GLOBAL SIGNIFICANCE OF $\delta^{34}S$ OF INORGANIC AND ORGANIC SULFUR PHASES ACROSS THE PERMIAN-TRIASSIC TRANSITION

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The ~251 Ma ago Permian/Triassic (P-Tr) extinction was the most severe of the Phanerozoic extinctions, with a disappearance of 95 % of marine species (e.g. Erwin et al., 2002) over a relatively short time interval (~60 ± 48 kyr; Burgess et al., 2014). Still, no consensus about the causes exists, with the most popular explanations including i) massive volcanic activity associated with the Siberian flood basalts; and ii) global anoxia and euxinia (e.g. Grice et al., 2005; Whiteside and Grice, 2016) during the formation of the supercontinent Pangea. Either of these processes could have been responsible for the profound impact on the global S-cycle shown by isotopic variations of inorganically bound S-phases (sulfate and pyrite; e.g. Kaiho et al., 2006; Gorjan et al., 2007). Here we complement the isotopic analysis of inorganic S with bulk organic S and, for the first time, organosulfur compounds in two Permian-Triassic boundary (PTB) sections from I) a carbonate dominated Global Stratotype Section and Point (GSSP) at Meishan-1 (South China) and II) a mud-rock sequence at Hovea-3 (Western Australia).

The Meishan-1 PTB section shows an isotopically distinct event horizon beginning at the top of bed 22 (~ 4 m below P-Tr extinction) and leading up to the top of bed 24 (just below the extinction and ~40 cm below PTB). In the event horizon total reduced inorganic sulfur (TRIS ≈ pyrite) shows a profound ^{34}S enrichment (from -30 to -13 ‰). Compound specific $\delta^{34}S$ analysis of dibenzothiophene (DBT) reveals a simultaneous ^{34}S depletion (from -17 to -24 ‰). Following the extinction (located in bed 25) $\delta^{34}S$ of TRIS and DBT return to near pre-event levels whereas kerogen S becomes depleted by 12 ‰. This novel data set suggests that DBT represents a sub-fraction of kerogen S that was isotopically sensitive to the changes in depositional setting (e.g. water column redox conditions etc.) during the extinction event, unlike the bulk kerogen which showed constant $\delta^{34}S$ values. An inverse relationship evident in the $\delta^{34}S$ profiles of TRIS and DBT suggests the disproportionation of a common reduced S source (HS_X^-). This isotopic excursion coincided with an increase in abundance of organic sulfur, reflected by decreasing TRIS/(TRIS+KerogenS) values, which likely favoured OM sulfurisation over pyritisation.

A more moderate ~ 4 ‰ ^{34}S depletion of TRIS and ~ 1.5 ‰ ^{34}S enrichment of DBT was measured across the relatively condensed PTB section suspected in Hovea-3. The direction and lower magnitude of the $\delta^{34}S$ variations was in contrast to the Meishan data, and may be due to higher abundances of kerogen S and moreso inorganic S deposited at this site. The contrasting $\delta^{34}S$ behaviour of the different S-phases across these 2 PTB sections implies a greater sensitivity to local basin conditions (e.g. water column redox conditions) or lithology than coincident global events such as volcanic activity (e.g. elevated influx of volcanic S species).

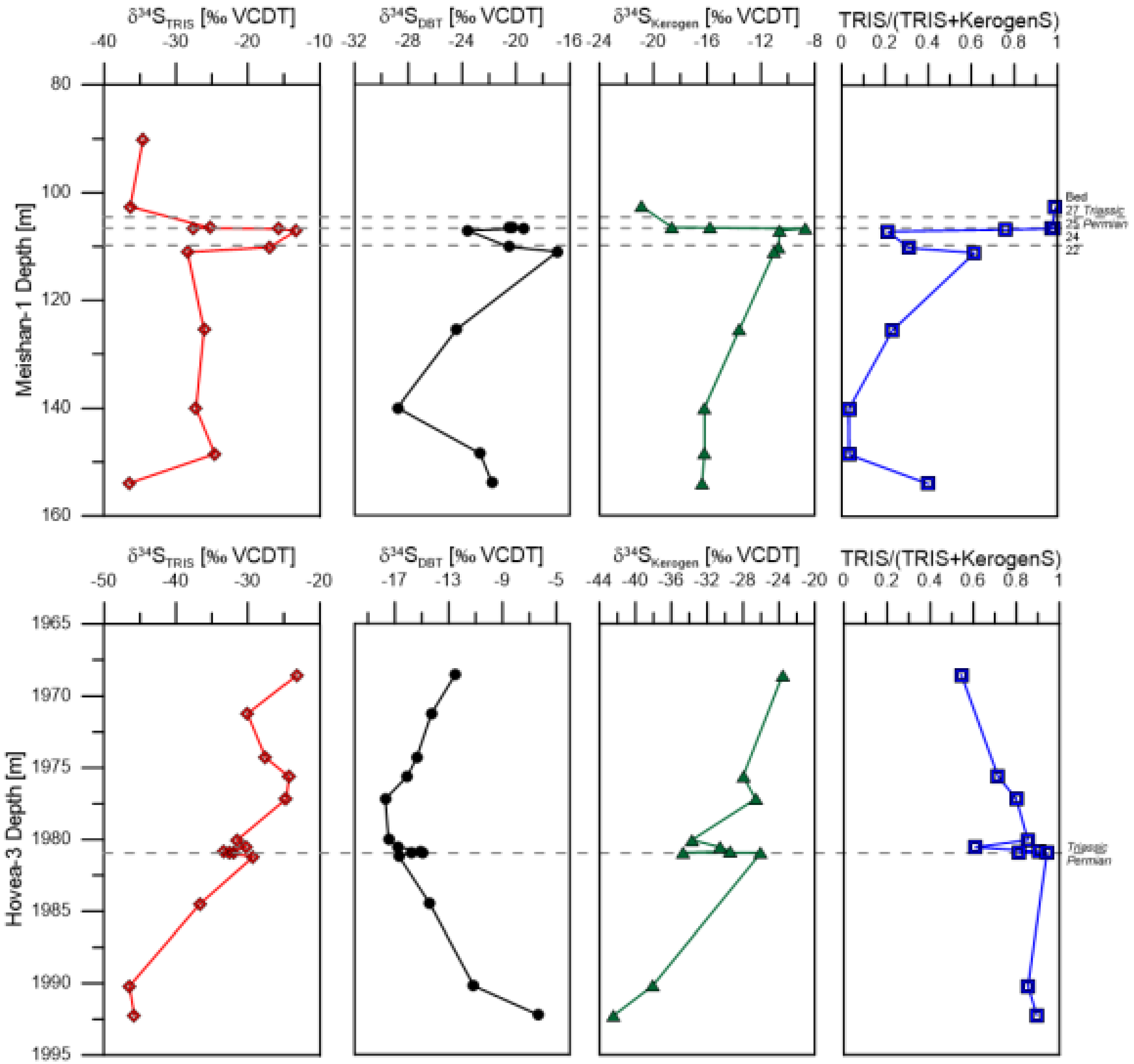

Figure 1 *δ34S profile of total reduced sulfur (TRIS, red), dibenzothiophene (DBT, black), and kerogen bound S (green) as well as fractional abundance of inorganic vs organic S (TRIS/(TRIS+KerogenS), blue) for PTB sections in Meishan-1 (top, extinction in bed 25, PTB in bed 27, implied as dashed lines) and Hovea-3 (bottom, PTB indicated as dashed line).*

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