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Photic zone euxinia in the central Rhaetian Sea prior the Triassic-Jurassic boundary

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ABSTRACT

Shortly after the deposition of black shales in the Rhaetian Sea (Central European Basin, CEB), the Triassic/Jurassic (Tr/J) boundary witnessed one of the Big Five mass extinction events in Earth's history. Aiming at a better understanding of paleoenvironmental changes in the (geochemically) less well-known middle to late Rhaetian (German subdivision), we studied samples from a cored borehole from the central Rhaetian Sea in NW Germany (Hebelermeer 2). Biomarkers, palynomorphs and bulk geochemistry all support a marine/brackish setting with inputs from terrestrial plants. Dinosteranes were found throughout the core, most likely suggesting the spread of dinoflagellates. It is widely accepted that volcanic exhalations during the development of the Central Atlantic Magmatic Province (CAMP) had a major impact on marine and terrestrial environments in the earliest Jurassic e.g., the development of photic zone euxinia and H_2S poisoning of benthic life. There is evidence from the studied core, however, that comparable conditions already thrived in the central Rhaetian Sea during the middle Rhaetian. A first indication of euxinia/anoxia is evident from low to very low total organic carbon versus total sulfur (TOC/TS) ratios (~<1) with a minimum preceding the Tr/J boundary (0.03). The latter very low value hints at a decoupling of S and C cycles and eventually abiogenic pyrite formation. Water-column anoxia during the middle Rhaetian is indicated by the occurrence of the biomarker gammacerane, which records ciliates living at the O_2-H_2S chemocline. The strongest support for a stratified water column even with photic zone euxinia comes from high abundances of isorenieratane. This biomarker is a pigment of anoxygenic phototrophic green sulfur bacteria, which use H_2S for photosynthesis. Our data point to perturbations in the biogeochemical cycles of sulfur and carbon already in the middle Rhaetian, which are possibly linked to early volcanic activities and SO_2, H_2S, and CO_2 eruptions.
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1. Introduction

The Triassic-Jurassic (Tr/J) boundary marks one of the most important mass extinction events in the Phanerozoic (Hesselbo et al., 2002; Hesselbo et al., 2004; Jaraula et al., 2013; Kasprak et al., 2015; Raup and Sepkoski, 1982; Williford et al., 2014). It is linked to the development of extensive and large igneous provinces (i.e. Central Atlantic Magmatic Province; CAMP; Marzoli et al., 1999) in the context of the breakup of the super-continent Pangaea. A similar scenario can be envisaged for the Permian/Triassic boundary extinction (Siberian Trap volcanism; Renne et al., 1995). Mechanisms such as massive CO_2, SO_2, and thermogenic methane emissions with subsequent perturbations in the carbon and sulfur cycles were crucial for mass extinctions in the marine and terrestrial realms (for the Tr/J boundary see Beerling and Berner (2002); Hesselbo et al. (2002); Richoz et al. (2012)). Ocean acidification, eutrophication of the seas due to increased continental weathering and phosphate and iron run-off, resulting in anoxia and photic zone euxinia, are believed to have played a major role during both extinction events (see for review van de Schootbrugge and Wignall, 2015). In case of the Tr/J boundary, the major event is recorded as a globally occurring, negative carbon isotope excursion (initial-CIE) in, e.g., sedimentary organic carbon (Hesselbo et al., 2002), alkanes of terrestrial plants (Williford et al., 2014) and fossil leaf (Ruhl and Kürschner, 2011). The exact timing of the onset of magmatic activities, biogeochemical changes, and mass extinction, however, is still a matter of discussion. Based on $^{187}Os/^{188}Os$ data, Kuroda et al. (2010) suggested early Rhaetian volcanism, and also Ruhl and Kürschner (2011) proposed from stable carbon isotope data a Rhaetian age for the initial CAMP activities. This data is in accordance with a marked drop of biodiversity already during the Rhaetian (Kiessling et al., 2007; McElwain et al., 2007). Early Rhaetian magmatic activities are proposed to be expressed by a "precursor-CIE" (Ruhl and Kürschner, 2011).

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One of the key arguments for the linkage of H_2S poisoning and the Tr/J marine mass extinction – comparable to a possible Permian/Triassic kill mechanism (Wignall and Hallam, 1992; Grice et al., 2005; Kump et al., 2005; Meyer et al., 2008) – comes from the occurrence of isorenieratane in earliest Jurassic sediments of the Rhaetian Sea (Richoz et al., 2012; Whiteside and Grice, 2016). This biomarker is produced by anoxygenic phototrophic green-sulfur bacteria, which require a hydrogen sulfide (H_2S) environment in the photic zone. This environmental situation is termed photic zone euxinia. Jaraula et al. (2013) observed isorenieratane in a sedimentary succession from the southern United Kingdom (St. Audrie's Bay), and as isorenieratane was also found in samples deposited slightly before the Tr/J boundary, it was postulated that episodic photic zone euxinia could have occurred temporarily before the onset of the Jurassic. However, the general conclusion of the study was that photic zone euxinia is directly linked to CAMP, the initial CIE, and the Tr/J boundary (Jaraula et al., 2013). Following the interpretation above it has to be considered though that: the studied sections neither record the (i) situation in the central Rhaetian Sea (Fig. 1; e.g. proximal position of core Mariental 1; Richoz et al., 2012) nor (ii) did samples of (middle) Rhaetian age receive much attention (e.g. core Rosswinkel FR 204-201; Richoz et al., 2012). This time interval, however, is crucial in understanding late Triassic changes (Kiessling et al., 2007).

To bridge this gap, we studied an interval of a core from the central Rhaetian Sea (Fig. 1; Hebelermeer 2 site). This sequence includes black shales with high contents of total organic carbon (TOC) as well as laminated shales/silt stones, which are generally indicative of a low energy system and the deposition below storm wave base. Our work focused on the interval covering the Middle Rhaetian to the Lower Jurassic. We used bulk carbon and sulfur geochemistry, palynomorphs, and extractable hydrocarbon biomarkers to reconstruct palaeoenvironmental changes in the Rhaetian Sea.

2. Regional geology and paleogeography

The working area is located in an intracontinental depositional setting, which traditionally has been referred to as the Germanic Basin of the Triassic period. In recent literature, this well-established term has progressively been abandoned in favor of Southern Permian Basin (e.g. van Wees et al., 2000) or Central European Basin, CEB (e.g. Fischer et al., 2012), a term applicable for the Permian to Jurassic depositional area within central Europe. In this study, we follow the term CEB, and we use the name Rhaetian Sea for the western part of the CEB, which was presumably permanently flooded during the terminal Triassic. Conditions were most likely brackish in its central parts, and clastic input was shed from the Bohemian and Fennoscandian Highs (Fischer et al., 2012; Fig. 1). In the central parts, laminated shales were periodically deposited, while in the eastern part of the sea deltaic successions occurred. Repeated marine ingressions came from the SW through the Burgundy Alemannic Gateway and from the NW (Fischer et al., 2012). During the late Triassic (middle Keuper), the CEB was affected by synsedimentary extensional tectonism resulting in an uplift of salt structures, which locally were truncated by Lower Jurassic strata (Maystrenko et al., 2013, with further references).

The Hebelermeer 2 core presented herein was retrieved from the central part of the former Rhaetian Sea (Fig. 1; Fischer et al., 2012). Bio- and lithostratigraphic subdivisions of the core are based on detailed micro- and macrofossil studies as well as on lithologic characters of the

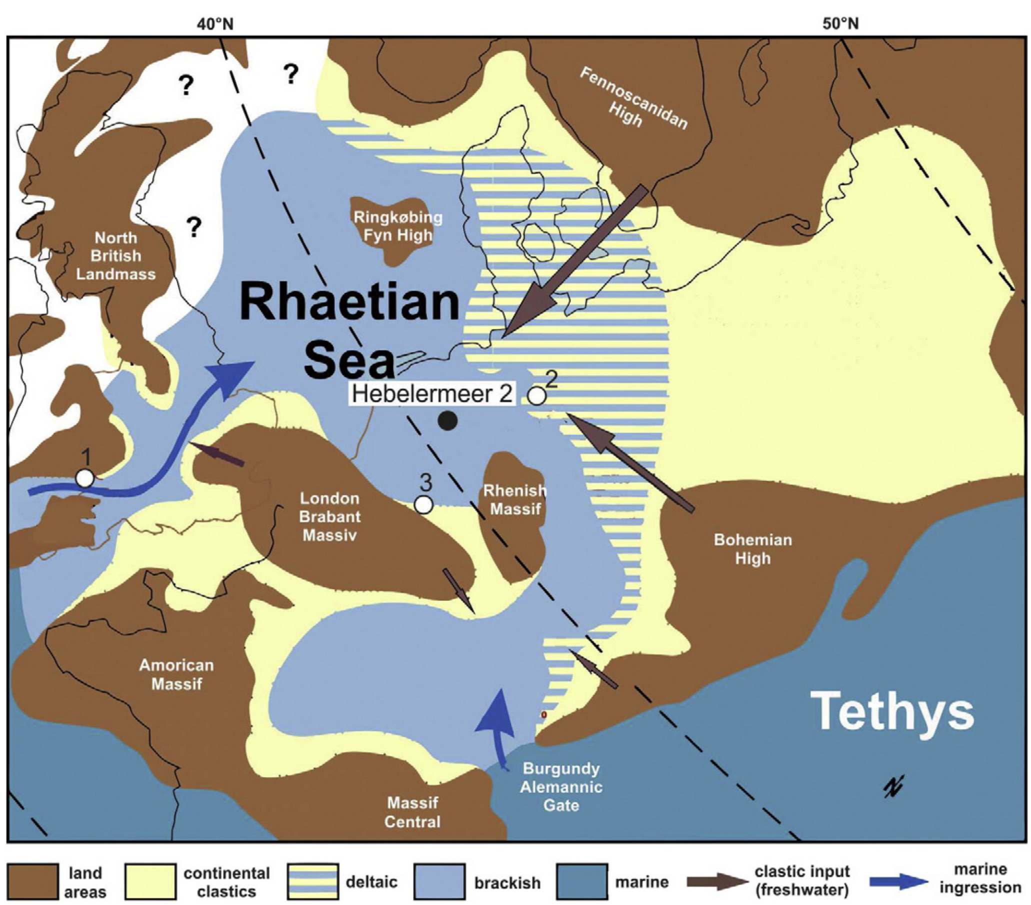

Fig. 1. Hebelermeer 2 drillcore site near Meppen in northern Germany and the paleogeographic situation during the middle Rhaetian. 1 = position of the St. Audrie's sequence in S UK (Hesselbo et al., 2004); 2 = Mariental 1 in northern Germany (van de Schootbrugge et al., 2009; Heunisch et al., 2010); 3 = Rosswinkel in Luxemburg (Richoz et al., 2012). The paleogeographic map including the paleolatitudes was modified after Fischer et al. (2012) and references therein.

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