Pyrite sulfur isotopes reveal glacial–interglacial environmental changes

Virgil Pasquier, Pierre Sansjofre, Marina Rabineau, Sidonie Révillon, Jennifer Houghton, David A. Fike

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

V. Pasquier[1], P. Sansjofre [1], M. Rabineau[1], S. Revillon[1,2] J. Houghton[3], D. A. Fike[3]

[1] IUEM, UMR CNRS 6538 « Laboratoire Géosciences Océan », Université de Bretagne Occidentale, 29280 Plouzane, France

[2] SEDISOR, IUEM, Place Nicolas Copernic, 29280, Plouzane, France

[3] Department of Earth and Planetary Sciences, Washington University, St. Louis, MO 63130, United States

Correspondence and requests for materials should be addressed to V.P. (virgil.pasquier@univ-brest.fr).

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

Keywords: Pyrite Sulfur isotopes – Glacial/Interglacial – Sedimentation Rate – Local environment changes.

Abstract:

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 fractionations. As such, variations in the sulfur isotopic composition ($\delta^{34}S$) of sedimentary sulfate and sulphide phases over Earth history can be used to infer substantive changes to the Earth's surface environment, including the rise of atmospheric oxygen. Such inferences assume that individual $\delta^{34}S$ records reflect temporal changes in the global sulfur cycle; this assumption may 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 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 far shorter than the residence time of marine sulfate, any change in the $\delta^{34}S_{pyr}$ record necessarily corresponds to local environmental changes. The stratigraphic variations (>76.8‰) in the isotopic data reported here are among the largest ever observed in pyrite, and are in phase with glacial-interglacial sea level and temperature changes. In this case, the dominant control appears to be glacial-interglacial variations in sedimentation rates. These results suggest that there exist important but previously overlooked depositional controls on sedimentary sulfur isotope records, 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 information can be derived from pyrite $\delta^{34}S$ records.

Significant Statement

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 biogeochemical perturbations. Sediments collected on the shelf of the Gulf of Lion, revealed remarkable sulfur isotopic fluctuations in sedimentary pyrite over the last 500,000 years, ranging between -44.0‰ and 32.3‰. We suggest this pattern is related to changes in the local environmental deposition, specifically sedimentation modulating connectivity with the overlying water column and resulting microbial activity. Besides providing new understanding of an important and poorly constrained aspect of past glacial-interglacial transitions, our results are critically important because they question the degree to which changes in sulfur isotopes in pyrite reflect global biogeochemical processes versus local depositional conditions.

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The sulfur biogeochemical cycle helps regulate Earth's surface redox conditions through a variety of abiotic and biological reactions (1). These diverse reactions are often associated with distinctive stable isotopic fractionations of sulfur species (2, 3). As such, changes in the sulfur isotopic composition ($\delta^{34}S$) of sedimentary phases over Earth history are often used to infer substantive changes to the Earth's surface environment, including the rise of atmospheric oxygen, the oxygenation of the oceans, and episodes of metazoan evolution and mass extinction (2-6). Much of past efforts to reconstruct the ancient sulfur cycle has used sulfate evaporite minerals (gypsum and anhydrite), barium-sulfate (barite), or carbonate-associated sulfate (i.e. sulfate bound into carbonate lattice, CAS) – all proxies that are generally thought to accurately reflect the $\delta^{34}S$ composition seawater sulfate (2, 7). Additional constraints on ancient biogeochemical cycling have been placed through the analysis of $\delta^{34}S$ records from sedimentary pyrites, either in 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 $\delta^{34}S$ records reflect the isotopic composition of seawater sulfate and, further, that changes in these values indicate large-scale temporal changes in the global sulfur cycle. However, a subset of records of sulfur cycling from certain intervals on Earth have shown substantial spatial and stratigraphic variability that is not easily reconciled with them reflecting the behavior of the global sulfur cycle (e.g., 14). Rather, it has been suggested that some $\delta^{34}S$ 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 from the Gulf of Lion deposited over the last 500,000 years associated with the last five glacial-interglacial transitions. Gulf of Lion is located in the North-Western Mediterranean basin and is characterized by a wide continental shelf (70 km) that was sub-aerially exposed during glacial periods over the Late Quaternary (15, 16). This study is based on borehole PRGL 1-4 (Fig. 1), drilled in the framework of the EU PROMESS project (http://www.pangaea.de/Projects/PROMESS1/), which sampled a 300 m long continuous record of the Bourcart and Herault canyons' interfluve sediment sequence on the upper slope of the Gulf of Lion (Fig. 1). The water depth of the core (298 m) ensures continued deposition under well oxygenated conditions during glacial and interglacial periods with sedimentation rates that enable high-resolution records and where the changing proximity to the continental shelf results in variable detrital input. Given these characteristics, this drill core represents a record of glacial-interglacial deposition that is uniquely positioned to assess the environmental dependence of $\delta^{34}S_{pyr}$ signatures in marine sediments.

Results and Discussion

A total of 131 pyrite sulfur isotopes analyses have been performed along the 300 m PRGL1-4 core, spanning the last 5 glacial-interglacial transitions (see Supporting Information Fig. 1). Throughout the core, pyrite shows extreme variations in $\delta^{34}S$ from -44.0‰ to 32.3‰, while pyrite contents vary between 0.02 and 1.69 weight %. No clear trend was observed between $\delta^{34}S_{pyr}$ and the pyrite content, nor between $\delta^{34}S_{pyr}$ and the iron content (see Supporting Informations S1 and S2). Complementary analysis of organic carbon isotopes ($\delta^{13}C_{org}$) was 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%.

A clear distinction in pyrite $\delta^{34}S_{pyr}$ values is observed between glacial and interglacial periods (Fig. 2) as deduced from the oxygen isotope curve obtained from planktonic foraminifera [*G. bulloïdes*] and the associated updated age model published on the same core (17). Distinctly different bimodal distributions are observed between glacial (*sensu stricto,* i.e., cold substages) periods with high $\delta^{34}S$ values and high isotopic variability (average $\delta^{34}S$ = -15.2‰ ± 9.0‰, n = 46) and the interglacial (*sensu stricto,* i.e., warm substages) periods characterized by low $\delta^{34}S$ and low isotopic variability (average $\delta^{34}S$ =-41.6‰ ± 2.2‰, n = 19; Fig. 2). The increased variability observed during glacial times provides insights into the suite of process and their inherent temporal fluctuations that are likely to regulate the observed changes in $\delta^{34}S_{pyr}$. Specifically, the lowered sea level during glacial times brought the site of deposition closer to the shore and source of detrital materials. These shallower, more proximal settings are subjected to short-term, stochastic variations in depositional conditions (17), including sediment characteristics (organic carbon loading, sedimentation rates; physical reworking) and benthic ecology (bioturbation, presence of microbial mats) that can impact pyrite formation and eventual $\delta^{34}S$ composition. Within the glacial and interglacial sediments, the $\delta^{34}S$ values and variability can be further understood as a function of temperature, as reconstructed from alkenone records (18, 19). For example, warmer intervals during interglacial time are associated with more negative $\delta^{34}S$ values (Fig. 2).

Over the last two glacial-interglacial cycles, where the time reconstruction is best constrained, pyrite $\delta^{34}S$ values in PRGL1-4 are modulated by and track depositional conditions across glacial-interglacial cycles (Fig. 3). During glacial times, higher $\delta^{34}S_{pyr}$ values are associated with lower sea levels, and low $\delta^{13}C_{org}$ values, which are often attributed to greater input of terrestrial organic matter (20). Interestingly, because of their increased proximity to shore, glacial deposits are also associated with increased sedimentation rates (21) and are characterized by decreased porosity intervals (see Supporting Information Fig. 2). In such nearshore environments, the rapid sediment burial ensures that a higher concentration of labile organic matter (supported by our TOC values) gets into the sediment without undergoing aerobic respiration. As such, a larger fraction of more easily metamobilizable (i.e., less degraded by oxic 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 $\delta^{34}S$ are often interpreted to reflect changes in the global sulfur biogeochemical cycle, such as intervals of enhanced pyrite burial or variations in the marine sulfate reservoir (9, 24). However, in this case, these strata were deposited over an interval of 500 kyr, much less than the residence time (13 Myr; ref. 25) of sulfate in the modern ocean. While these sediments were deposited in the Gulf of Lion, the Mediterranean Sea maintained connectivity with the global ocean and retained marine sulfate abundances and isotopic compositions during glacial-interglacial periods, based on both the abundance and isotopic composition of sulfate porewater profiles (26) and the continuous sea water infill of Mediterranean Sea by Atlantic water through the Gilbraltar Strait since ~4.4 Ma (27, 28). Thus, continued connectivity with the ocean and the short timescale of deposition preclude any substantive change in the parent sulfate reservoir, such as might arise from prolonged variation in the burial flux of pyrite, during deposition of these sediments. How then is this variation in pyrite $\delta^{34}S$ to be interpreted?

Two possible mechanisms present themselves to explain the observed data – both fundamentally driven by glaciation induced environmental changes: one reflecting changes in the inherent metabolic activity of sulfur cycling microbes in the sediments; the other, changes in the connectivity of porewaters to the overlying water column. In the former, isotopic fractionation during microbial sulfur cycling is typically dominated by microbial sulfate reduction (3) and a change in pyrite $\delta^{34}S$ can result from variations in the rate of cell-specific sulfate reduction (csSRR) in these sediments (29). Specifically, there is a well-documented relationship whereby faster rates of csSRR are associated with decreased isotopic fractionation between the parent sulfate and the produced sulfide (29, 30). Thus, our data could indicate faster csSRR during glacial times, possibly driven by enhanced input of more easily metabolizable organic matter and/or enhanced terrestrial nutrient input (as supported by lower organic carbon isotopic values, see Supplementary Fig. 1). In contrast, slower csSSR would characterize interglacial times associated with more limited (both in abundance and reactivity) organic matter resources and 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 involves a change in the connectivity of sedimentary porewaters where pyrites are forming with the overlying water column (32). Such a change could be the natural result of the increased sedimentation rates and decreased porosity during glacial times (Supplementary Fig. 2), both of which act to more effectively isolate porewaters from ready communication with seawater. This 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 microbial activity naturally leads to an increase in the resulting biogenic $\delta^{34}S_{H2S}$, which eventually forms pyrite following reaction with available iron. The increased variability in $\delta^{34}S_{pyr}$ during glacial times can be understood as the natural response to increased short-term fluctuations in depositional conditions that characterize shallower water environments more proximal to the shore. During interglacial times, the return to slower sedimentation rates and higher porosity, driven in part by the admixture of foraminifera (Supplementary Fig. 2), results in 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 therefore in the resulting $\delta^{34}S_{pyr}$) in these intervals. While the relationship between sedimentation rate and $\delta^{34}S_{pyr}$ indicates a dominant control by sedimentation (Fig. 4), it should be noted that these two mechanisms are not mutually exclusive. Indeed, all things being equal, increased csSRR will inherently lead to more closed system behavior because it represents enhanced sulfate consumption relative to the diffusive exchange of sulfate. Further, there is a general trend toward increasing rates of sulfate reduction with increasing sedimentation rate (33).

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

Implication for deep time records:

Many deep time studies make use of direct proxies for seawater sulfate, such as carbonate-associated 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 $\delta^{34}S_{pyr}$ excursions in the rock record are also associated with shallowing-upwards depositional sequences formed during sea level lowstands. The present study is particularly relevant for considering the ~10-30‰ positive excursions in $\delta^{34}S_{pyr}$ that are associated with the initiation and termination of the end-Ordovician 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 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 $\delta^{34}S_{pyr}$ excursions could also be explained by local changes in depositional conditions, particularly changes in sedimentation that modulate connectivity with the overlying water column (e.g. Fig. 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 $\delta^{34}S_{pyr}$ excursions, found in sections around the world associated with the end Ordovician glaciation, would then be the result of synchronous local changes in environmental conditions in basins around the world, changes driven globally by sea level fluctuations during the onset and 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 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 $\delta^{34}S$ can be a valuable new proxy for reconstructing local paleoenvironmental and sedimentological conditions throughout Earth history.

Materials and Methods:

Pyrite Sulfur ($\delta^{34}S_{pyrite}$ and S content)

Pyrite sulfur from the samples was extracted using the chromium reduction method (40-42). This method allows a recovering of all reduced inorganic sulfur present in sedimentary samples (pyrite, element sulfur and iron monosulfide phases). During extraction, samples were reacted with ~25 mL of 1M reduced chromium chloride ($CrCl_2$) solution and 25 mL of 6N HCl for four hours in a specialized extraction line under a Nitrogen atmosphere. The liberated hydrogen sulfide was reacted in a silver nitrate (0.1M) trap, recovering the sulfide as Ag_2S; reproducibility was under 5% for repeated analyse. Residual Ag_2S were rinsed three times using Mili-Q water, centrifuged then the dried until complete dryness. The Ag_2S powders were homogenized prior to being analysed, then 450 µg was loaded into tin capsules with excess V_2O_5. The Ag_2S was analysed measuring $^{34}S/^{32}S$ ratio following online combustion with a Thermo Delta V Plus coupled with a Costech ECS 4010 Elemental Analyser at Washington University in St Louis. Pyrite sulfur composition are expressed in standard delta notation as per mil (‰) deviations from Vienna Canyon Diablo Troilite (VCDT) with an analytical error of <0.5‰.

Organic carbon analyses ($\delta^{13}C_{org}$ and TOC)

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

Acknowledgements

This work was supported by the "Laboratoire d'Excellence" LabexMER (ANR-10-LABX-19) and co-funded by a grant from the French government under the program "Investissements d'Avenir", and by a grant from the Regional Council of Brittany. The drilling operation was conducted within the European Commission Project PROMESS (contract EVR1-CT-2002-40024). Engineers of FUGRO-BV and the captain and crew of the Amige drilling vessel *Bavenit* are thanked for their dedication during the cruise. The European Promess shipboard party and colleagues at Ifremer are also thanked for previous contributions of data acquisition and processing. The authors warmly acknowledge C. Liorzou who kindly helped during the analytical preparation of samples, and O. Lebeau for assistance on the EA-IRMS in Brest.

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Figure Legends

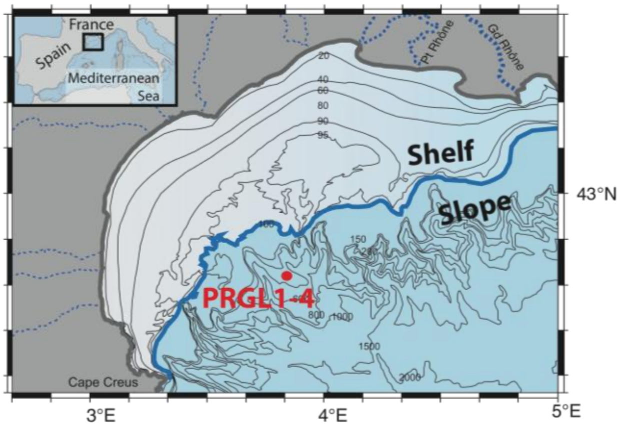

Figure 1: Map of the Gulf of Lion with the position of the PRGL1-4 core (42.690N; 3.838E). The bold grey line highlights the present shoreline position and the contours reflect modern water depths. The bold blue line corresponds to the shoreline position during the last-glacial period (low sea level).

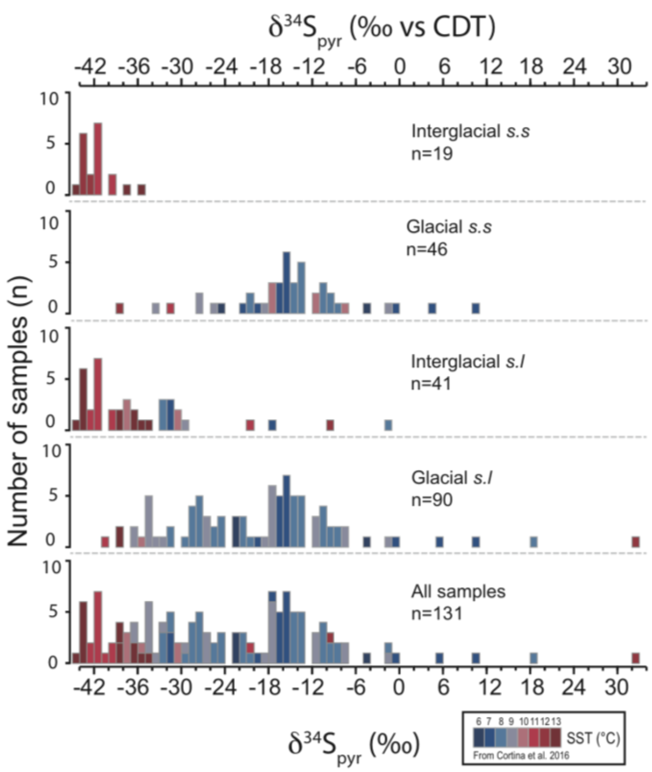

Figure 2: Histogram of pyrite $\delta^{34}S$ (this study) as a function of glacial/interglacial periods, color-

coded by temperature obtained from the relative composition of C_{37} unsaturated alkenones (18, 19). Sensu stricto (s.s.) refers to the warm substages of the interglacials and cold substages during glacials. The sensu latto (s.l.) includes all the data within interglacial or glacial periods.

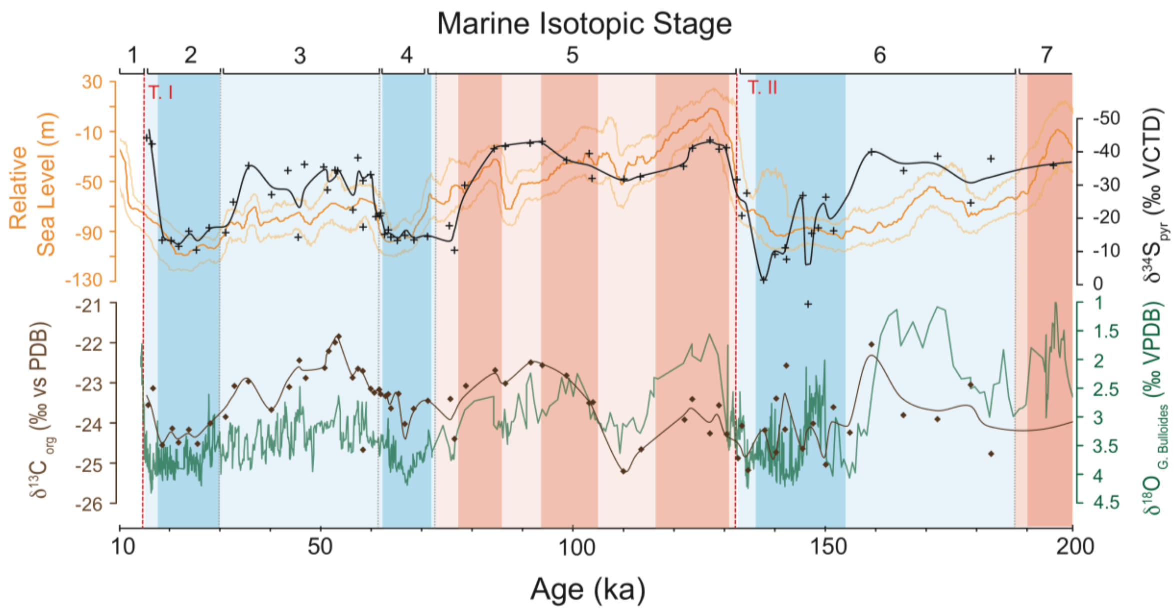

Figure 3: Glacial-interglacial geochemical records. $\delta^{34}S_{pyr}$ (black crosses; black line representing LOESS regression, this study), $\delta^{13}C_{org}$ (brown diamonds and brown line (LOESS regression), this study), reconstructed sea levels (orange) from the Red Sea, and $\delta^{18}O_{G.\ Bulloides}$ (green) for the last 6 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 vertical bands represent the glacial times with corresponding cold substages (i.e. *sensu-stricto*) in darker blue. Red bands correspond to interglacials periods with warm substages (i.e. *sensu-stricto*) highlighted in dark pink. Vertical pink dashed lines reflect glacial termination (T.) times according to ref. 44; vertical black dashed lines reflect scheme of marine stages according to ref. 45.

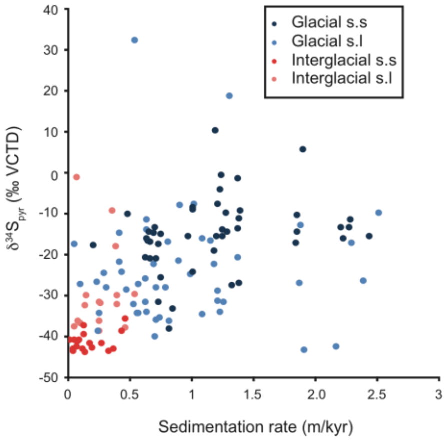

Figure 4: The relationship between sedimentation rate (m kyr^{-1}) and $\delta^{34}S_{pyr}$. Sedimentation rates are calculated using the linear relationship between depth in borehole and the update age model derived from ref. 17. Light / dark blues circles correspond to cold substages (i.e. respectively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