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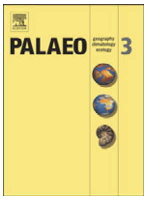

Tracking the redox history and nitrogen cycle in the pelagic Panthalassic deep ocean in the Middle Triassic to Early Jurassic: Insights from redox-sensitive elements and nitrogen isotopes

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ABSTRACT

In order to clarify the redox history of the central Panthalassic Ocean in the Middle Triassic (Anisian) to Early Jurassic (Toarcian), we determined the abundances of major, trace and rare earth elements, and organic carbon and total nitrogen isotopes from well-exposed shales interbedded with deep-sea cherts from Inuyama, southwest Japan. A distinct positive Ce anomaly accompanying high Mn and weak Mo enrichments was detected in the transitional sequence across the Tr–J boundary, which indicates deposition under a more oxic condition than at any other period in the study section. The oxic period lasted for 130–170 kyr, and coincided with a faunal turnover at the end of the Triassic. On the other hand, strong enrichments of U, V, Mo, TOC and TN in Anisian and Toarcian black shales suggest deep ocean anoxia in both intervals. Highly concentrated Mo contents in some black shales indicate euxinia in the pelagic Panthalassic deep ocean. $\delta^{15}N_{TN}$ values are low, down to −2.0 ‰, in such black shales enriched in redox-sensitive elements, compared with other shales. This low $\delta^{15}N_{TN}$ values during recurrent oceanic euxinic events in the Anisian may indicate strong assimilation of ammonium, but the possibility of enhanced nitrogen fixation cannot be ruled out especially for the Toarcian anoxic event. This work provides the first documentation of the long-term redox history in the pelagic Panthalassic deep ocean, from the Middle Triassic to the Early Jurassic, based on redox-sensitive elements in shales, and it reveals probable links between oceanic redox changes and biological activity.

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1. Introduction

The interval from the Middle Triassic to the Early Jurassic coincided with the time of onset of the main breakup of Pangea, the opening of Tethys Ocean, and the shrinkage of their counterpart, the Panthalassic Ocean. This interval was also a period of global-biotic changes, such as the mass extinction at the Triassic–Jurassic (Tr–J) boundary, and the Toarcian Oceanic Anoxic Event (T-OAE) (e.g., Jenkyns, 1988, 2010; Alroy, 2010). These events were likely linked to major redox changes in the Tethys (McArthur et al., 2008; Pearce et al., 2008; Quan et al., 2008; Bonis et al., 2010; Pálfy and Zajzon, 2012; Richoz et al., 2012; Jaraula et al., 2013; French et al., 2014; Kemp and Izumi, 2014; Kasprak et al., 2015) and Panthalassic Oceans (Hori, 1993; Hori et al., 2007). In addition to sea level changes (e.g., Hallam and Wignall, 1999), anomalous events occurred in both marine and terrestrial environments, such as global-scale intense volcanism and bolide impacts within less than a few million years (Cohen et al., 1999; Cohen and Coe, 2002, 2007; Olsen et al., 2002a, 2002b; Cohen et al., 2004; Tanner and Kyte, 2005; Tanner et al., 2008; Kuroda et al., 2010). The evidence for widespread anoxia in Middle Triassic and Early Jurassic shelf sedimentary rocks has been independently confirmed by multi-geochemical proxies and lithological changes (e.g., Jenkyns, 1988; Quan et al., 2008; Bonis et al., 2010; Mazzini et al., 2010; Izumi et al., 2012; Pálfy and Zajzon, 2012; Song et al., 2012; Richoz et al., 2012; Jaraula et al., 2013; French et al., 2014; Kemp and Izumi, 2014; Kasprak et al., 2015).

The redox condition of seawater is generally classified on the basis of the concentrations of dissolved oxygen and hydrogen sulfide as follows: oxic (>2.0 mL O_2 L^{-1}), dysoxic or suboxic (0.2–2.0 mL O_2 L^{-1}), anoxic-nonsulfidic (<0.2 mL O_2 L^{-1}, 0 mL H_2S L^{-1}), and anoxic-sulfidic or euxinic (nearly 0 mL O_2 L^{-1}, >0 mL H_2S L^{-1}) (Tyson and Pearson, 1991). A quantitative documentation of paleo-redox history

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is paramount for an improved understanding of the conditions of sedimentation in the pelagic Panthalassic Ocean, and of the associated biotic changes in the Middle Triassic to Early Jurassic.

Deep-sea bedded cherts in the Mino-Tanba belt in southwestern Japan provide key information about the pelagic oceanic sedimentation from the Middle Triassic to Early Jurassic (Fig. 1A; e.g., Isozaki et al., 1990; Matsuda and Isozaki, 1991). The chert beds are mostly red due to the presence of hematite, which is indicative of well-oxygenated depositional conditions. In contrast, the intercalated dark gray radiolarian cherts provide evidence for the anoxic events in the pelagic Panthalassic Ocean (Hori, 1993). Many previous studies have reported redox proxies in deep-sea sediments in Japan, such as sulfur isotope ratios (Kajiwara et al., 1994; Takahashi et al., 2013, 2015), trace element concentrations and/or rare earth element (REE) abundance patterns (Ishiga et al., 1996; Kato et al., 2002; Hori et al., 2007; Algeo et al., 2011; Takahashi et al., 2014, 2015), the size of framboidal pyrite grains (Algeo et al., 2010; Wignall et al., 2010; Takahashi et al., 2015), and variations in iron-bearing mineral species (Nakao and Isozaki, 1994; Kubo et al., 1996; Matsuo et al., 2003; Sato et al., 2012). These studies, except for Wignall et al. (2010), focused on particular sequences around the Permian–Triassic (P–T) or Tr–J boundaries. Wignall et al. (2010) presented a redox history of the Panthalassic Ocean from the Permian to Jurassic on the basis of pyrite framboid size analysis, and suggested there were three phases of euxinia during this period. However, their redox estimation method depends on the occurrence of pyrite, and its application is limited to pyrite-bearing beds. Therefore, the long-term redox history in the pelagic Panthalassic Ocean from the Middle Triassic to Early Jurassic is still unclear, because of limited redox indices.

Redox-sensitive element concentrations in sediments are well correlated with the above-mentioned redox classification, and have long been used as paleo-redox proxies (Brumsack, 1980, 2006; Wignall and Myers, 1988; Dean et al., 1999; Algeo and Maynard, 2004; Tribovillard et al., 2006). In this work, we focus on shales interbedded with deep-sea cherts because the shales have a greater potential than the cherts for preserving enrichments of redox-sensitive elements due to their low depositional rate, as shown by Hori et al. (2000). In order to establish a precise stratigraphic column, we made a new detailed geological map of the bedded cherts, mudstones and sandstones along the Kiso River together with the minor folds in bedded cherts using high-resolution color aerial photos taken with an unmanned aerial vehicle (UAV) (Figs. 2 and 3). On the basis of the redox-sensitive element concentrations obtained from shales, we reconstruct the redox history of the pelagic Panthalassic deep ocean from the Middle Triassic to Early Jurassic. Moreover, we have determined the isotopic compositions of total nitrogen and organic carbon in the shales, the first of which has not been reported before. The aim of this paper is to decipher the secular changes in oceanic redox conditions on a global scale and their influence on biological activity at that time.

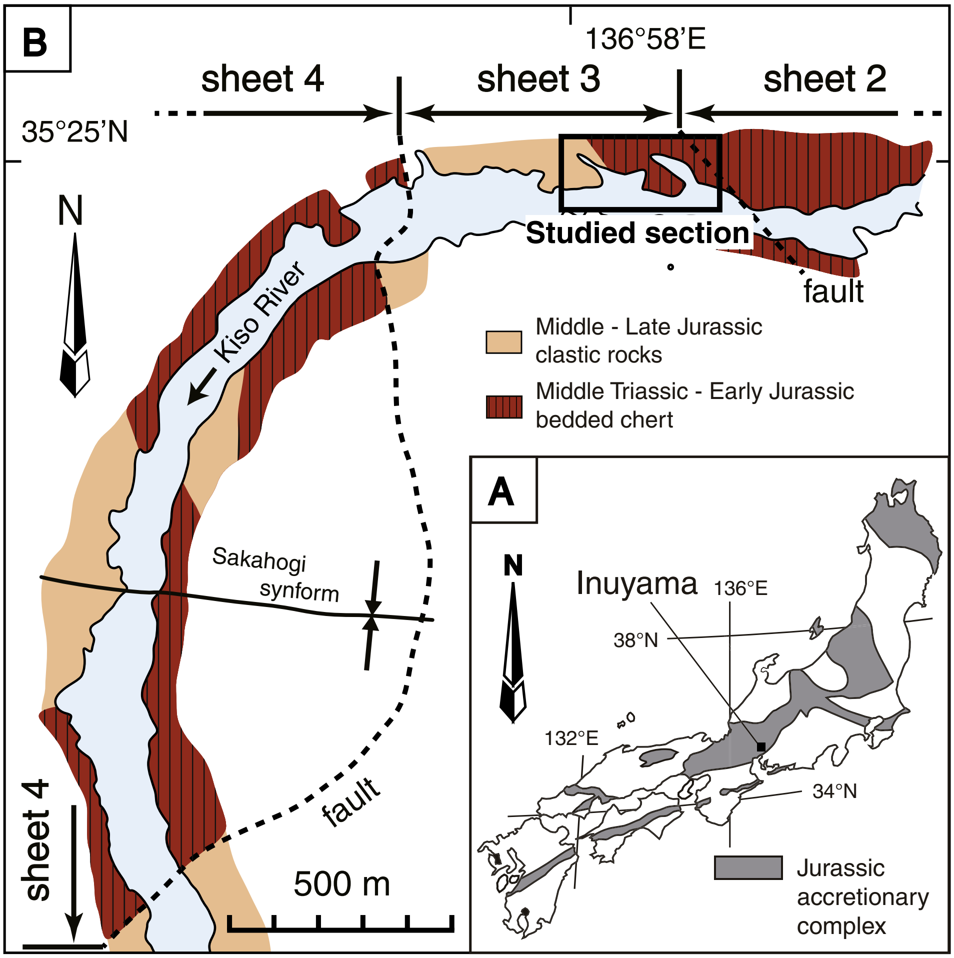

Fig. 1. (A) Simplified geological map of the Japanese Islands and the location of the Inuyama area. The shaded areas represent Jurassic accretionary complexes. (B) Geological map of the Inuyama area in the Mino-Tanba belt, showing imbricated coherent-type units of Jurassic accretionary complexes (modified from Matsuda and Isozaki (1991) and Kimura and Hori (1993)). White areas represent post-Jurassic cover sediments. Note the tectonic repetition of the same stratigraphic sequences of Middle Triassic to Early Jurassic bedded cherts and Middle to Late Jurassic clastic sediments. Six units (the sheets 1–6) are repeated by bedding-parallel faults, and our studied section geologically corresponds to the sheets 2 and 3.

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