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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 through diverse abiotic and biological reactions that have distinctive stable isotopic 27 fractionations. As such, variations in the sulfur isotopic composition (δ^{34} S) of sedimentary sulfate 28 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 individual δ^{34} S records reflect temporal changes in the global sulfur cycle; this assumption may 31 32 be well grounded for sulfate-bearing minerals, but is less well established for pyrite-based records. Here, we investigate alternative controls on the sedimentary sulfur isotopic composition 33 34 of marine pyrite by examining a 300 m drill core of Mediterranean sediments deposited over the past 500,000 years and spanning the last five glacial-interglacial periods. Because this interval is 35 far shorter than the residence time of marine sulfate, any change in the $\delta^{34}S_{pvr}$ record necessarily 36 corresponds to local environmental changes. The stratigraphic variations (>76.8‰) in the 37 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 perspective on the origin of variability in such records and suggests novel paleoenvironmental 43 information can be derived from pyrite δ^{34} S records. 44

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47 Significant Statement

48 Sulfate is a major oxidant in the global ocean with a long residence time (13 Myr). As such, changes in sulfur isotopes ratio $({}^{34}S/{}^{32}S)$ of marine sulfur phases are often attributed to global 49 biogeochemical perturbations. Sediments collected on the shelf of the Gulf of Lion, revealed 50 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 reflect global biogeochemical processes versus local depositional conditions. 57

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The sulfur biogeochemical cycle helps regulate Earth's surface redox conditions through a 61 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 isotopic composition (δ^{34} S) of sedimentary phases over Earth history are often used to infer 64 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 the δ^{34} S composition seawater sulfate (2, 7). Additional constraints on ancient biogeochemical 70 cycling have been placed through the analysis of δ^{34} S records from sedimentary pyrites, either in 71 72 parallel with direct proxies for sulfate (4, 6, 8, 9), or on their own (10-13). Inferences about past biogeochemical cycling are based on the assumption that the δ^{34} S records reflect the isotopic 73 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 has been suggested that some δ^{34} S records have the potential to be impacted by local depositional conditions (2) – and further that these records may provide new insights into paleo-environmental conditions. This intriguing idea has, however, not yet been appropriately tested.

Here we examine the sulfur isotopic record preserved in pyrite ($\delta^{34}S_{pyr}$) from sediments 81 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), drilled the EU project 86 in framework of the PROMESS 87 (http://www.pangaea.de/Projects/PROMESS1/), which sampled a 300 m long continuous record 88 of the Bourcart and Herault canyons' interfluve 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 δ^{34} S_{pvr} signatures in marine sediments. 94

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 Fig. 1). Throughout the core, pyrite shows extreme variations in δ^{34} S from -44.0% to 32.3%, 99 100 while pyrite contents vary between 0.02 and 1.69 weight %. No clear trend was observed between $\delta^{34}S_{pvr}$ and the pyrite content, nor between $\delta^{34}S_{pvr}$ and the iron content (see Supporting 101 Informations S1 and S2). Complementary analysis of organic carbon isotopes ($\delta^{13}C_{oro}$) was 102 103 conducted and these values vary between -25.3‰ and -21.8‰ with no clear trends between $\delta^{13}C_{org}$ and total organic carbon (TOC) contents, which vary between 0.35% and 0.84%. 104

105 A clear distinction in pyrite $\delta^{34}S_{pyr}$ values is observed between glacial and interglacial 106 periods (Fig. 2) as deduced from the oxygen isotope curve obtained from planktonic foraminifera 107 [*G. bulloïdes*] 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)

periods with high δ^{34} S values and high isotopic variability (average δ^{34} S = -15.2‰ ± 9.0‰, n = 109 110 46) and the interglacial (*sensu stricto*, i.e., warm substages) periods characterized by low δ^{34} S and low isotopic variability (average $\delta^{34}S = -41.6\% \pm 2.2\%$, n = 19; Fig. 2). The increased 111 112 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 $\delta^{34}S_{pvr}$. Specifically, the lowered sea level during glacial times brought the site of deposition closer to the 114 115 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 δ^{34} S composition. Within the glacial and interglacial sediments, the δ^{34} S values and variability 119 can be further understood as a function of temperature, as reconstructed from alkenone records 120 121 (18, 19). For example, warmer intervals during interglacial time are associated with more negative δ^{34} S values (Fig. 2). 122

123 Over the last two glacial-interglacial cycles, where the time reconstruction is best constrained, pyrite δ^{34} S values in PRGL1-4 are modulated by and track depositional conditions 124 across glacial-interglacial cycles (Fig. 3). During glacial times, higher $\delta^{34}S_{pvr}$ values are 125 associated with lower sea levels, and low $\delta^{13}C_{org}$ values, which are often attributed to greater 126 127 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).

In contrast, decreased and less variable $\delta^{34}S_{pyr}$ values are associated with the transition into and during interglacial times. These are associated with warmer temperatures and higher sea levels, as well as increased $\delta^{13}C_{org}$ values, indicative of increased marine input (23). Sediments deposited during interglacial periods are also associated with lower sedimentation rates (because of landward migration of the shoreline) and increased foraminiferal abundance, resulting in intervals of higher porosity (21; see Supplementary Fig. 2). As sedimentation rates decrease, organic matter spends more time in the zone of aerobic respiration. Therefore, less (and less
reactive) organic matter remains for sulfate-reducing bacteria under these conditions.

Stratigraphic variations in pyrite δ^{34} S are often interpreted to reflect changes in the global 142 sulfur biogeochemical cycle, such as intervals of enhanced pyrite burial or variations in the 143 144 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 Gilbraltar 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 δ^{34} S to be interpreted? 154

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 change in pyrite δ^{34} S can result from variations in the rate of cell-specific sulfate reduction 160 161 (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 csSSR would characterize interglacial times 167 associated with more limited (both in abundance and reactivity) organic matter resources and 168 more stable nutrient input.

Assuming that pyrite is formed mainly in the pore-water environment, as it is expected 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 increased porewater $\delta^{34}S_{SO4}$ through ongoing microbial sulfate reduction (32). In turn, this 176 microbial activity naturally leads to an increase in the resulting biogenic $\delta^{34}S_{\rm H2S},$ which 177 eventually forms pyrite following reaction with available iron. The increased variability in $\delta^{34}S_{nvr}$ 178 during glacial times can be understood as the natural response to increased short-term 179 180 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 constant supply of seawater sulfate results in a stable, low value for porewater $\delta^{34}S_{SO4}$ (and 184 therefore in the resulting δ^{34} S_{pvr}) in these intervals. While the relationship between sedimentation 185 rate and $\delta^{34}S_{pvr}$ indicates a dominant control by sedimentation (Fig. 4), it should be noted that 186 these two mechanisms are not mutually exclusive. Indeed, all things being equal, increased 187 188 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 δ^{34} 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 δ^{34} S_{pyr} data presented here also shed light on the 196 possible origins of similar variability in this proxy in deep time.

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Implication for deep time records:

Many deep time studies make use of direct proxies for seawater sulfate, such as carbonateassociated sulfate (CAS), which are generally thought to reflect marine sulfate with little fractionation (e.g., 7; but see 34). Indeed, studies utilizing direct proxies for seawater sulfate (e.g., 9, 24, 35, 36) can provide powerful insights into ancient biogeochemical conditions. In many cases, however, no direct proxy of seawater sulfate is present and stratigraphic records of $\delta^{34}S_{pyr}$ are used to reconstruct global biogeochemical cycling and redox change (e.g., 10-13). In other cases, the isotopic offsets between coeval $\delta^{34}S$ records from sulfate and pyrite are used to reconstruct marine sulfate levels or the types of microbial metabolism present (e.g., 4, 8). With few exceptions (e.g., 6), these $\delta^{34}S_{pyr}$ records are not interpreted in the context of local depositional or facies change.

Interestingly, many of the reports showing positive $\delta^{34}S_{pvr}$ excursions in the rock record are 209 210 also associated with shallowing-upwards depositional sequences formed during sea level 211 lowstands. The present study is particularly relevant for considering the $\sim 10-30\%$ positive excursions in δ^{34} S_{pyr} that are associated with the initiation and termination of the end-Ordovician 212 213 Hirnantian glaciation and mass extinction (e.g., 6, 10, 11,6, 12, 13). Depositional environments at this time experienced a magnitude (~100 m) and timescale (~ 10^5 yr) of sea level change that 214 215 would have been comparable to those influencing the Pleistocene sediments of the Gulf of Lion. Our data suggest that rather than reflecting a change in the global sulfur cycle, these $\delta^{34}S_{pvr}$ 216 217 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 get preserved in sedimentary records. The temporal coincidence of the Hirnantian $\delta^{34}S_{pyr}$ 220 221 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 explaining other stratigraphic $\delta^{34}S_{pyr}$ excursions in Earth history, particularly those associated 225 226 with changing depositional facies and lacking a direct proxy for the marine sulfate reservoir (e.g., 37-39). As such, the data presented here show that pyrite δ^{34} S can be a valuable new proxy for 227 228 reconstructing local paleoenvironmental and sedimentological conditions throughout Earth 229 history.

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231 Materials and Methods:

232 *Pyrite Sulfur* ($\delta^{34}S_{pyrite}$ 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 (CrCl₂) 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 Ag₂S; 239 reproducibility was under 5% for repeated analyse. Residual Ag₂S were rinsed three times using Mili-Q water, centrifuged then the dried until complete dryness. The Ag₂S powders were 240 homogenized prior to being analysed, then 450 μ g was loaded into tin capsules with excess V₂O₅. 241 The Ag₂S was analysed measuring ${}^{34}S/{}^{32}S$ ratio following online combustion with a Thermo 242 243 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%.

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Organic carbon analyses ($\delta^{l^3}C_{org}$ 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 (1σ) 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.

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

The bold grey line highlights the present shoreline position and the contours reflect modern water depths. The bold blue line corresponds to the shoreline position during the last-glacial period (low sea level).



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

403 coded by temperature obtained from the relative composition of C_{37} 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 latto (s.l.) includes all the data within interglacial or glacial periods.



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Figure 3: Glacial-interglacial geochemical records. $\delta^{34}S_{pyr}$ (black crosses; black line representing 407 LOESS regression, this study), $\delta^{13}C_{org}$ (brown diamonds and brown line (LOESS regression), this 408 study) reconstructed sea levels (orange) from the Red Sea, and $\delta^{18}O_{G, Bulloides}$ (green) for the last 6 409 410 Marine isotopic stages (10 to 200 kyr). Relative Sea Level (orange line) superimposed with 95% of probability interval (light orange lines) from ref. 43 and $\delta^{18}O_{G,Bulloides}$ from ref. 17, 21. Blue 411 vertical bands represent the glacial times with corresponding cold substages (i.e. sensu-stricto) in 412 413 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.





418 **Figure 4:** The relationship between sedimentation rate (m kyr⁻¹) and $\delta^{34}S_{pyr}$. 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*).