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1           **Pyrite sulfur isotopes: a new proxy for glacial-interglacial environmental changes**

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16  
17           **Author Contributions** DF, PS, MR and SR conceived the work. VP did the sampling. VP and  
18           JH carried out sulfur isotopic analyses. VP, DF, PS, MR, JH and SR wrote the paper and most of  
19           the Supplementary Information. All authors discussed the interpretation of the results and  
20           contributed to the manuscript.

21  
22           **Keywords:** Pyrite Sulfur isotopes – Glacial/Interglacial – Sedimentation Rate – Local  
23           environment changes.

24

25 **Abstract:**

26 The sulfur biogeochemical cycle plays a key role in regulating Earth's surface redox  
27 through diverse abiotic and biological reactions that have distinctive stable isotopic  
28 fractionations. As such, variations in the sulfur isotopic composition ( $\delta^{34}\text{S}$ ) of sedimentary sulfate  
29 and sulphide phases over Earth history can be used to infer substantive changes to the Earth's  
30 surface environment, including the rise of atmospheric oxygen. Such inferences assume that  
31 individual  $\delta^{34}\text{S}$  records reflect temporal changes in the global sulfur cycle; this assumption may  
32 be well grounded for sulfate-bearing minerals, but is less well established for pyrite-based  
33 records. Here, we investigate alternative controls on the sedimentary sulfur isotopic composition  
34 of marine pyrite by examining a 300 m drill core of Mediterranean sediments deposited over the  
35 past 500,000 years and spanning the last five glacial-interglacial periods. Because this interval is  
36 far shorter than the residence time of marine sulfate, any change in the  $\delta^{34}\text{S}_{\text{pyr}}$  record necessarily  
37 corresponds to local environmental changes. The stratigraphic variations ( $>76.8\text{‰}$ ) in the  
38 isotopic data reported here are among the largest ever observed in pyrite, and are in phase with  
39 glacial-interglacial sea level and temperature changes. In this case, the dominant control appears  
40 to be glacial-interglacial variations in sedimentation rates. These results suggest that there exist  
41 important but previously overlooked depositional controls on sedimentary sulfur isotope records,  
42 especially associated with intervals of substantial sea level change. This work provides important  
43 perspective on the origin of variability in such records and suggests novel paleoenvironmental  
44 information can be derived from pyrite  $\delta^{34}\text{S}$  records.

45

46

47 **Significant Statement**

48 Sulfate is a major oxidant in the global ocean with a long residence time (13 Myr). As such,  
49 changes in sulfur isotopes ratio ( $^{34}\text{S}/^{32}\text{S}$ ) of marine sulfur phases are often attributed to global  
50 biogeochemical perturbations. Sediments collected on the shelf of the Gulf of Lion, revealed  
51 remarkable sulfur isotopic fluctuations in sedimentary pyrite over the last 500,000 years, ranging  
52 between -44.0‰ and 32.3‰. We suggest this pattern is related to changes in the local  
53 environmental deposition, specifically sedimentation modulating connectivity with the overlying  
54 water column and resulting microbial activity. Besides providing new understanding of an  
55 important and poorly constrained aspect of past glacial-interglacial transitions, our results are  
56 critically important because they question the degree to which changes in sulfur isotopes in pyrite  
57 reflect global biogeochemical processes versus local depositional conditions.

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61 The sulfur biogeochemical cycle helps regulate Earth's surface redox conditions through a  
62 variety of abiotic and biological reactions (1). These diverse reactions are often associated with  
63 distinctive stable isotopic fractionations of sulfur species (2, 3). As such, changes in the sulfur  
64 isotopic composition ( $\delta^{34}\text{S}$ ) of sedimentary phases over Earth history are often used to infer  
65 substantive changes to the Earth's surface environment, including the rise of atmospheric oxygen,  
66 the oxygenation of the oceans, and episodes of metazoan evolution and mass extinction (2-6).  
67 Much of past efforts to reconstruct the ancient sulfur cycle has used sulfate evaporite minerals  
68 (gypsum and anhydrite), barium-sulfate (barite), or carbonate-associated sulfate (i.e. sulfate  
69 bound into carbonate lattice, CAS) – all proxies that are generally thought to accurately reflect  
70 the  $\delta^{34}\text{S}$  composition seawater sulfate (2, 7). Additional constraints on ancient biogeochemical  
71 cycling have been placed through the analysis of  $\delta^{34}\text{S}$  records from sedimentary pyrites, either in  
72 parallel with direct proxies for sulfate (4, 6, 8, 9), or on their own (10-13). Inferences about past  
73 biogeochemical cycling are based on the assumption that the  $\delta^{34}\text{S}$  records reflect the isotopic  
74 composition of seawater sulfate and, further, that changes in these values indicate large-scale  
75 temporal changes in the global sulfur cycle. However, a subset of records of sulfur cycling from  
76 certain intervals on Earth have shown substantial spatial and stratigraphic variability that is not  
77 easily reconciled with them reflecting the behavior of the global sulfur cycle (e.g., 14). Rather, it

78 has been suggested that some  $\delta^{34}\text{S}$  records have the potential to be impacted by local depositional  
79 conditions (2) – and further that these records may provide new insights into paleo-environmental  
80 conditions. This intriguing idea has, however, not yet been appropriately tested.

81 Here we examine the sulfur isotopic record preserved in pyrite ( $\delta^{34}\text{S}_{\text{pyr}}$ ) from sediments  
82 from the Gulf of Lion deposited over the last 500,000 years associated with the last five glacial-  
83 interglacial transitions. Gulf of Lion is located in the North-Western Mediterranean basin and is  
84 characterized by a wide continental shelf (70 km) that was sub-aerially exposed during glacial  
85 periods over the Late Quaternary (15, 16). This study is based on borehole PRGL 1-4 (Fig. 1),  
86 drilled in the framework of the EU PROMESS project  
87 (<http://www.pangaea.de/Projects/PROMESS1/>), which sampled a 300 m long continuous record  
88 of the Bourcart and Herault canyons' interfluvial sediment sequence on the upper slope of the Gulf  
89 of Lion (Fig. 1). The water depth of the core (298 m) ensures continued deposition under well  
90 oxygenated conditions during glacial and interglacial periods with sedimentation rates that enable  
91 high-resolution records and where the changing proximity to the continental shelf results in  
92 variable detrital input. Given these characteristics, this drill core represents a record of glacial-  
93 interglacial deposition that is uniquely positioned to assess the environmental dependence of  
94  $\delta^{34}\text{S}_{\text{pyr}}$  signatures in marine sediments.

95

## 96 **Results and Discussion**

97 A total of 131 pyrite sulfur isotopes analyses have been performed along the 300 m  
98 PRGL1-4 core, spanning the last 5 glacial-interglacial transitions (see Supporting Information  
99 Fig. 1). Throughout the core, pyrite shows extreme variations in  $\delta^{34}\text{S}$  from -44.0‰ to 32.3‰,  
100 while pyrite contents vary between 0.02 and 1.69 weight %. No clear trend was observed  
101 between  $\delta^{34}\text{S}_{\text{pyr}}$  and the pyrite content, nor between  $\delta^{34}\text{S}_{\text{pyr}}$  and the iron content (see Supporting  
102 Information S1 and S2). Complementary analysis of organic carbon isotopes ( $\delta^{13}\text{C}_{\text{org}}$ ) was  
103 conducted and these values vary between -25.3‰ and -21.8‰ with no clear trends between  
104  $\delta^{13}\text{C}_{\text{org}}$  and total organic carbon (TOC) contents, which vary between 0.35% and 0.84%.

105 A clear distinction in pyrite  $\delta^{34}\text{S}_{\text{pyr}}$  values is observed between glacial and interglacial  
106 periods (Fig. 2) as deduced from the oxygen isotope curve obtained from planktonic foraminifera  
107 [*G. bulloides*] and the associated updated age model published on the same core (17). Distinctly  
108 different bimodal distributions are observed between glacial (*sensu stricto*, i.e., cold substages)

109 periods with high  $\delta^{34}\text{S}$  values and high isotopic variability (average  $\delta^{34}\text{S} = -15.2\text{‰} \pm 9.0\text{‰}$ ,  $n =$   
110 46) and the interglacial (*sensu stricto*, i.e., warm substages) periods characterized by low  $\delta^{34}\text{S}$   
111 and low isotopic variability (average  $\delta^{34}\text{S} = -41.6\text{‰} \pm 2.2\text{‰}$ ,  $n = 19$ ; Fig. 2). The increased  
112 variability observed during glacial times provides insights into the suite of process and their  
113 inherent temporal fluctuations that are likely to regulate the observed changes in  $\delta^{34}\text{S}_{\text{pyr}}$ .  
114 Specifically, the lowered sea level during glacial times brought the site of deposition closer to the  
115 shore and source of detrital materials. These shallower, more proximal settings are subjected to  
116 short-term, stochastic variations in depositional conditions (17), including sediment  
117 characteristics (organic carbon loading, sedimentation rates; physical reworking) and benthic  
118 ecology (bioturbation, presence of microbial mats) that can impact pyrite formation and eventual  
119  $\delta^{34}\text{S}$  composition. Within the glacial and interglacial sediments, the  $\delta^{34}\text{S}$  values and variability  
120 can be further understood as a function of temperature, as reconstructed from alkenone records  
121 (18, 19). For example, warmer intervals during interglacial time are associated with more  
122 negative  $\delta^{34}\text{S}$  values (Fig. 2).

123 Over the last two glacial-interglacial cycles, where the time reconstruction is best  
124 constrained, pyrite  $\delta^{34}\text{S}$  values in PRGL1-4 are modulated by and track depositional conditions  
125 across glacial-interglacial cycles (Fig. 3). During glacial times, higher  $\delta^{34}\text{S}_{\text{pyr}}$  values are  
126 associated with lower sea levels, and low  $\delta^{13}\text{C}_{\text{org}}$  values, which are often attributed to greater  
127 input of terrestrial organic matter (20). Interestingly, because of their increased proximity to  
128 shore, glacial deposits are also associated with increased sedimentation rates (21) and are  
129 characterized by decreased porosity intervals (see Supporting Information Fig. 2). In such  
130 nearshore environments, the rapid sediment burial ensures that a higher concentration of labile  
131 organic matter (supported by our TOC values) gets into the sediment without undergoing aerobic  
132 respiration. As such, a larger fraction of more easily metamobilizable (i.e., less degraded by oxic  
133 processes) organic matter is available for sulfate reduction (22).

134 In contrast, decreased and less variable  $\delta^{34}\text{S}_{\text{pyr}}$  values are associated with the transition into  
135 and during interglacial times. These are associated with warmer temperatures and higher sea  
136 levels, as well as increased  $\delta^{13}\text{C}_{\text{org}}$  values, indicative of increased marine input (23). Sediments  
137 deposited during interglacial periods are also associated with lower sedimentation rates (because  
138 of landward migration of the shoreline) and increased foraminiferal abundance, resulting in  
139 intervals of higher porosity (21; see Supplementary Fig. 2). As sedimentation rates decrease,

140 organic matter spends more time in the zone of aerobic respiration. Therefore, less (and less  
141 reactive) organic matter remains for sulfate-reducing bacteria under these conditions.

142 Stratigraphic variations in pyrite  $\delta^{34}\text{S}$  are often interpreted to reflect changes in the global  
143 sulfur biogeochemical cycle, such as intervals of enhanced pyrite burial or variations in the  
144 marine sulfate reservoir (9, 24). However, in this case, these strata were deposited over an  
145 interval of 500 kyr, much less than the residence time (13 Myr; ref. 25) of sulfate in the modern  
146 ocean. While these sediments were deposited in the Gulf of Lion, the Mediterranean Sea  
147 maintained connectivity with the global ocean and retained marine sulfate abundances and  
148 isotopic compositions during glacial-interglacial periods, based on both the abundance and  
149 isotopic composition of sulfate porewater profiles (26) and the continuous sea water infill of  
150 Mediterranean Sea by Atlantic water through the Gibraltar Strait since ~4.4 Ma (27, 28). Thus,  
151 continued connectivity with the ocean and the short timescale of deposition preclude any  
152 substantive change in the parent sulfate reservoir, such as might arise from prolonged variation in  
153 the burial flux of pyrite, during deposition of these sediments. How then is this variation in pyrite  
154  $\delta^{34}\text{S}$  to be interpreted?

155 Two possible mechanisms present themselves to explain the observed data – both  
156 fundamentally driven by glaciation induced environmental changes: one reflecting changes in the  
157 inherent metabolic activity of sulfur cycling microbes in the sediments; the other, changes in the  
158 connectivity of porewaters to the overlying water column. In the former, isotopic fractionation  
159 during microbial sulfur cycling is typically dominated by microbial sulfate reduction (3) and a  
160 change in pyrite  $\delta^{34}\text{S}$  can result from variations in the rate of cell-specific sulfate reduction  
161 (csSRR) in these sediments (29). Specifically, there is a well-documented relationship whereby  
162 faster rates of csSRR are associated with decreased isotopic fractionation between the parent  
163 sulfate and the produced sulfide (29, 30). Thus, our data could indicate faster csSRR during  
164 glacial times, possibly driven by enhanced input of more easily metabolizable organic matter  
165 and/or enhanced terrestrial nutrient input (as supported by lower organic carbon isotopic values,  
166 see Supplementary Fig. 1). In contrast, slower csSRR would characterize interglacial times  
167 associated with more limited (both in abundance and reactivity) organic matter resources and  
168 more stable nutrient input.

169 Assuming that pyrite is formed mainly in the pore-water environment, as it is expected  
170 under oxygenated (non euxinic) water column (31), an alternative mechanism to explain our data

171 involves a change in the connectivity of sedimentary porewaters where pyrites are forming with  
172 the overlying water column (32). Such a change could be the natural result of the increased  
173 sedimentation rates and decreased porosity during glacial times (Supplementary Fig. 2), both of  
174 which act to more effectively isolate porewaters from ready communication with seawater. This  
175 decreased connectivity effectively isolates the local porewater sulfate reservoir, leading to  
176 increased porewater  $\delta^{34}\text{S}_{\text{SO}_4}$  through ongoing microbial sulfate reduction (32). In turn, this  
177 microbial activity naturally leads to an increase in the resulting biogenic  $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ , which  
178 eventually forms pyrite following reaction with available iron. The increased variability in  $\delta^{34}\text{S}_{\text{pyr}}$   
179 during glacial times can be understood as the natural response to increased short-term  
180 fluctuations in depositional conditions that characterize shallower water environments more  
181 proximal to the shore. During interglacial times, the return to slower sedimentation rates and  
182 higher porosity, driven in part by the admixture of foraminifera (Supplementary Fig. 2), results in  
183 enhanced communication between porewater and seawater. In this relatively open system, the  
184 constant supply of seawater sulfate results in a stable, low value for porewater  $\delta^{34}\text{S}_{\text{SO}_4}$  (and  
185 therefore in the resulting  $\delta^{34}\text{S}_{\text{pyr}}$ ) in these intervals. While the relationship between sedimentation  
186 rate and  $\delta^{34}\text{S}_{\text{pyr}}$  indicates a dominant control by sedimentation (Fig. 4), it should be noted that  
187 these two mechanisms are not mutually exclusive. Indeed, all things being equal, increased  
188 csSRR will inherently lead to more closed system behavior because it represents enhanced sulfate  
189 consumption relative to the diffusive exchange of sulfate. Further, there is a general trend toward  
190 increasing rates of sulfate reduction with increasing sedimentation rate (33).

191 The magnitude and directionality of the relationship between water depth and pyrite  $\delta^{34}\text{S}$   
192 observed here agree with predictions previously made (2) but never rigorously tested and provide  
193 a powerful new way to reconstruct paleo-environmental conditions in sedimentary environments,  
194 particularly the degree to which sedimentary porefluids may have been in communication with  
195 the overlying water column. In addition, the  $\delta^{34}\text{S}_{\text{pyr}}$  data presented here also shed light on the  
196 possible origins of similar variability in this proxy in deep time.

197

### 198 **Implication for deep time records:**

199 Many deep time studies make use of direct proxies for seawater sulfate, such as carbonate-  
200 associated sulfate (CAS), which are generally thought to reflect marine sulfate with little  
201 fractionation (e.g., 7; but see 34). Indeed, studies utilizing direct proxies for seawater sulfate



202 (e.g., 9, 24, 35, 36) can provide powerful insights into ancient biogeochemical conditions. In  
203 many cases, however, no direct proxy of seawater sulfate is present and stratigraphic records of  
204  $\delta^{34}\text{S}_{\text{pyr}}$  are used to reconstruct global biogeochemical cycling and redox change (e.g., 10-13). In  
205 other cases, the isotopic offsets between coeval  $\delta^{34}\text{S}$  records from sulfate and pyrite are used to  
206 reconstruct marine sulfate levels or the types of microbial metabolism present (e.g., 4, 8). With  
207 few exceptions (e.g., 6), these  $\delta^{34}\text{S}_{\text{pyr}}$  records are not interpreted in the context of local  
208 depositional or facies change.

209 Interestingly, many of the reports showing positive  $\delta^{34}\text{S}_{\text{pyr}}$  excursions in the rock record are  
210 also associated with shallowing-upwards depositional sequences formed during sea level  
211 lowstands. The present study is particularly relevant for considering the ~10-30‰ positive  
212 excursions in  $\delta^{34}\text{S}_{\text{pyr}}$  that are associated with the initiation and termination of the end-Ordovician  
213 Hirnantian glaciation and mass extinction (e.g., 6, 10, 11, 6, 12, 13). Depositional environments at  
214 this time experienced a magnitude (~100 m) and timescale ( $\sim 10^5$  yr) of sea level change that  
215 would have been comparable to those influencing the Pleistocene sediments of the Gulf of Lion.  
216 Our data suggest that rather than reflecting a change in the global sulfur cycle, these  $\delta^{34}\text{S}_{\text{pyr}}$   
217 excursions could also be explained by local changes in depositional conditions, particularly  
218 changes in sedimentation that modulate connectivity with the overlying water column (e.g. Fig.  
219 4). In this scenario, it is local sedimentological changes that impact how records of sulfur cycling  
220 get preserved in sedimentary records. The temporal coincidence of the Hirnantian  $\delta^{34}\text{S}_{\text{pyr}}$   
221 excursions, found in sections around the world associated with the end Ordovician glaciation,  
222 would then be the result of synchronous local changes in environmental conditions in basins  
223 around the world, changes driven globally by sea level fluctuations during the onset and  
224 termination of the Hirnantian glaciation. Local environmental controls could be relevant for  
225 explaining other stratigraphic  $\delta^{34}\text{S}_{\text{pyr}}$  excursions in Earth history, particularly those associated  
226 with changing depositional facies and lacking a direct proxy for the marine sulfate reservoir (e.g.,  
227 37-39). As such, the data presented here show that pyrite  $\delta^{34}\text{S}$  can be a valuable new proxy for  
228 reconstructing local paleoenvironmental and sedimentological conditions throughout Earth  
229 history.

230

## 231 **Materials and Methods:**

232 *Pyrite Sulfur ( $\delta^{34}\text{S}_{\text{pyrite}}$  and S content)*

233 Pyrite sulfur from the samples was extracted using the chromium reduction method (40-  
234 42). This method allows a recovering of all reduced inorganic sulfur present in sedimentary  
235 samples (pyrite, element sulfur and iron monosulfide phases). During extraction, samples were  
236 reacted with ~25 mL of 1M reduced chromium chloride ( $\text{CrCl}_2$ ) solution and 25 mL of 6N HCl  
237 for four hours in a specialized extraction line under a Nitrogen atmosphere. The liberated  
238 hydrogen sulfide was reacted in a silver nitrate (0.1M) trap, recovering the sulfide as  $\text{Ag}_2\text{S}$ ;  
239 reproducibility was under 5% for repeated analyse. Residual  $\text{Ag}_2\text{S}$  were rinsed three times using  
240 Mili-Q water, centrifuged then the dried until complete dryness. The  $\text{Ag}_2\text{S}$  powders were  
241 homogenized prior to being analysed, then 450  $\mu\text{g}$  was loaded into tin capsules with excess  $\text{V}_2\text{O}_5$ .  
242 The  $\text{Ag}_2\text{S}$  was analysed measuring  $^{34}\text{S}/^{32}\text{S}$  ratio following online combustion with a Thermo  
243 Delta V Plus coupled with a Costech ECS 4010 Elemental Analyser at Washington University in  
244 St Louis. Pyrite sulfur composition are expressed in standard delta notation as per mil (‰)  
245 deviations from Vienna Canyon Diablo Troilite (VCDT) with an analytical error of <0.5‰.

246

#### 247 *Organic carbon analyses ( $\delta^3\text{C}_{org}$ and TOC)*

248 Prior to Organic carbon and Nitrogen analyses, the carbonated fraction was removed from  
249 bulk samples using excess 1.5 HCl digestion during 48h. During digestion centrifuge tube were  
250 placed in ultrasonic bath to increase the mechanical separation of clay and calcium carbonates.  
251 After total dissolution residues were washed three times with distilled water, centrifuged then  
252 dried at 50°C. The residual powders were homogenized and prior to analyses 30 mg were loaded  
253 into tin capsule. Analyses were performed using an Elemental Analyser (EA, Flash 2000 -  
254 ThermoScientific) coupled to an isotope ratio mass spectrometer (Delta V+ Thermo Scientific  
255 EA-IRMS) at the Pôle de Spectométrie Océan (PSO, Brest, France). Carbon is given as delta  
256 notation as per mil deviation from Pee Dee Belemnite (PDB), with an analytical error of <0.2‰  
257 ( $1\sigma$ ) for organic carbon isotopes. Total Organic Carbon (TOC) were measured using the Thermal  
258 Conductivity Detector (TCD) of the Flash EA 2000, ThermoScientific at PSO, Brest, France.

259

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270

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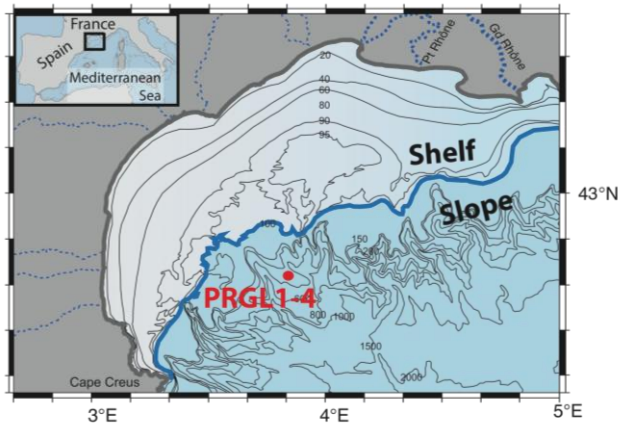
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394 **Figure Legends**

395



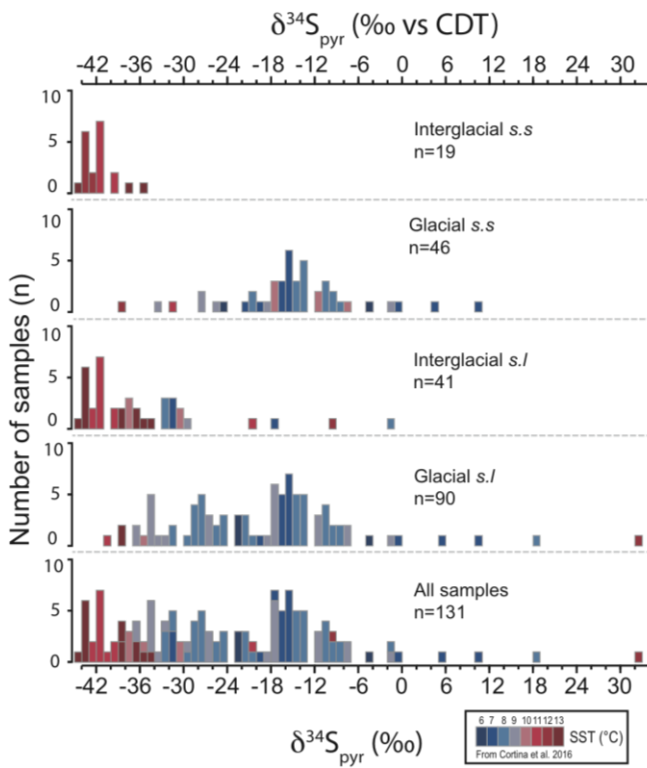
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397 **Figure 1:** Map of the Gulf of Lion with the position of the PRGL1-4 core (42.690N; 3.838E).

398 The bold grey line highlights the present shoreline position and the contours reflect modern water

399 depths. The bold blue line corresponds to the shoreline position during the last-glacial period

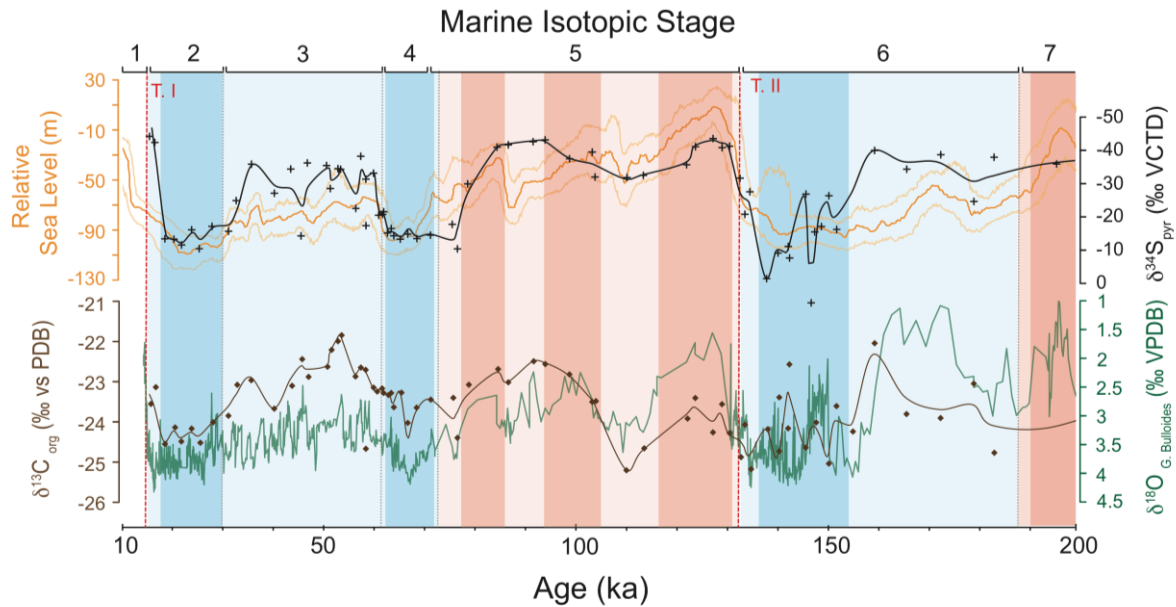
400 (low sea level).



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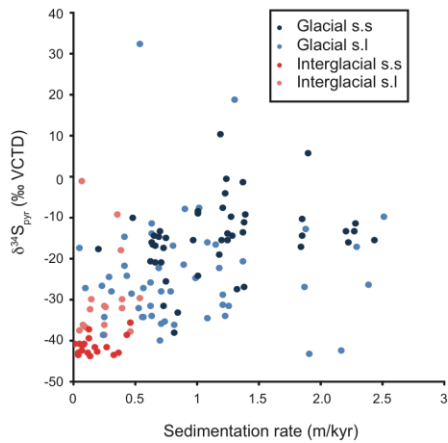
402 **Figure 2:** Histogram of pyrite  $\delta^{34}\text{S}$  (this study) as a function of glacial/interglacial periods, color-

403 coded by temperature obtained from the relative composition of C<sub>37</sub> unsaturated alkenones (18,  
404 19). *Sensu stricto* (s.s.) refers to the warm substages of the interglacials and cold substages during  
405 glacials. The *sensu lato* (s.l.) includes all the data within interglacial or glacial periods.



406  
407 **Figure 3:** Glacial-interglacial geochemical records.  $\delta^{34}\text{S}_{\text{pyr}}$  (black crosses; black line representing  
408 LOESS regression, this study),  $\delta^{13}\text{C}_{\text{org}}$  (brown diamonds and brown line (LOESS regression), this  
409 study), reconstructed sea levels (orange) from the Red Sea, and  $\delta^{18}\text{O}_{\text{G. Bulloides}}$  (green) for the last 6  
410 Marine isotopic stages (10 to 200 kyr). Relative Sea Level (orange line) superimposed with 95%  
411 of probability interval (light orange lines) from ref. 43 and  $\delta^{18}\text{O}_{\text{G. Bulloides}}$  from ref. 17, 21. Blue  
412 vertical bands represent the glacial times with corresponding cold substages (i.e. *sensu-stricto*) in  
413 darker blue. Red bands correspond to interglacials periods with warm substages (i.e. *sensu-*  
414 *stricto*) highlighted in dark pink. Vertical pink dashed lines reflect glacial termination (T.) times  
415 according to ref. 44; vertical black dashed lines reflect scheme of marine stages according to ref.  
416 45.





417  
 418 **Figure 4:** The relationship between sedimentation rate ( $\text{m kyr}^{-1}$ ) and  $\delta^{34}\text{S}_{\text{pyr}}$ . Sedimentation rates  
 419 are calculated using the linear relationship between depth in borehole and the update age model  
 420 derived from ref. 17. Light / dark blues circles correspond to cold substages (i.e. respectively  
 421 sensu-lato and *sensu-stricto*) whereas light / dark red circles refer to warm substages (i.e.  
 422 respectively sensu-lato and *sensu-stricto*).  
 423