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Volatile earliest Triassic sulfur cycle: A consequence of persistent low seawater sulfate concentrations and a high sulfur cycle turnover rate?

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ABSTRACT

Marine biodiversity decreases and ecosystem destruction during the end-Permian mass extinction (EPME) have been linked to widespread marine euxinic conditions. Changes in the biogeochemical sulfur cycle, microbial sulfate reduction (MSR), and marine dissolved sulfate concentrations during the Permian-Triassic transition can provide insights into the role of ocean chemistry change in the largest mass extinction in Earth history. In this study, we constrain marine dissolved sulfate concentrations using the MSR-trend method of Algeo et al. [Algeo, T.J., Luo, G.M., Song, H.Y., Lyons, T.W., Canfield, D.E., 2015. Reconstruction of secular variation in seawater sulfate concentrations. Biogeosciences 12, 2131–2151] on sulfur (S) isotope records from Iran (the Kuh-e-Ali Bashi and Zal sections) and Hungary (the Bálvány North and Bálvány East sections). This empirically derived transfer function is based on the S isotope fractionation between sulfate and sulfide associated with MSR in natural aquatic environments. This fractionation is proxied by the difference in S isotope compositions between chromium-reducible sulfur (CRS) and carbonate-associated sulfate (CAS), i.e., $\Delta^{34}S_{CAS\text{-}CRS}$. We show that, despite region-specific redox conditions, $\Delta^{34}S_{CAS\text{-}CRS}$ exhibits a nearly invariant value of 15–16‰ in both study sections. By comparing our record with a $\Delta^{34}S_{sulfate\text{-}sulfide}$ density distribution for modern marine sediments, we deduce that porewater Rayleigh distillation, carbonate diagenesis, and other effects are unlikely to have appreciably altered the S isotope offset between CRS and CAS in the study sections. In addition, differences in sedimentary regimes and organic carbon (OC) fluxes between the Iranian and Hungarian sections exclude major influence of the electron donor on MSR-S isotope fractionation and point to a more universal control, i.e., contemporaneous seawater sulfate concentration.

The MSR-trend transfer function yielded estimates of seawater sulfate of 0.6–2.8 mM for the latest Permian to earliest Triassic, suggesting a balanced oceanic S-cycle with equal S inputs and outputs and no major changes in sulfate concentrations during this interval. However, a secular trend toward heavier $\delta^{34}S_{CAS}$ (by >5‰) in the earliest Triassic can be explained only by increasing the turnover rate of the S-cycle (by ca. one order of magnitude) and a concomitant change in terrestrial S sources in a box model experiment. Exposure of evaporite deposits having a high $\delta^{34}S$ may account for the source change, with a possible role for the Siberian Traps volcanism by magmatic remobilization of Cambrian rock salt. A high sulfur cycle turnover rate would have left the ocean system vulnerable to development of widespread euxinic conditions, posing a sustained threat to marine life during the Early Triassic.

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1. Introduction

The reconstruction of ancient oceanic ion concentrations is critical to an understanding of the evolution of atmospheric oxygen levels (Berner and Canfield, 1989; Canfield et al., 2000), biogeochemical cycles (Strauss, 1999), and biomineralization evolutionary pathways (Stanley

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and Hardie, 1998). Perturbations of the marine dissolved inorganic carbon and sulfate pools have been linked to the end-Permian mass extinction and the subsequent delayed recovery of marine ecosystems during the Early Triassic (Holser et al., 1989; Newton et al., 2004; Payne et al., 2004; Song et al., 2014). These perturbed oceanic chemical reservoirs may be indicative of unusual environmental conditions triggered by, e.g., intense volcanism, water-column stagnation, and fluctuations in nutrient cycling and bioproductivity (Payne et al., 2004; Song et al., 2014).

Palaeo-seawater sulfate concentrations ($[SO_4]_{aq}$) have been the focus of a number of recent studies in an attempt to explain large temporal and spatial variation in carbonate-associated sulfate (CAS)-sulfur isotope records. In Permian-Triassic (P-Tr) successions, $\delta^{34}S_{CAS}$ values can exhibit pronounced bed-to-bed fluctuations and large differences between contemporaneous sections around the world (Luo et al., 2010; Song et al., 2014). Furthermore, concurrent secular variations in the isotopic composition of seawater DIC and sulfate pools, as evidenced by carbonate-C isotope and CAS-S isotope fluctuations, have been interpreted to reflect low $[SO_4]_{aq}$ (Luo et al., 2010; Song et al., 2014). Several methods have been applied in attempts to quantitatively reconstruct ancient $[SO_4]_{aq}$, including sulfate concentrations in fluid inclusions of evaporite deposits (Horita et al., 2002) and CAS concentrations in carbonates (Hurtgen et al., 2002). However, these proxies are hampered by insufficient stratigraphic coverage of evaporite deposits and the propensity of diagenetic alteration to reduce CAS concentrations (Lyons et al., 2004). Another method of reconstructing ancient $[SO_4]_{aq}$ is based on the maximum observed rate of secular variation in CAS-sulfur isotope records, ($\frac{d\delta^{34}S_{CAS}}{dt}$), which becomes more limited as $[SO_4]_{aq}$ increases (Kah et al., 2004; Song et al., 2014). However, this "rate method" depends on the development of contemporaneous imbalances in sulfate fluxes into and out of the global ocean and generally provides a maximum (rather than a mean) estimate of $[SO_4]_{aq}$ (Algeo et al., 2015).

The present study aims to reconstruct a robust and independently derived record of variation in $[SO_4]_{aq}$ for the latest Permian to earliest Triassic ocean through application of the empirically derived "microbial sulfate reduction (MSR)-trend method" of Algeo et al. (2015). The basis for this reconstruction is the S isotope fractionation associated with MSR which discriminates against the heavier isotope (^{34}S), depleting the product (H_2S) by ~50‰ relative to the source sulfate in modern marine environments (Rees, 1973; Canfield and Teske, 1996), but with both smaller and larger fractionations observed in some natural systems and laboratory experiments (Kaplan and Rittenberg, 1964; Sim et al., 2011). The origin of this isotope partitioning has been sought in internal cellular processes that regulate energy flows, with reduction first of adenosine 5′-phosphosulfate and then of sulfite by a suite of enzymes as the most important reactions (Fike et al., 2015). Based on these considerations, cell-specific sulfate reduction rates can be envisioned to modulate the magnitude of sulfur isotope fractionation, and a likely rate-limiting step is the supply of organic substrate (Leavitt et al., 2013). Chemostat experiments and porewater dissolved sulfate-S and -O isotope profiles can be explained by an inverse relation between the availability of the electron donor (organic substrate) and the magnitude of S isotope fractionation during MSR (Antler et al., 2013; Leavitt et al., 2013). However, similar observations in culture experiments have been made regarding a relation between sulfate concentration and the magnitude of MSR-S isotope fractionation (Habicht et al., 2002). Although, the exact cell internal mechanisms controlling isotope fractionation during MSR remain elusive (Fike et al., 2015), the pronounced correlation between dissolved sulfate concentrations and $\Delta^{34}S_{sulfate\text{-}sulfide}$ from a compendium of natural aquatic environments, as provided by Algeo et al. (2015), suggests an overarching control of dissolved sulfate levels on MSR isotope fractionation, at least, on the macro-scale.

In order to apply this MSR-trend method to the P-Tr sediment record, we used $\delta^{34}S$ data from cogenetic sedimentary sulfides (chromium-reducible sulfur—CRS) and sulfates (CAS) from two sites in NW Iran, Kuh-e-Ali Bashi and Zal, for which sedimentary sulfur isotope records were published by Schobben et al. (2015), and two sites in Hungary, Bálvány North and Bálvány East, for which we report new sedimentary sulfur isotope records. The Iranian succession was deposited in an open-marine setting in the middle of the Tethys Ocean, whereas the Hungarian succession represents an outer ramp facies. These two geographically and bathymetrically distinct localities were selected to investigate perturbations in P-Tr ocean chemistry. Differences in sedimentary environments and organic carbon fluxes between the study sites are important in demonstrating that a general control, i.e., contemporaneous seawater sulfate concentration, was the dominant influence on $\Delta^{34}S_{sulfate\text{-}sulfide}$.

To further enhance our understanding of influences on sulfur isotope fractionation between cogenetic sedimentary sulfates and sulfides, we compiled published S isotope data for sediments and porewaters covering a range of burial depths and from various natural environments. This approach, a frequentist inference, was then employed to determine the frequency with which sedimentary S isotope parameters (i.e., absolute isotope values and S isotope offset) could have appeared in P-Tr sediments. To minimize local, non-representative effects on $[SO_4]_{aq}$ estimates, we identified long-term first-order trends in both the CRS-S and CAS-S isotope records by means of statistical smoothing, and we diagnosed the potential effects of diagenetic overprinting on these proxy records. Our ultimate aim is an assessment of the influence of $[SO_4]_{aq}$ and S-cycling on the end-Permian mass extinction and subsequent Early Triassic recovery period.

2. Geological and stratigraphic setting

2.1. Northwestern Iran

The P-Tr boundary interval was sampled at two sites in NW Iran, at Kuh-e-Ali Bashi (38°94′00″ N, 45°52′00″E) and Zal (38°73′30″ N, 45°58′00″ E). These sites were located on the NW Iranian terrane, a part of the peri-equatorial Cimmerian microcontinent separating the Palaeotethys and Neotethys oceans, during the study interval (Fig. 1) (Muttoni et al., 2009). The *Paratirolites* Limestone Member, the youngest pre-EPME carbonate formation in NW Iran, is composed of red nodular limestone beds with thicknesses of ~20–30 cm that are separated by shaly intervals with thicknesses from a few mm to ~25 cm. This formation contains a pre-extinction fauna that is rich in ammonites and brachiopods, representing a deep-shelf setting (Ghaderi et al., 2014; Leda et al., 2014). It is conformably overlain by the clay-rich Aras Member (formerly "Boundary Clay") of the Elikah Formation (Ghaderi et al., 2014), the base of which corresponds to the EPME horizon (Kozur, 2007). These predominantly siliciclastic deposits, which contain some conspicuous ostracod-rich layers, have been interpreted as a

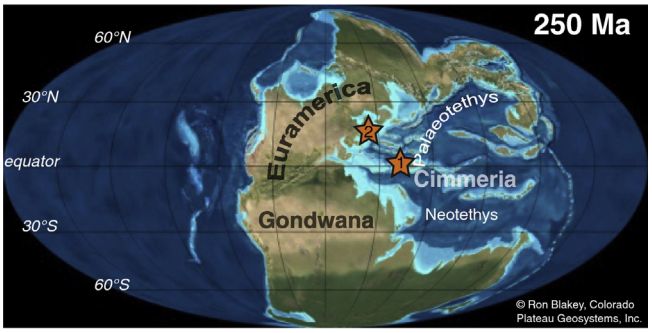

Fig. 1. Early Triassic global palaeogeography. The red stars depict the P-Tr study locales at Kuh-e-Ali Bashi and Zal in NW Iran (1), and at Bálvány North and Bálvány East in northern Hungary (2). Base map adapted from Colorado Plateau Geosystems website (http://jan.ucc.nau.edu/~rcb7/). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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