Seawater sulfate cycling during the Late Palaeocene Thermal Maximum

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The novel carbonate-associated sulfate (CAS) technique was applied to ocean core samples from ODP Site 1051B (Northwest Atlantic) to generate a unique, high resolution palaeorecord of seawater SO₄ isotopes ($\delta^{34}S_{CAS}$ and $\delta^{18}O_{CAS}$) during the Late Palaeocene Thermal Maximum (LPTM). The aim of the study was to further understand the sulfur cycle within the context of a well-defined period of abrupt and significant global environmental change by examining variations in the isotopic compositions of sulfate-S and sulfate-O preserved as CAS in marine carbonates. Because both $\delta^{34}S$ and $\delta^{18}O$ in marine sulfate respond to different processes and on different timescales, the dual system was used to gain insights into events during the LPTM.

Extreme positive isotope anomalies in both $\delta^{34}S_{CAS}$ (+29%*o*) and $\delta^{18}O_{CAS}$ (+24%*o*) were coincident with the carbon isotope excursion (CIE) that typifies the LPTM, and resulted from incorporation of diagenetic celestite (SrSO₄) during sample preparation. This is an issue to be aware of in the construction of future high resolution CAS records. Overall, after extrapolating across the positive isotope anomaly, the results showed covariation between $\delta^{34}S_{CAS}$ and $\delta^{18}O_{CAS}$ with a significant and sharp decrease ($\delta^{34}S_{CAS}$, +21 to +16%*c*; $\delta^{18}O_{CAS}$, +17 to +15%*c*) initiated prior to the CIE and a smaller sharp increase ($\delta^{34}S_{CAS}$, +15 to +18%*c*; $\delta^{18}O_{CAS}$, +14 to +16%*c*) in the CIE recovery interval.

The specific events that drive these changes are unclear, but it is particularly significant that changes in the sulfur cycle occurred prior to the onset of the CIE, and may have been linked to its trigger mechanism. Possible candidates for this sudden change to lighter CAS isotopes are an increase in weathering and/or volcanic fluxes of sulfate to the oceans. The oceanic sulfate pool was probably much smaller at this time making it more responsive to changing input fluxes. The subsequent shift back to heavier values in the CIE recovery interval may represent a partial cessation of these increased fluxes. CAS isotopic changes also incorporate a component affected by cycling of sulfur in organic rich sediments driven by bacterial sulfate reduction and sulfide oxidation, but the contribution of this is difficult to assess.