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Mo and U Isotope Evidence of Ocean Euxinia during the End-Permian Mass Extinction

Juan Carlos SILVA-TAMAYO[1,3], Stefan WEYER[2], Paul B. WIGNALL[3], Jonathan L. PAYNE[1], Robert J. NEWTON[3], Nadjia NEUBERT[2], Annika BRUESKE[2], Kimberly LAU[1] and Katharine MAHER[1]

1 Department of Geological and Environmental Sciences, Stanford University, USA
2 Institut fur Mineralogie, Leibniz Universitat Hannover, Germany
3 Department of Earth and Environment, University of Leeds, U.K.

The end-Permian mass extinction was the most severe biological crisis in Earth's history. Marine anoxia and photic zone euxinia have been proposed as kill mechanisms contributing to the mass extinction. However, the timing and extent of ocean anoxia before, during, and after the extinction interval remain poorly quantified.

Molybdenum and uranium isotope geochemistry and trace metal enrichment factors (EF=Element/Thorium PAAS) of marine sediments are promising tools to evaluate global oceanic oxygenation. Here we use the evolution of the Mo and U isotopic compositions and trace metal EF (Mo, U, Cr, V) of black shales and carbonates deposited along the Panthalassan, Paleotethys and Neotethys oceans to investigate the extend of ocean oxygenation during the Permian-Triassic transition.

Black shales deposited along the Panthalassan and Neotethys display increasing trace metal EF in the interval predating the onset of extinction. A marked decrease in the trace metal EF occurs at the main extinction level and persisted to the biostratigraphic Permian-Triassic boundary. An increase in the trace element EF occurs in the lowermost Triassic. Black shales below the extinction horizon display $\delta^{98/95}$Mo and $\delta^{238/235}$U values suggesting increasing basin euxinia under a well-oxygenated ocean. A global rapid shift towards negative $\delta^{98/95}$Mo and $\delta^{238/235}$U values coincides with the main extinction level. The coupled decreases in $\delta^{98/95}$Mo and $\delta^{238/235}$U values, together with the decrease in trace metal EF, suggests increased areas of euxinic sedimentation in the oceans during the extinction interval. The subsequent increase in $\delta^{98/95}$Mo and $\delta^{238/235}$U, along with increasing trace element EF in the analysed shales, suggests slightly more oxygenated conditions during earliest Triassic time. These data are consistent with enhanced anoxia and euxinia as contributing kill mechanisms.

Increased global temperatures during the late Permian would have, on the other hand, resulted on decreased latitudinal ocean temperature gradients and on increased delivery of freshwaters to the oceans along tropical and sub-tropical latitudes; thus reducing ocean circulation. Global warming would have also reduced the introduction of atmospheric oxygen through its direct exchange with high latitude cold ocean water. The combination of reduced oceanic circulation and reduced introduction of oxygen along high latitudes would have prevented the delivery of oxygen to the subtropical and tropical oceans. The enhanced delivery of freshwaters to the tropical and subtropical oceans would have also promoted enhanced supply of phosphate and other bioessencial trace metals to the global ocean. In fact the increase in phosphate availability in the oceans resulting in high productivity in the oxygenated shallow oceans has been proposed as a mechanism further promoting eutrophication and the decrease in oceanic oxygenation leading to extinction.

Under eutrophic conditions, increased shallow ocean productivity would have been further fertilized by the increased availability of bioessential trace metals. This scenario explains the increase in bioessential trace metals in both, carbonates and black shales before the extinction, and is consistent with increasing anoxia and euxinia during this interval. The sharp decrease in trace metals EF at the extinction level and predominantly low trace metal EF displayed by the carbonate record spanning the main extinction level and lowermost Triassic interval suggests low concentrations of trace metals in the oceans. Enhanced continental weathering and runoff of bioessential elements to the oceans would have continued during and after the interval postdating the extinction, due to high pCO_2 and global warm temperatures. The low carbonate trace metal EF during this interval suggests continued scavenging of bioessential trace metals in large areas of euxinic and anoxic sedimentation in the global oceans. As trace metals are essential for nitrogen fixation and photosynthesis, the low trace metal EF during the extinction level and the early Triassic support the hypothesis that enhanced anoxia/euxinia would have delayed the recovery of life in the global oceans. It also highlights the important role that the availability of bioessential trace metals in the ocean may have had on the recovery of life.

* Corresponding author. E-mail: cuore@stanford.edu