# Multiple S isotope ratios of glacial vs. interglacial pyrite: Insight into the controls on diagenetic signals in marine sediments

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S isotope ratios ($\delta^{34}S$) in sedimentary pyrite are used to constrain fluxes in the biogeochemical S cycle, seawater chemistry, the oxidation state of Earth's surface environment, and degradation pathways of organic matter in marine sediments. Stratigraphic variation in $\delta^{34}S$ values is typically interpreted to reflect changes in S cycling on a basinal or even global scale. Recently, it was shown that pyrites hosted in Pleistocene (<500ka) western Mediterranean sediments show pronounced $\delta^{34}S$ variation (up to 76‰) in phase with glacial-interglacial cycles. Hypotheses to explain this variation in S isotope ratios involve local changes in (i) fractionation of S isotopes during microbial sulfate reduction and/or (ii) the effects of sedimentological factors (e.g., sedimentation rate, grain size, porosity) on the openness of the sedimentary system. To discern between these two hypotheses, we measured multiple S isotope ratios ($\delta^{34}S$, $\Delta^{33}S$ and $\Delta^{36}S$) on the same pyrites. We find that interglacial sediments are characterized by positive and homogenous $\Delta^{33}S$ values, which are associated with strongly negative $\delta^{34}S$ values. Such a combination of values is consistent with the preservation of large microbial fractionation in an open system, where porewater sulfate readily exchanges with the overlying water column. During glacial stages we observe a decrease of $\Delta^{33}S$-anomalies accompanied with a $^{34}S$ enrichment. Using model calculations, we suggest that this results from a progressive distillation of porewater sulfate under pseudo-closed-system conditions. Furthermore, we suggest that the change in system openness between glacial and interglacial times is related to changes in sedimentation rate and grain size. These findings show an important role of the depositional environment on the isotopic characteristics transferred to the sedimentary rock record, which must be accounted for in the interpretation of bulk pyrite $\delta^{34}S$ records over Earth history.