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^{57}Fe Mössbauer analysis of the Upper Triassic-Lower Jurassic deep-sea chert: Paleo-redox history across the Triassic-Jurassic boundary and the Toarcian oceanic anoxic event

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Abstract We investigated the paleo-redox change across the Triassic-Jurassic (T-J) boundary (~200 Ma) and the Early Toarcian oceanic anoxic event (T-OAE; ~183 Ma) recorded in the Upper Triassic to Lower Jurassic pelagic deep-sea cherts in the Inuyama area, Central Japan. The present ^{57}Fe Mössbauer spectroscopic analysis for these cherts identified five iron species, i.e., hematite (α-Fe_2O_3), pyrite (FeS_2), paramagnetic Fe^{3+}, and two paramagnetic Fe^{2+} with different quadrupole splittings. The occurrence of hematite and pyrite in deep-sea cherts essentially indicates primary oxidizing and reducing depositional conditions, respectively. The results confirmed that oxidizing conditions persisted in deep-sea across the T-J boundary. In contrast, across the T-OAE, deep-sea environment shifted to reducing conditions. The first appearance of the gray pyrite-bearing chert marked the onset of the deep-sea oxygen-depletion in the middle Pliensbachian, i.e., clearly before the shallow-sea T-OAE.

Keywords Mössbauer spectroscopy · Iron · Deep-sea chert · Redox · Toarcian

1 Introduction

Pelagic deep-sea cherts in ancient accretionary complexes are useful to reconstruct oceanic paleo-environments, because pre-Jurassic deep-sea floors have been lost from the Earth's surface by the oceanic subduction. Accessory iron-bearing minerals in deep-sea cherts, such as hematite and pyrite, have been used as redox indicators

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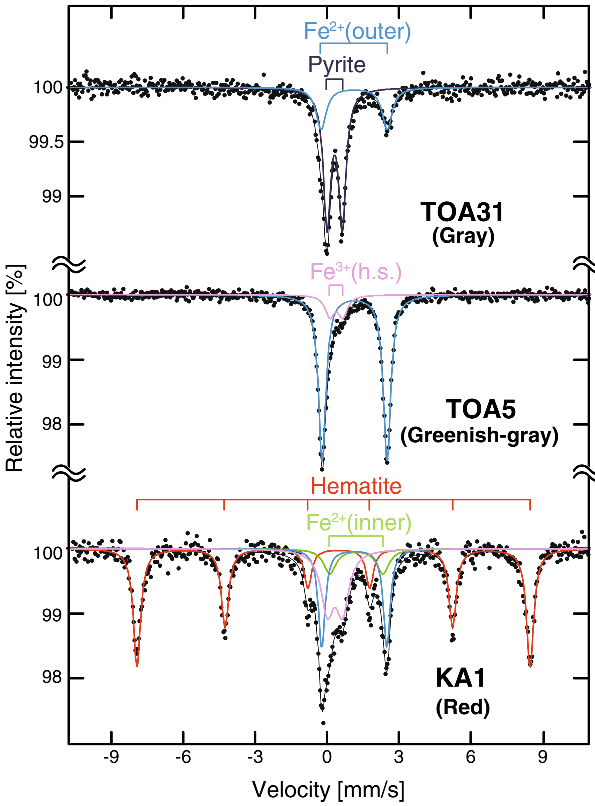

Fig. 1 Mössbauer spectra of the analyzed cherts at Katsuyama, Central Japan. KA1, TOA5, and TOA31 are representative of *red*, *greenish-gray*, and *gray* cherts, respectively

for ancient deep-sea environments, as in the case of the Permian-Triassic boundary Superanoxia [1, 2]. In order to analyze paleo-redox history across the Triassic-Jurassic (T-J) boundary (∼200 Ma) and the Early Toarcian Oceanic Anoxic Event (T-OAE; ∼183 Ma), this study examined the Mössbauer spectra of the Upper Triassic to Lower Jurassic deep-sea cherts in the Inuyama area, Central Japan.

2 Sample and method

The Upper Triassic to Lower Jurassic pelagic deep-sea cherts at the Katsuyama section in Inuyama record the Triassic-Jurassic boundary and the T-OAE intervals [3–5]. The T-J boundary lies in the red cherts, whereas the T-OAE interval lies in organic-rich black cherts above the grayish cherts. Chert samples were prepared following the same procedure as previous studies [2, 6]. Mössbauer spectra were measured with an Austin Science S-600 Mössbauer spectrometer using a 1.11 GBq $^{57}Co/Rh$ source at room temperature (293 K). Mössbauer spectra were fitted by a least-square method with restrictions of intensity and half width of peaks. All doublets were treated as symmetric. Peak positions of pyrite were constrained as in previous studies [2, 6]. The presence of pyrite crystals was also checked under the microscope.

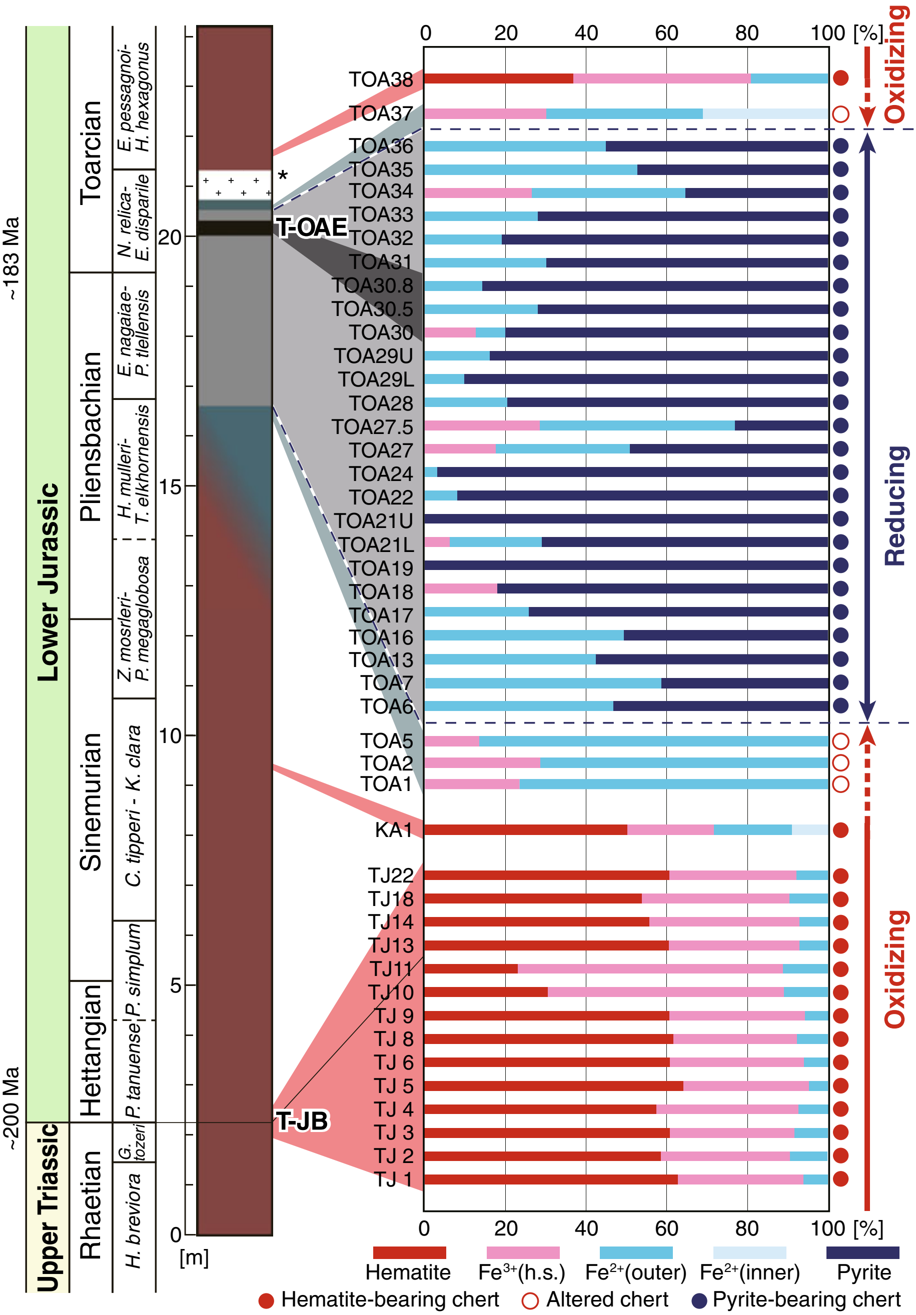

Fig. 2 Stratigraphic column showing the color and the iron-species composition of the Upper Triassic to Lower Jurassic pelagic deep-sea cherts at Katsuyama, Central Japan. * shows white massive chert. Radiolarian assemblage-zones are from [4, 5]

3 Results and discussion

The Mössbauer analysis for 45 chert samples identified five iron species from the analyzed deep-sea cherts (Fig. 1); hematite (α-Fe_2O_3), pyrite (FeS_2), paramagnetic Fe^{3+}(high spin; h.s.), and two types of paramagnetic Fe^{2+}(h.s.), i.e., Fe^{2+}(outer) with larger quadrupole splitting (QS) and Fe^{2+}(inner) with smaller QS. Red cherts contain hematite, Fe^{3+}(h.s.), Fe^{2+}(outer), and occasionally Fe^{2+}(inner), suggesting their primary deposition in oxidizing conditions. The grayish colored cherts are classified into two groups; i.e. ones with pyrite, Fe^{2+}(outer), and occasionally Fe^{3+}(h.s.), and the others mainly with Fe^{2+}(outer) and some Fe^{3+}(h.s.) without pyrite. The former group with framboidal pyrites was likely deposited primarily under reducing conditions, whereas the latter group without pyrite was likely altered from primary hematite-bearing red cherts [6]. Fe^{3+}(h.s.) and Fe^{2+}(outer) are likely included in clay minerals such as illite or chlorite. Fe^{2+}(inner) may be contained in siderite ($FeCO_3$)-like amorphous mineral that is derived from hematite by the post-depositional alteration.

4 Paleo-redox history

Figure 2 shows the secular change of paleo-redox in the studied Upper Triassic to Lower Jurassic deep-sea cherts. As for the T-J boundary, consistent occurrence of the red hematite-bearing cherts (TJ1–22) suggests that the deep-sea environment remained in oxidizing condition across the T-J boundary. In contrast, the mid-Pliensbachian to Toarcian interval (~4 m thick) consists of the framboidal pyrite-bearing gray cherts (TOA6–36), suggesting their deposition under reducing conditions. In addition, organic-rich black cherts (TOA30–30.8) corresponding to the shallow-sea T-OAE occur in the middle of this interval. The greenish-gray cherts (TOA1–5, 37), immediately below and above the reducing interval, contain mainly Fe^{2+}(outer) without pyrite nor hematite. They represent altered parts from the primary hematite-bearing cherts, in accordance with a recent study [6]. The onset of the reducing condition in deep-sea is marked by the first appearance of the gray pyrite-bearing chert (TOA6), lying ~3.5 m below the T-OAE black cherts (TOA30–30.8), at the *Hsuum mulleri-Trillus elkhornensis* (Radiolaria) Zone [4, 5], i.e. in the Lower Pliensbachian. This indicates that the deep-sea environment changed from oxidizing to reducing clearly before the shallow-sea T-OAE, and persisted in the reducing condition much longer than the shallow-sea environment.

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