High resolution isotope and trace element ratios during the Triassic/Jurassic mass-extinction

Introduction, the T/J mass-extinction

The Triassic-Jurassic boundary event is widely known as a time period when one of the biggest first order (one of the "BigFive") mass extinctions of the history of life occurred (Raup & Sepkoski, 1982). This extinction event is coinciding with observed perturbations in many biogeochemical cycles and also with the main activity of the flood basalt volcanism of the Central Atlantic Magmatic Province (CAMP LIP) (Pálfy & Zajzon, 2012). Brachiopods were also affected by the end-Triassic mass extinction and a compositional turnover is observed in their communities (Tomašových & Siblík, 2007). The main geochemical hallmarks of the event are the characteristic carbon isotope excursions (CIE) in the uppermost Rhaetian followed by a main negative shift just below the Triassic-Jurassic boundary. This observation could be followed in every $\delta^{13}C$ records in several section globally (Hesselbo et al., 2002; van de Schootbrugge et al., 2008; Ruhl & Kürschner, 2011). Similar, but a more gentle isotope excursion was also observed in the Uppermost Rhaetian just before the "main" isotope anomalies preceding the mass extinction (Mette at al., 2012). The carbon isotope excursions are also connected to black shale deposition in several localities like in the Kössen Basin of the western Tethys, suggesting sever, anoxic conditions in the bottom seawater (Bonis & Kürschner, 2010). The negative $\delta^{13}C$ anomalies are suggesting the elevated amount of the light ^{12}C in the ocean-atmosphere system, possibly linked to volcanic degastion of isotopically light carbon by CO_2 due to the CAMP volcanism (Hesselbo et al., 2002; Ruhl et al., 2011). The elevated amount of CO_2 in the Earth-systems was leading to severe greenhouse conditions and also to ocean acidification as a result of undersaturated ocean respect to $CaCO_3$. The absence of coral reefs and other carbonate precipitating organisms at the extinction horizon and also reduction of their size and shell thickness are supporting this hypothesis (Berner & Beerling, 2007; Martindale et al., 2012).

What can the brachiopods tell us? Recent studies on their geochemical composition

Brachiopods are present during the whole Phanerozoic Era in the fossil record. Articulate brachiopods are secreting calcite shells with low and intermediate Mg content. This feature suggest a good resistance against post depositional chemical alternations (Brand et al., 2003). This ability against diagenesis and also they high abundance in the stratigraphic record makes them excellent carriers of the isotopic paleo-environmental signals of the ambient see water as archives (Parkinson et al., 2005). Based on recent examples several studies are showing that brachiopods are incorporating stable isotopes into their shells close to equilibrium with the ambient seawater (Brand et al., 2003; Yamamoto et al., 2010, 2013; Takayanagi et al., 2013; Brand et al., 2013). The shell structure of most articulate brachiopods are layered, usually it is composed of an outer primary layer and an inner, secondary layer with fibrous calcite crystals (Cusack et al., 2008), but in some cases they could have a tertiary layer as well. In case of most of the species only the secondary (and tertiary) layer is which is incorporating the stable isotope signals of the environment in equilibrium (Brand et al., 2015). Mg/Ca ratio is also a very useful paleo-environmental proxy which shows close relation to temperature and the salinity. Furthermore the observed fluctuation of the ratio of these two elements in long terms during the Phanerozoic could be connected to big tectonic movements like changes in the spreading rate of the ocean crust trough time (Ries, 2004). The temperature dependence of Mg/Ca ratio is also found in the carbonate material of brachiopod shells (Pérez-Huerta et al., 2008; Butler et al., 2015). Studies are also showing that the primary layer of the brachiopod shell is containing more Mg than the secondary layer and there are also some differences in the Mg/Ca ratio of the two layers. Furthermore high resolution transect analysis are suggesting seasonal changes in the Mg/Ca ratio which could reflect that brachiopods can be also a useful tool for estimating paleo-seasonality (Pérez-Huerta et al., 2008). Recent studies on clumped isotope composition of modern brachiopods are also suggesting that the brachiopod carbonate material could be also useful for clumped isotope paleo-thermometry (Henkes et al., 2013)

Summary: the need of brachiopod data from the T/J boundary

The T/J mass extinction is one of the biggest extinction event in the Phanerozoic and also connected to one of the most sever environmental change in the Mesozoic. That is why a precise and reliable data is obviously needed to better understand the Earth-system and its driver mechanisms and brachiopods could be a powerful tool for this. So far numerous studies were yielding isotope data from this spectacular time interval, but brachiopod data is still very rare. Only a few data is available now from the Late Triassic (Korte et al., 2005; Mette et al., 2012; Ullmann et al., 2014) and Veizer & Prokoph (2015) were collected the oxygen isotope data from the whole Phanerozoic which contains the data around the T/J boundary as well.

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