Major Perturbation in Sulfur Cycling at the Triassic/Jurassic Boundary

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Supporting Online Material

Materials and Methods

The ratio of sulfur stable isotopes ($^{34}S/^{32}S$) was measured by elemental analyzer continuous-flow isotope-ratio mass spectrometry (EA-CF-IRMS) at the ISOLAB, University of Washington. Sulfur species in the samples underwent flash combustion in a Eurovector elemental analyzer and were thus converted to SO_2. Within the EA, SO_2 was separated by gas chromatography. A Thermo Finnigan Conflo III was then used to introduce the reference SO_2 and the sample SO_2 gas into a Thermo Finnigan MAT253 isotope-ratio mass spectrometer. Compared to other sulfur isotope mass spectrometry techniques (e.g. dual inlet), EA-CF-IRMS allows a much faster data output.

Finely grounded shale samples and sulfate and sulfide reference material ($BaSO_4$ internal laboratory standard and NIST-NBS127 and Ag_2S NIST-NZ1) were introduced in the EA packed in tin-foil cups. For each cup an amount of sample and standard corresponding to 50-100μg of S was weighed and V_2O_5 (from 1mg for light samples up to 10-20 mg for the heaviest samples) was added to each cup to aid combustion.

The elemental analyzer configuration used here was similar to that described by Fry *et al.* (2002) and Baublys *et al.* (2004). Samples were dropped in a quartz reaction tube and small volume of O_2 was injected to induce the flash combustion. The reaction tube was packed with 8-10 cm of sulfur-grade copper wires used to reduced S oxides to SO_2, framed by layers of quartz

chips and quartz wool (see Baublys *et al.*, 2004) and heated to 1050°C. A helium flow then flushed the sulfur dioxide through a second quartz tube heated to 890°C and packed with SiO_2 to buffer the oxygen isotopes in SO_2. Any water was removed by a magnesium perchlorate column and SO_2 was purified in a 80 cm sulfur GC Teflon column heated at 80°C.

The analytical precision (1σ) measured on replicates of our internal laboratory standard during each run was $\leq 0.2‰$. The average analytical precision (1σ) on sample duplicates was higher (0.6‰) which we attribute to sample heterogeneity.

To test the relative isotopic contribution of various sulfur species, sample fractions containing different sulfur species were isolated by chemical processing. The bulk fraction, with no chemical treatment, represents the sum of all possible S species within the samples: sulfide, sulfate, carbonate associated sulfate and organic-S. Carbonate-associated sulfates were removed from the HCl-washed fraction (2N hydrochloric acid, 36-72 hours at 60°C) leaving insoluble sulfates, sulfides and organic-S. A few samples were treated with NaClO (5.5%, 12-14h, 60ºC) and HNO3 (6N, 24-48h, 60ºC) in order to oxidize organic sulfur and sulfide and isolate a possible barite component. These samples showed barite sulfur levels below detection limits or too low (<0.03 wt.%) to significantly influence isotopic measurements. Insoluble sulfate contributions are thus ignored in the following discussion.

Mass Balance Calculation

Taking the value of 11 mM as the long term baseline for $[SO_4^{2-}]_{seawater}$ (*25*), a quantity of sulfate equivalent to a 10.8 mM concentration must be removed from the ocean to bring $[SO_4^{2-}]_{seawater}$ to 0.2 mM and cause isotopic fractionation during BSR to fall below 10‰. Given a modern mass of sulfate in the oceans of 3.79×10^{18} kg, a concentration of 28 mM, and a slightly larger ocean volume in the Jurassic (1.39 vs. 1.37×10^{9} km^3) (*30*), a 10.8 mM equivalent represents 1.48×10^{18} kg sulfate that must have been removed from the ocean to bring $[SO_4^{2-}]$

]$_{seawater}$ to 0.2 mM. The onset of the positive excursion occurs over the 2.7 m interval between 132.9 m and 135.7 m. If the entire 250 m of section represents 8 Myr (4 Myr Rhaetian, 3 Myr Hettangian, 1 Myr Sinemurian time) then 2.7 m represents 86.4 kyr. A flux of 1.71×10^{13} kg/yr would be necessary to remove the required quantity of sulfate in that amount of time.
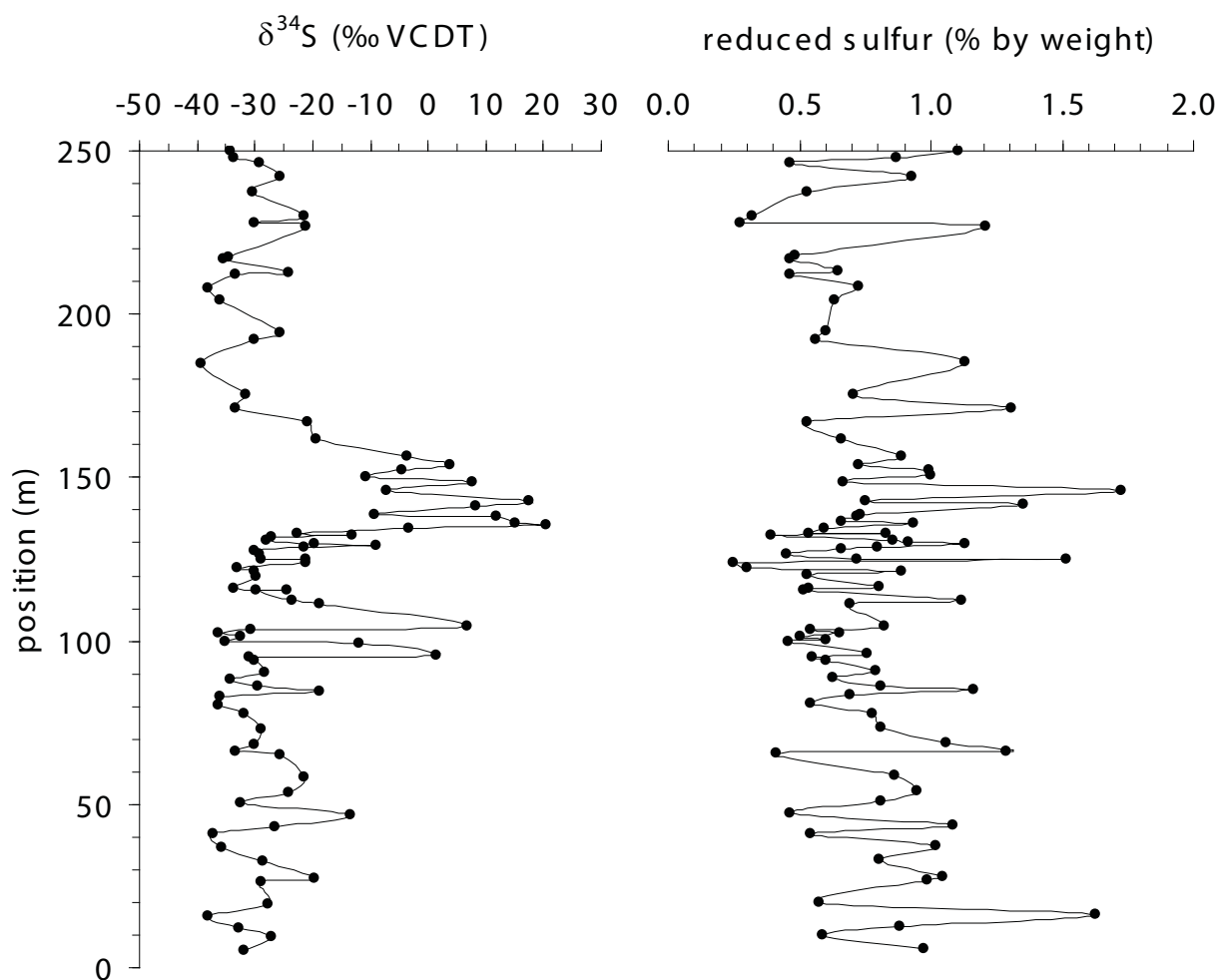

Figure DR1. δ^{34}S and weight percent reduced sulfur (total sulfide plus organic sulfur). The latter was determined after treatment with 10% HCl.
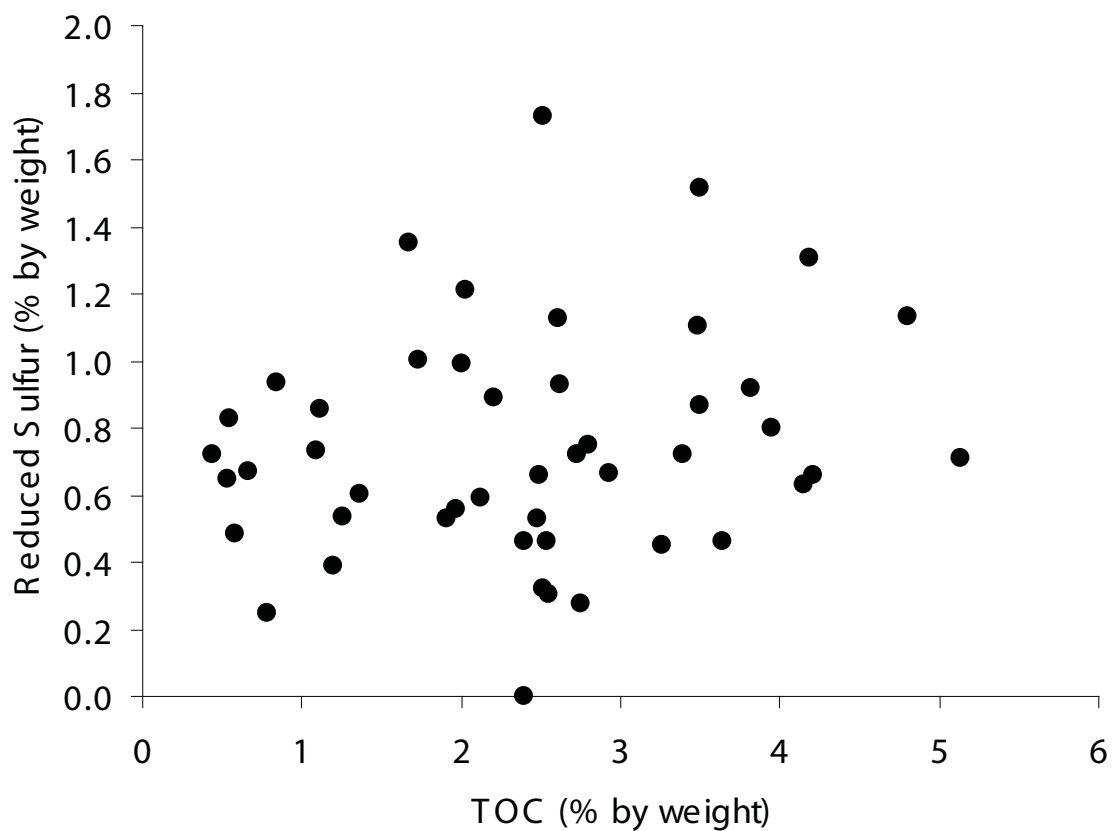
Figure DR2. Total Organic Carbon (TOC) by weight versus weight percent reduced sulfur (total sulfide plus organic sulfur). Both quantities were determined after treatment with 10% HCl.