}} \right| \end{aligned} \quad (36)$$

250

251 We assign a lower bound of 0 to the seven scaling factors (carbonate weathering, organic carbon  
 252 weathering, carbonate degassing, organic carbon degassing, sulfate weathering, pyrite weathering and  
 253 pyrite degassing) and assign no bound to the scaling factor of sulfate degassing (since this scaling factor  
 254 is solved from the other seven scaling factors). The model runs from 570 to 300 Ma and fails at various  
 255 time steps for different scenarios. In addition, some scaling factors are required to fluctuate significantly  
 256 within a geologically short time interval, which is physically implausible. For example, with the  
 257 carbonate weathering scaling factor (fig. 5B), extremely large fluctuations (for example, a drop from 1 to  
 258 0 in 20 million years during Ordovician for Scenario 3 and 4) are required.

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#### 260 SENSITIVITY TESTS OF CARBONATE $\delta^{13}\text{C}$ ON $\text{O}_2$ LEVELS

261 We argue that the most poorly constrained, yet impactful input parameter for GEOCARBSULF is  
 262 the carbonate  $\delta^{13}\text{C}$  values chosen for given time bin, which tightly controls the burial rate of organic  
 263 carbon. Due to the complexity surrounding the empirical carbonate  $\delta^{13}\text{C}$  records, the  $\delta^{13}\text{C}$  of buried  
 264 carbonate in the Paleozoic used in GEOCARBSULF may not be the true average  $\delta^{13}\text{C}$  of the ocean (for  
 265 example, Saltzman and Thomas, 2012), thus influencing the predicted  $\text{O}_2$  level. As demonstrated in Royer  
 266 and others (2014) and Mills and others (2016), the atmospheric  $\text{O}_2$  predicted by isotope mass balance is  
 267 highly sensitive to assumed carbonate  $\delta^{13}\text{C}$ . Assuming all the weathering and degassing fluxes of carbon  
 268 and sulfur are the same with the fluxes in the original GEOCARBSULF (that is, all scaling factors are 1),  
 269 it is straightforward to apply the new method to solve carbonate  $\delta^{13}\text{C}$  for different  $\text{O}_2$  scenarios. Since we  
 270 only have 1 unknown parameter (carbonate  $\delta^{13}\text{C}$ ), we could directly solve this parameter and its solution  
 271 is as follows:

$$272 \delta^{13}\text{C} = \frac{F_{bg} \cdot \Delta^{13}\text{C} + F_{wcy} \cdot \text{dlcy} + F_{wca} \cdot \text{dlca} + F_{wgy} \cdot \text{dlgy} + F_{wga} \cdot \text{dlga} + F_{mc} \cdot \text{dlca} + F_{mg} \cdot \text{dlga}}{F_{wcy} + F_{wca} + F_{wgy} + F_{wga} + F_{mc} + F_{mg}} \quad (37)$$

273 As shown in figure 6, the carbonate  $\delta^{13}\text{C}$  required to fit each  $\text{O}_2$  scenario is consistently within the  
 274 range of  $\delta^{13}\text{C}$  records through the Paleozoic, and almost always within 2SD of the long term running  
 275 average. The overall evolving trends of the required  $\delta^{13}\text{C}$  across all scenarios and the  $\delta^{13}\text{C}$  record are

276 similar, and the CO<sub>2</sub> predicted is similar to that from the original GEOCARBSULF model (fig. 7). In all  
277 scenarios, the organic carbon burial rate increased through the Devonian (fig. 8A) and the pyrite burial  
278 rate decreased through the Paleozoic (fig. 8B).

279         Instead of calculating  $\Delta^{13}\text{C}$  based on its relationship with O<sub>2</sub> levels, we could also derive  $\Delta^{13}\text{C}$   
280 through time from the geologic records (Hayes and others, 1999)), similar to what we did for  $\Delta^{34}\text{S}$ . We  
281 note that the compilation of Hayes and others (1999) may not represent the true global average  $\Delta^{13}\text{C}$   
282 because the  $\delta^{13}\text{C}$  of organic carbon used to calculate  $\Delta^{13}\text{C}$  is based solely on marine organic matter.  
283 Despite this, the required carbonate  $\delta^{13}\text{C}$  values still fall into the range of the  $\delta^{13}\text{C}$  record after this update  
284 (fig. 9B).

285         Besides carbonate  $\delta^{13}\text{C}$ , the initial sulfate proportion within the upper continental crust (50% of  
286 the total sulfur) at 570 Ma assumed in the original formulation GEOCARBSULF is considered unlikely  
287 based on several recent  $f_{\text{py}}$  estimates (for example, Canfield and Farquhar, 2009; Halevy and others, 2012)  
288 which argue for limited sulfate burial in the Precambrian and Early Cambrian. Therefore, as an initial  
289 attempt, we reduced the initial sulfate proportion in the crust from 50% to 20%, which is in qualitative  
290 agreement with the work of Canfield and Farquhar (2009). To maintain a realistic  $\delta^{34}\text{S}$  value of the sulfate  
291 reservoirs after this proportion change, the  $\delta^{34}\text{S}$  values of initial young and old pyrite in the original  
292 GEOCARBSULF are also adjusted (from -10‰ to 0‰). This change is not unreasonable, as the  $\delta^{34}\text{S}$  of  
293 buried sedimentary pyrite was 5.7‰ at 570 Ma and was even higher than 5.7‰ in the Precambrian (Wu  
294 and others, 2010). Therefore, assigning 0‰ to the initial sedimentary pyrite is conservative. After these  
295 modifications, the required carbonate  $\delta^{13}\text{C}$  is more enriched at each time step (fig. 10 vs fig. 6) but still  
296 fits reasonably well with the isotope records. The CO<sub>2</sub> predictions are again similar to the original  
297 GEOARBSULF (fig. 11).

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## DISCUSSION

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301

Our sensitivity tests demonstrate that it is impossible to maintain a low atmospheric O<sub>2</sub> in the  
early Paleozoic followed by an O<sub>2</sub> rise to ~ 30% by the Late Carboniferous through varying only the

302 weathering and degassing fluxes of different rock reservoirs in GEOCARBSULF. Even over the short  
303 time interval where the model ran successfully and maintained consistent O<sub>2</sub> levels, some weathering and  
304 degassing rate variations were extreme, indicating inefficiency of these parameters in controlling  
305 atmospheric O<sub>2</sub>. While these results confirm that inorganic weathering and degassing fluxes can alter the  
306 predictions drawn from carbon isotope mass balance (Shields and Mills, 2017), they also suggest that the  
307 dominant influence on O<sub>2</sub> variability over most of the Phanerozoic was not the weathering rates of  
308 organic carbon and pyrite but their burial rates (Bernier, 2006b).

309 By removing the extreme negative feedback from the sulfur system and changing the input  
310 carbonate  $\delta^{13}\text{C}$  within the geological data range, we can maintain a low O<sub>2</sub> level in GEOCARBSULF  
311 before the Devonian (or before the Silurian in the case of Scenario 4 — see fig. 4). This model output is  
312 in great contrast with that of Royer and others (2014), which could not produce low O<sub>2</sub> levels in the early  
313 Paleozoic. Compared with figure 3B, which also couldn't maintain a low O<sub>2</sub> level even after updating the  
314  $\delta^{13}\text{C}$  and  $\Delta^{34}\text{S}$ , our model outputs indicate that uncertainties in the variations in marine  $\delta^{13}\text{C}$  is the biggest  
315 hurdle in predicting O<sub>2</sub>. Our method also argues for a relative constant organic carbon burial rate through  
316 Ordovician and Silurian, and a continuous increase of organic carbon burial rate through Devonian (fig.  
317 8A), which correlates with the diversification of vascular plants. Our predicted  $\delta^{13}\text{C}$  is generally less  
318 variable than the observed record through this time (fig. 6 and 10). However, the empirical  $\delta^{13}\text{C}$  of old  
319 platform carbonates, similar to modern shallow water carbonates, were likely influenced by many factors  
320 such as: diagenetic processes, mineralogical variability, vital effects caused by calcifying organisms, local  
321 water mass restriction, and carbon cycle perturbations (Brand and others, 2009; Mii and others, 1999;  
322 Panchuk and others, 2006; Saltzman and Thomas, 2012; Veizer and others, 1999). For example, the  $\delta^{13}\text{C}$   
323 of brachiopods exhibit substantial regional heterogeneity, with high values in the Russian Platform, low  
324 values in western North America, and intermediate values in the midcontinent (Grossman and others,  
325 2008). Given this variability, the exact global curve of the carbonate  $\delta^{13}\text{C}$  through the Paleozoic is poorly  
326 known. Our modeling approach serves as an indirect way to inspect the global average carbonate  $\delta^{13}\text{C}$  and  
327 bears significance for promoting further research on this issue.



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#### FIGURE CAPTIONS

478 Fig. 1. Long-term carbon, sulfur, and oxygen cycles in GEOCARBSULF. Carbon cycle consists of fluxes  
 479 between carbon in the surficial system including atmosphere, ocean, biosphere and soil (**C**), young  
 480 organic carbon (**G<sub>y</sub>**), old organic carbon (**G<sub>a</sub>**), young carbonate (**C<sub>y</sub>**) and old carbonate (**C<sub>a</sub>**). Specifically,  
 481 these fluxes are organic carbon burial (**F<sub>bg</sub>**), oxidative weathering of young organic carbon (**F<sub>wgy</sub>**) and old  
 482 organic carbon (**F<sub>wga</sub>**), degassing of organic carbon from volcanism, metamorphism and diagenesis (**F<sub>mg</sub>**),  
 483 organic carbon transfer from young to old reservoir (**F<sub>yog</sub>**), carbonate burial (**F<sub>bc</sub>**), weathering of young  
 484 carbonate (**F<sub>wcy</sub>**) and old carbonate (**F<sub>wca</sub>**), degassing of carbonate from volcanism, metamorphism and  
 485 diagenesis (**F<sub>mc</sub>**), and carbonate transfer from young to old reservoir (**F<sub>yoc</sub>**). Sulfur cycle consists of fluxes  
 486 between sulfur in the surficial system including atmosphere, ocean, biosphere and soil (**S**), young pyrite

487 sulfur ( $\mathbf{P}_y$ ), old pyrite sulfur ( $\mathbf{P}_a$ ), young gypsum sulfur ( $\mathbf{G}_y$ ) and old gypsum sulfur ( $\mathbf{G}_a$ ). Specifically,  
488 these fluxes include pyrite burial ( $\mathbf{F}_{bp}$ ), oxidative weathering of young pyrite ( $\mathbf{F}_{wpy}$ ) and old pyrite ( $\mathbf{F}_{wpa}$ ),  
489 degassing of pyrite from volcanism, metamorphism and diagenesis ( $\mathbf{F}_{mp}$ ), pyrite transfer from young to  
490 old reservoir ( $\mathbf{F}_{yop}$ ), gypsum burial ( $\mathbf{F}_{bs}$ ), weathering of young gypsum ( $\mathbf{F}_{wsy}$ ) and old gypsum ( $\mathbf{F}_{wsa}$ ),  
491 degassing of gypsum from volcanism, metamorphism and diagenesis ( $\mathbf{F}_{ms}$ ), and gypsum transfer from  
492 young to old reservoir ( $\mathbf{F}_{yos}$ ). As shown in Equation (1), the sources of atmospheric  $\text{O}_2$  are  $\mathbf{F}_{bg}$  and  $\mathbf{F}_{bp}$   
493 (represented by the red arrow). The sinks are  $\mathbf{F}_{wgy}$ ,  $\mathbf{F}_{wga}$ ,  $\mathbf{F}_{mg}$ ,  $\mathbf{F}_{wpy}$ ,  $\mathbf{F}_{wpa}$  and  $\mathbf{F}_{mp}$  (represented by the blue  
494 arrow).

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496 Fig. 2.  $\text{O}_2$  evolution patterns through the Paleozoic. The red curve represents the  $\text{O}_2$  prediction from the  
497 GEOCARBSULF model (Royer and others, 2014). The purple curve represents the  $\text{O}_2$  prediction from  
498 the baseline COPSE model (Bergman and others, 2004). The red line shows the approximate maximum  
499 atmospheric  $\text{O}_2$  level based on water column redox data (Canfield, 1998; Sperling and others, 2015). The  
500 blue line is the approximate  $\text{O}_2$  maximum, based on burning experiments and wildfire feedbacks  
501 (Glasspool and others, 2015; Watson and others, 1978), but geochemical mass balance studies suggest  
502  $p\text{O}_2$  levels as high as 35% may be permissible (Wildman and others, 2004). The brown shaded area  
503 represents the trend of atmospheric  $\text{O}_2$  evolution based on Mo isotopes (Dahl and others, 2010) and  
504 cerium anomaly records (Wallace and others, 2017).

505  
506 Fig. 3. Predicted  $\text{O}_2$  evolution from the GEOCARBSULF model with an initial  $\text{O}_2$  level of 1% and 5%.  
507 (A)  $\Delta^{34}\text{S}$  is derived from the old formulation ( $\text{O}_2$  dependency) in GEOCARBSULF. (B)  $\Delta^{34}\text{S}$  is derived  
508 from the geological records (Wu and others, 2010). The green line represents the predicted average  $\text{O}_2$   
509 level starting from 1% at 570 Ma and the red line represents the predicted average  $\text{O}_2$  level starting from  
510 5% at 570 Ma. The shaded area represents the average value  $\pm 1\text{SD}$ .

511

512 Fig. 4. Atmospheric O<sub>2</sub> evolution scenarios through the Paleozoic constructed in this study. Scenario 1  
513 and 2 try to simulate the O<sub>2</sub> level predicted by the cerium anomaly (Wallace and others, 2017). They keep  
514 O<sub>2</sub> at a low level (1% and 5% respectively) from the Early Cambrian to the Late Silurian and then force  
515 O<sub>2</sub> to rise to ~30% by the Late Carboniferous. Scenario 3 is atmospheric O<sub>2</sub> evolution after the baseline  
516 COPSE model (Bergman and others, 2004). Scenario 4 is a combination of atmospheric O<sub>2</sub> prediction  
517 after the baseline model and the updated COPSE model which integrates early plant colonization, biotic  
518 effects on silicate weathering and 25% increase in P weathering (Lenton and others, 2016).

519

520 Fig. 5. The scaling factors for various weathering fluxes required to reproduce different O<sub>2</sub> scenarios. (A)  
521 Scaling factor for organic carbon weathering rate. (B) Scaling factor for carbonate weathering rate. (C)  
522 Scaling factor for pyrite weathering rate. (D) Scaling factor for sulfate weathering rate. The shaded pink  
523 area represents the average value  $\pm$  2SD for Scenario 2. The error range for other scenarios is similar to  
524 that of Scenario 2. Different scenarios are described in figure 4.

525

526 Fig. 6. Carbonate  $\delta^{13}\text{C}$  required to reproduce the four oxygen scenarios through the Paleozoic, and how  
527 they correlate with geologic record. The grey dots are the carbonate  $\delta^{13}\text{C}$  compilation from Saltzman and  
528 Thomas (2012). The green dots are the  $\delta^{13}\text{C}$  of brachiopod shells from Veizer (1999). The orange dots are  
529 the  $\delta^{13}\text{C}$  of brachiopod shells compiled by Grossman and others (2008). The black line represents the  
530 moving average (10 Myrs) of all the carbonate  $\delta^{13}\text{C}$  records. The brown area represents the average value  
531  $\pm$  2SD. The shaded pink area represents the average value  $\pm$  2SD for Scenario 2. The error range for other  
532 scenarios is similar to that of Scenario 2. Different scenarios are described in figure 4.

533

534 Fig. 7. Atmospheric CO<sub>2</sub> predicted in the sensitivity tests of carbonate  $\delta^{13}\text{C}$  for different scenarios,  
535 compared with the CO<sub>2</sub> prediction from the original GEOCARBSULF (Royer and others, 2014).  
536 Different scenarios are described in figure 4.

537

538 Fig. 8. Organic carbon and pyrite sulfur burial rate predicted in the sensitivity tests of carbonate  $\delta^{13}\text{C}$  for  
539 different scenarios. (A) Organic carbon burial rate. (B) Pyrite sulfur burial rate. Notice that the pyrite  
540 burial rates for different scenarios are the same. Different scenarios are described in figure 4.

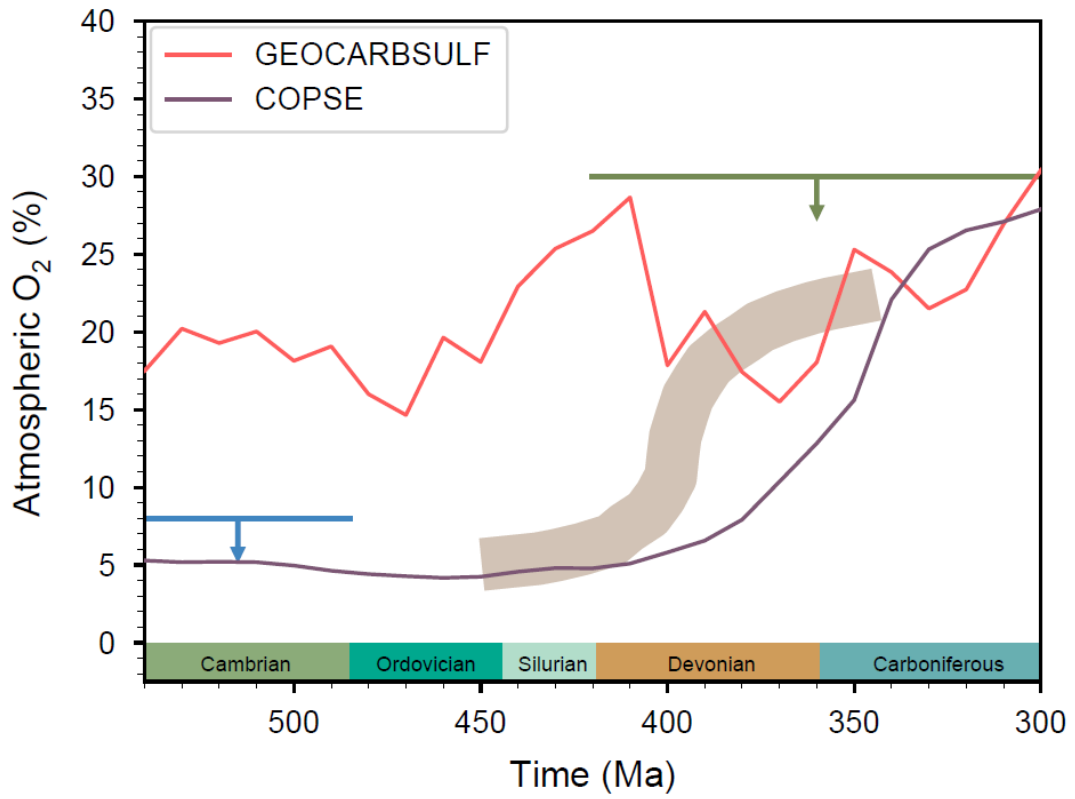
541  
542 Fig. 9.  $\Delta^{13}\text{C}$  from geological records and carbonate  $\delta^{13}\text{C}$  required to reproduce the four oxygen scenarios  
543 using this  $\Delta^{13}\text{C}$ . (A)  $\Delta^{13}\text{C}$  derived from Hayes and others (1999) through the Paleozoic. (B) Carbonate  
544  $\delta^{13}\text{C}$  required to reproduce the four oxygen scenarios using  $\Delta^{13}\text{C}$  derived from geological records. The  
545 symbols are described in figure 6. Different scenarios are described in figure 4.

546  
547 Fig. 10. Carbonate  $\delta^{13}\text{C}$  required to reproduce the four oxygen scenarios through the Paleozoic, assuming  
548 20% initial sulfate in the crust, and how they correlate with geologic record. The symbols are described in  
549 figure 6. Different scenarios are described in figure 4.

550  
551 Fig. 11. Atmospheric  $\text{CO}_2$  predicted in the sensitivity tests of carbonate  $\delta^{13}\text{C}$  for different scenarios  
552 assuming 20% initial sulfate in the crust, compared with the  $\text{CO}_2$  prediction from the original  
553 GEOCARBSULF (Royer and others, 2014). Different scenarios are described in figure 4.

554

Fig. 1



555

Fig. 2

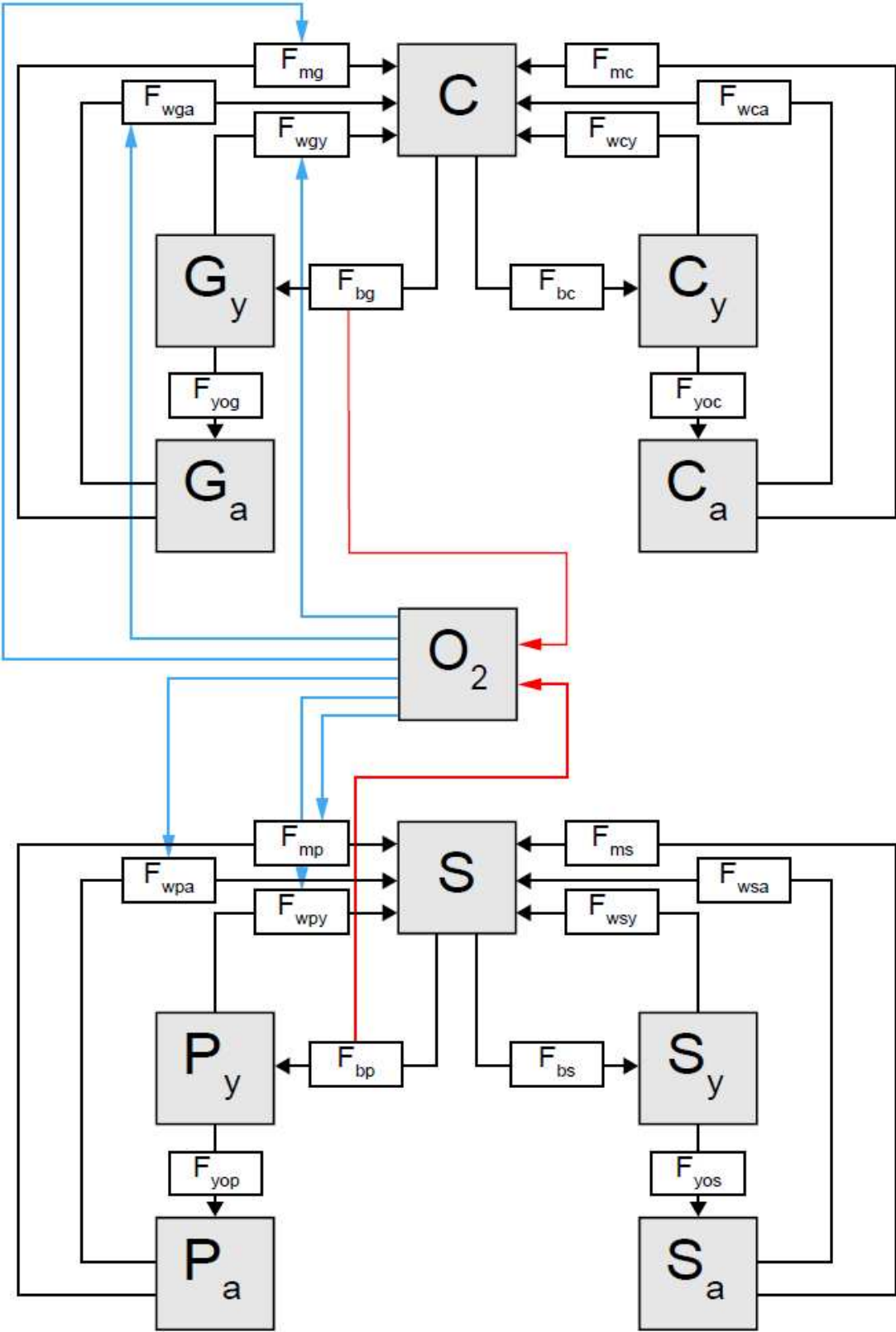
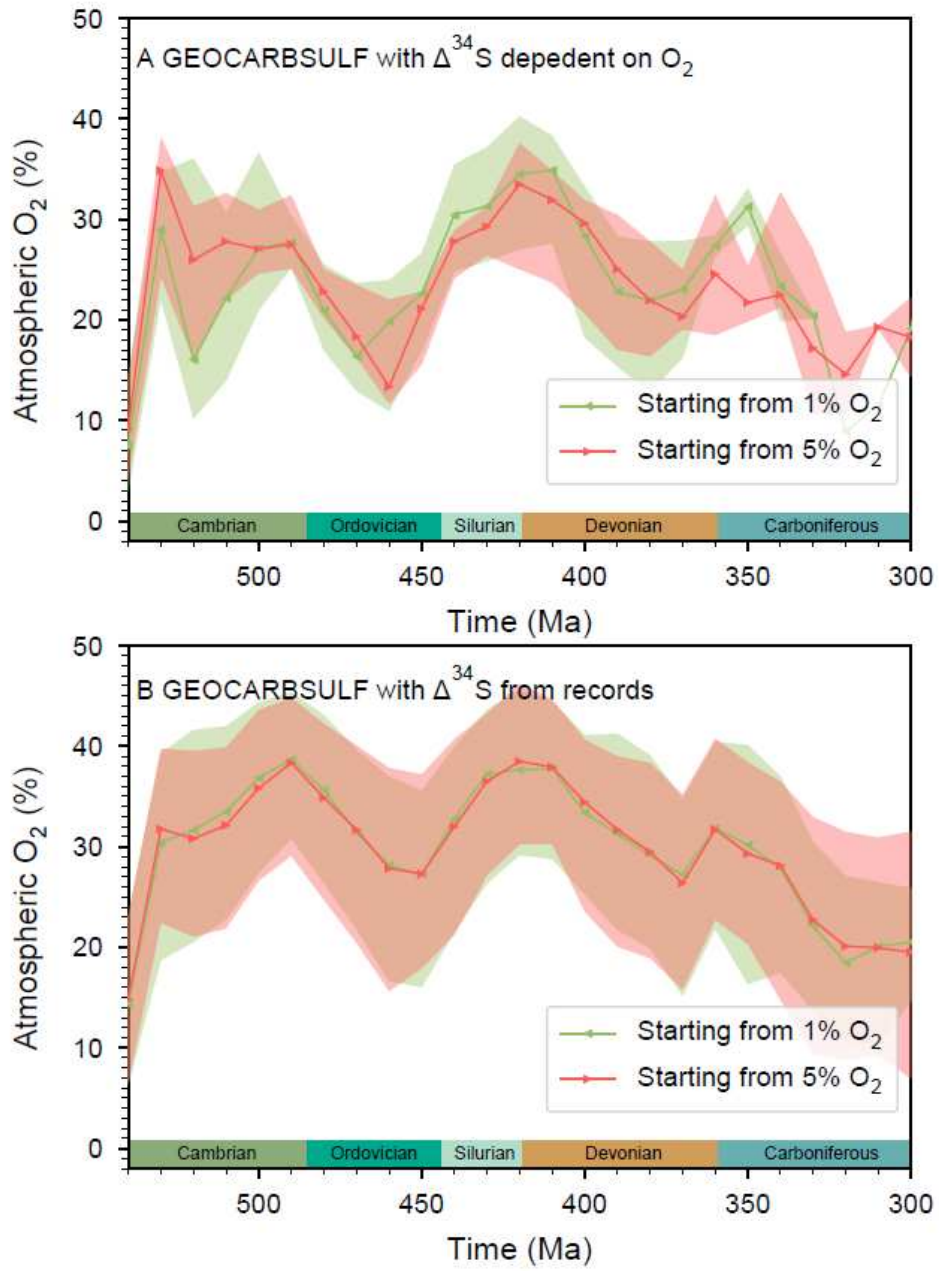
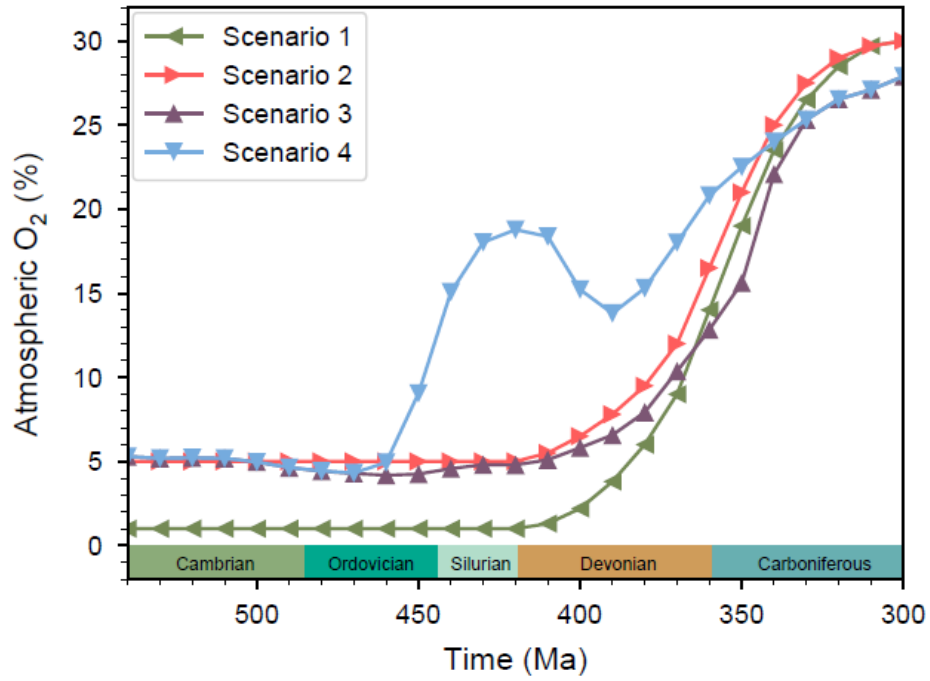


Fig. 3



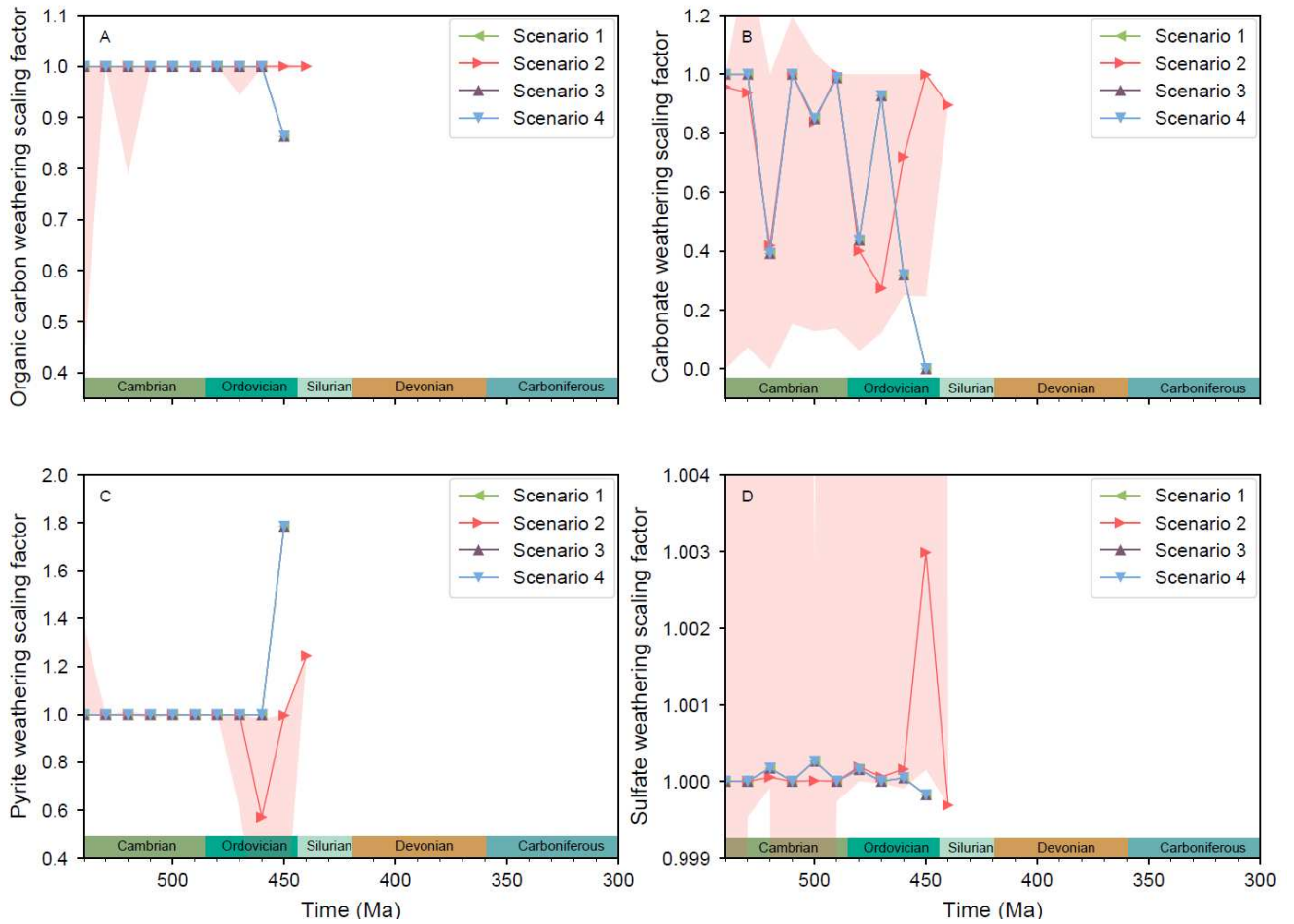
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Fig. 4



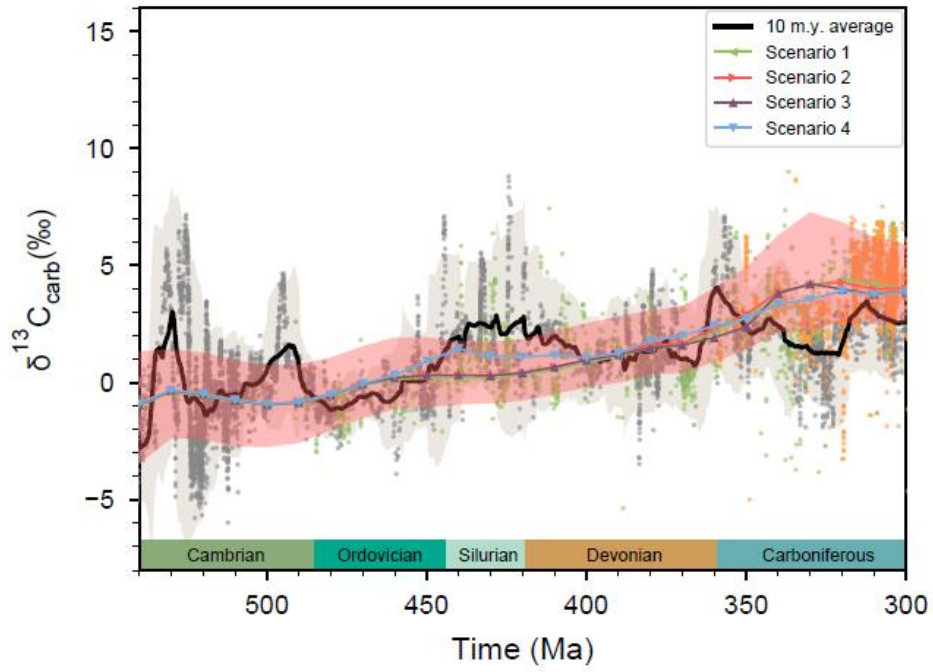
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Fig. 5



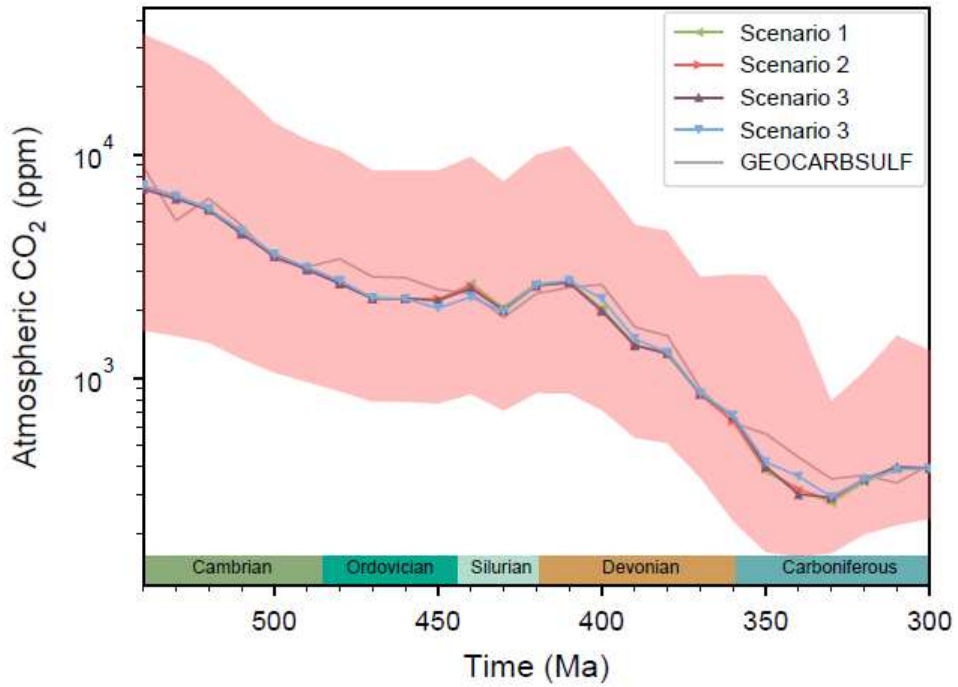
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Fig. 6



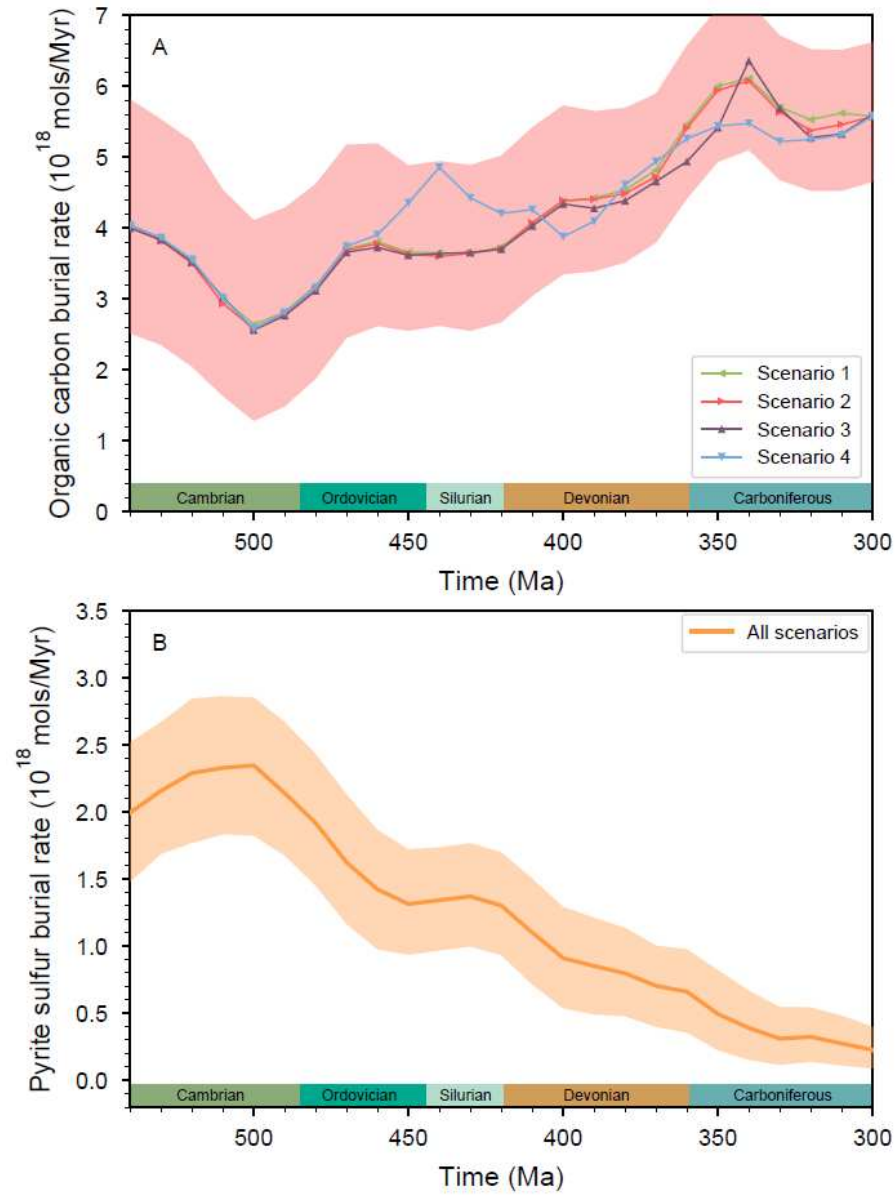
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Fig. 7



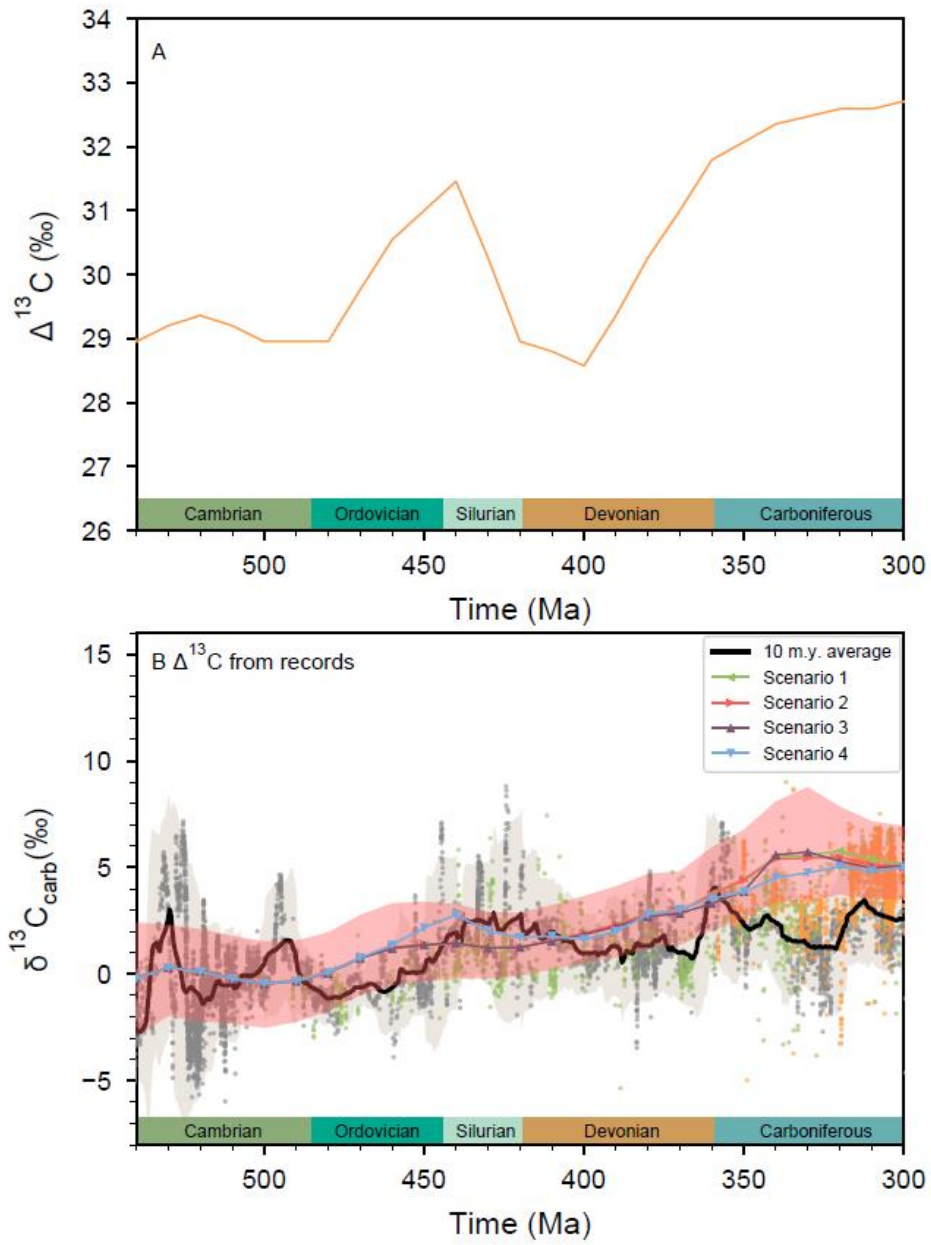
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Fig. 8



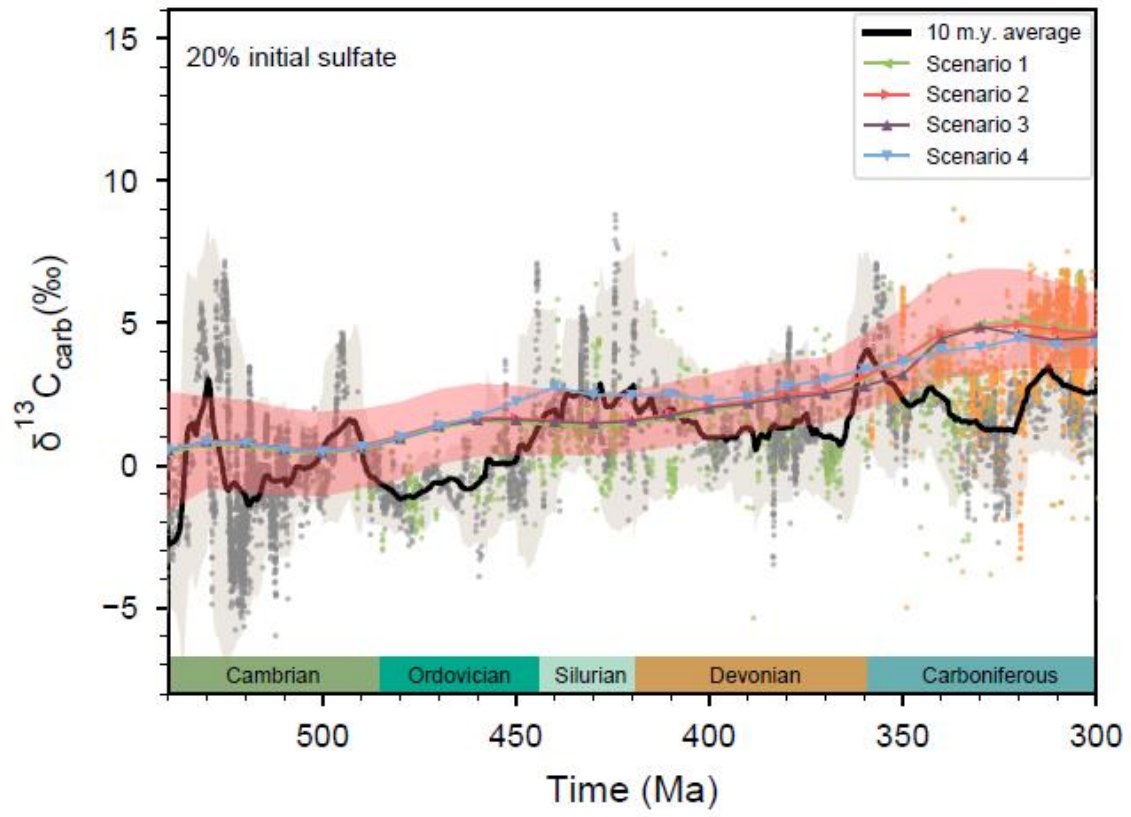
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Fig. 9



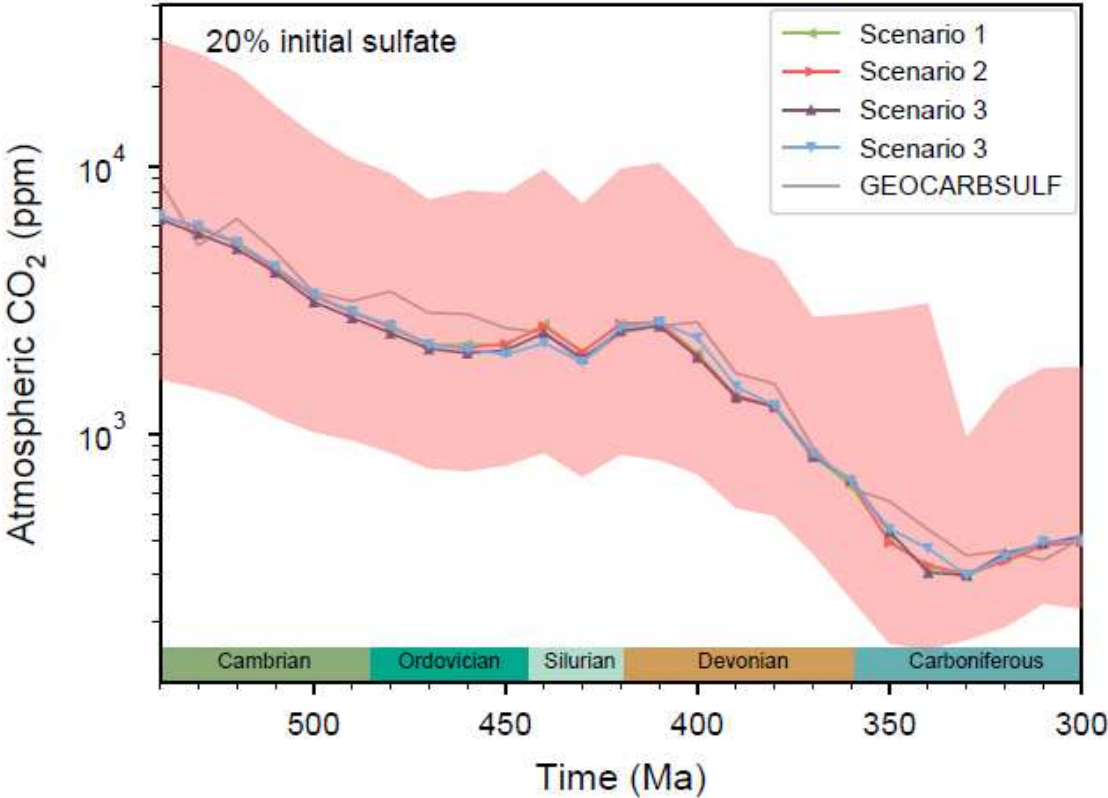
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Fig. 10



564

Fig. 11



565