Global and Planetary Change 69 (2009) 79–81

Contents lists available at ScienceDirect

Global and Planetary Change

journal homepage: www.elsevier.com/locate/gloplacha

Discussion

Comment on “Evaluation of palaeo-oxygenation of the ocean bottom cross the Permian–Triassic boundary” by Kakuwa (2008): Was the Late Permian deep-superocean really oxic?

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ARTICLE INFO

Article history:
Received 24 December 2008
Accepted 30 January 2009
Available online 15 February 2009

Keywords:
Permian-Triassic boundary
superanoxia
rare earth element (REE)
Ce anomaly
paleo-redox
deep-sea chert

ABSTRACT

Nearly 15 years after the proposal of the superanoxia concept (Isozaki, Y., 1994. Superanoxia across the Permo–Triassic boundary: record in accreted deep-sea pelagic chert in Japan. In: Embry, A.F., Beauchamp, B., Glass, D.J. (Eds.), Pangea: Global Environments and Resources. Memoir, Canadian Society of Petroleum Geologists, 17, pp. 805–812.), it is an appropriate timing to re-evaluate its geological context with the updated dataset. Kakuwa (Kakuwa, Y., 2008. Evaluation of palaeo-oxygenation of the ocean bottom across the Permian–Triassic boundary. Global and Planetary Change 63, 40–56.) lately discussed that the deep-sea anoxia across the Permian–Triassic boundary (P–TB) may have been much shorter than previously proposed, on the basis of ichnofabrics and geochemical data; however, his interpretations of the data do not appear straightforward nor persuading, and thus his claim is likely misled. Here we raise comments to his explanation on the following four issues: 1) invalid application of ichnofabric indices for shallow sea sediments to deep-sea cherts, 2) misinterpretation of Ce anomaly as a redox indicator, 3) improper application of various redox sensitive trace elements, and 4) questionable interpretations of δ^{34}S data of pyrites.

1. Bioturbation

Kakuwa (2008) used the ichnofabric indices of Droser and Bottjer (1986) that was established on the basis of sedimentary fabrics observed in continental shelf sediments. The direct application of this criterion to deep-sea sediments, however, appears misleading because the biota on shelves responsible for making ichnofabrics are essentially shallow marine dwellers that are remarkably different from those on deep-sea floors below CCD. The ichnofabrics in deep-sea sediments are likely formed by unique biological communities with different tolerance limit for poor oxygen availability. In order to discuss deep-sea ichnofabrics, we need more direct dataset for comparison from modern deep-sea sediments such as deep-sea drilling cores. The ichnofabric evidence for a strictly oxic condition in deep-sea chert emphasized by Kakuwa (2008) is therefore not yet validated and definitely needs further check. In addition, as to the enlarging digital images of burrows by assuming the proportional compaction of soft sediments after deposition, serious cautions are necessary because we may possibly fabricate non-existing morphology (artifact) through such a digital treatment of photo images.

2. Ce anomaly

Kakuwa (2008) used Ce anomalies in rare earth element (REE) abundance to evaluate paleo-redox state of deep-sea as Kato et al. (2002) did as well; however, Kakuwa's interpretation went too far beyond the reasonable resolution limit, leading to a wrong redox evaluation. First, subtle Ce anomalies almost close to none were overrated. According to Kakuwa (2008), the absence or weak positive Ce anomaly indicates an *oxic* condition (lines 64–65 of p.50 Right, “cherts have no to weak positive anomalies which may suggest oxidating environment still persisted”), whereas the absence or weak negative anomaly indicates an *anoxic* condition (lines 6–7 of p.51 Left, “the Spathian rocks generally have no to weak negative anomaly, and can be anoxic”). Although there were many paleo-redox studies using REE abundance to date (e.g., German and Elderfield, 1990; Murray et al., 1992; MacLeod and Irving, 1996; Kato et al., 2006), nobody has employed such unreliable or rather wrong criteria for evaluating redox conditions of marine sediments. Kakuwa's criteria are based on the notion that “pelagic red clays of slow sedimentation rates often have weak positive anomalies of Ce because Ce precipitates in sediments from seawater under oxidating environment with iron and manganese (Thomson et al., 1984), while anoxic blue muds have weak negative or no Ce anomalies (Toyoda et al., 1990)” as remarked in lines 50–55 of p.50 Left. However, the modern pelagic red clays reported by Thomson et al. (1984) have a weak positive Ce anomaly merely because the red

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0921-8181/$ – see front matter
doi:10.1016/j.gloplacha.2009.01.003

clays are an admixture of the authigenic (hydrogenetic) ferromanganese component with a positive Ce anomaly and the terrigenous component with no Ce anomaly. Due to removal of Ce from seawater by co-precipitation with the hydrogenetic ferromanganese materials, the overlying oxic seawater has a strong negative Ce anomaly. Some kinds of submarine sediments including pelagic carbonates (MacLeod and Irving, 1996), hydrothermal metalliferous (ferromanganese) sediments on flanks of mid-oceanic ridges (e.g., Ruhlin and Owen, 1986; Barrett and Jarvis, 1988; Ravizza et al., 1999; Kato et al., 2005a,b), and pelagic cherts (Murray et al., 1991, 1992) mimic REE signatures (e.g., striking depletion of Ce) of deep-sea waters. It should be kept in mind that we can reconstruct REE signatures of ancient seawaters only by using these appropriate sediments mimicking marine REE patterns. Therefore, Kakuwa's protocol determining redox conditions by small differences of Ce anomalies is irrelevant and thus wrong. After all, one of the main conclusions of Kakuwa (2008) claiming that “the oxic environment lasted from the Guadalupian to the early Changhsingian based on the Ce anomaly of cherts” is not acceptable.

Kakuwa made a similar mis-interpretation of Ce anomaly in the pre-P–TB carbonates from northwest Iran in his previous paper (Kakuwa and Matsumoto, 2006), in which he recognized the negative excursion of Ce in the carbonate sequence just prior to P–TB and interpreted that “the suboxic water mass associated with the Ce negative anomaly zone migrated and invaded into shallow carbonate shelf around 600 thousand years before the PTB”. They overestimated the slight negative excursion of Ce anomaly from −0.1 to −0.3, which is completely inconsistent with the much larger negative Ce anomaly values of the suboxic seawater mass, ranging from −1.5 to −0.5 in their Fig. 4, which are based on REE data of the Black Sea by German et al. (1991).

Furthermore, there are some doubts about the small negative Ce anomalies upended by Kakuwa because his data were obtained by INAA methods, and thus Pr data that are crucial for the estimation (calculation) of Ce anomaly are absent. He calculated a Ce anomaly by substituting Sm for Pr, but a true Ce anomaly value cannot be obtained by this calculation because there is sometimes an anomalous behavior of La in marine environments (Barrett and Jarvis, 1988; Bau and Dulski, 1996). Lanthanum enrichment (i.e., positive La anomalies), together with the well-known Ce depletion, has been identified in modern seawaters (e.g., Zhang et al., 1994; Alibo and Nozaki, 1999). Anomalous La enrichment can create false negative Ce anomalies in some cases. Therefore, REE datasets lacking Pr measurement should be avoided for the precise evaluation of Ce anomaly (see Kato et al., 2006), in particular for the subtle Ce anomaly as in the case of P–TB interval.

3. Redox sensitive trace elements

Trace elements including V, Mo, U, Cd and Re are commonly used in evaluating paleo-redox as reported in several key articles (e.g., Emerson and Huested, 1991; Thomson et al., 1993; Morford et al., 2005; Tribovillard et al., 2006). However, Kakuwa (2008) used these geochemical proxies without referring to these articles. His discussion contains critical errors in setting threshold values of these elements for redox evaluation that are not commonly used by major references but unique ones from ad hoc various marine sediments. These elements are called redox sensitive because they are very easily subject to post-depositional modification. Several elements such as Ni, Cu, Zn, and Cd are often delivered to organic C-rich sediments, but these elements are mostly lost without pyrite when organic matters are decayed. Thus, a simple-minded application of such redox sensitive element geochemistry as done by Kakuwa (2008) may easily lead to false interpretations.

4. $\delta^{34}S$ data of pyrite

Sulfur isotope ratio (commonly $\delta^{>34}S$) of pyrite has been discussed as supporting evidence for the assertion that the deep-sea anoxia across the P–TB was shorter than previously thought. Kakuwa (2008) has applied $\delta^{34}S$ data of pyrite in ancient marine sediments too far to discriminate redox (anoxic or oxic) conditions of overlying seawater. However, the discrimination between anoxic and oxic conditions on the basis of $\delta^{34}S$ values of pyrite is likely difficult. Because pyrite is generally regarded as an end product of the diagenesis of sulfur in marine sediments (e.g., Berner, 1984), the $\delta^{34}S$ values of pyrite in ancient sediments inevitably contain post-depositional diagenetic components, and thus the isotopic ratios should not be used as an indicator of redox conditions of overlying seawater. In fact, Jørgensen et al. (2004) and Neretin et al. (2004) demonstrated that the $\delta^{34}S$ of Black Sea deep-water sediments and the entire S–Fe chemistry are significantly altered by a secondary diagenetic overprint, and thus warned that the sulfur isotope signatures of pyrite in ancient rocks do not represent initial conditions of deposition during early diagenetic processes nor even pristine signatures of overlying water column. Ignoring such a warning, Kakuwa (2008) naively asserted that “In the case of the rock records, various influences of diagenesis should be carefully excluded and screening the data is required” in lines 31–32 of p.51 Left. As “careful exclusion and screening of the data” are substantially impossible, however, this will easily lead to arbitrary selection of data. In addition, $\delta^{34}S$ values greatly vary even among anoxic sediments of the Black Sea (>20‰), according to depositional conditions that were either open or closed, as reported by Calvert et al. (1996) to which Kakuwa (2008) referred. Therefore, Kakuwa's interpretation based on $\delta^{34}S$ values of pyrite also cannot support “his” secular change in redox.

5. Conclusions

Consequently, all lines of evidence presented by Kakuwa (2008) cannot lead to his conclusion that the Late Permian deep-sea was almost entirely oxic except for the interval immediately before the P–TB. Instead, the interpretation of Kato et al. (2002) that “the anoxic condition prevailed in the deep-sea pelagic regions for an extremely long period, much more than 10 Myr, from the middle Late Permian to early Early Triassic” still stands. On the basis of chemostratigraphic data, Isozaki (2007) and Isozaki et al. (2007) recently speculated that the superanoxic ocean stagnation probably had started slightly earlier than the G–LB when the global climate changed its mode from cooling to warming.

Regardless of Kakuwa's strange geochemical interpretations and emphasis in the text, what he concluded at the end is essentially the same as the previous idea of superanoxia; i.e. the Upper Permian to lower Middle Triassic deep-sea chert of Panthalassa recorded not fully oxic but unstable redox conditions, and the redox minimum was reached across the P–TB (Isozaki, 1994, 1997; Kato et al., 2002; Matsuo et al., 2003). For example, it is ironical that Kakuwa (2008) demonstrated a slight but clear redox drop during the early Late Permian (Wuchiapingian) in Fig. 13 somehow in a hesitated manner without showing any clear evidence. In other words, he actually admits that some redox change within his “oxic range” already started appreciably before the latest Changhsingian. This contradicts with his main message that the deep-sea was fully oxic throughout the Late Permian except for the latest Changhsingian. As the strict definition of redox levels is generally difficult for ancient sediments without accurate quantitative proxies, it is not practical to discuss sensitive conditions of strict oxic/suboxic(dysoxic)/anoxic boundaries based solely on qualitative (or semi-quatitative at best) measurements.

As to the Permian radiolarians, biostratigraphic resolution was greatly enhanced during the last decade; however, details of zonation and the correlation with other fossil (e.g., conodont) zones around the Guadalupian–Lopingian boundary are not yet in agreement among researchers. Most radiolarian paleontologists assign the *Follicucullus scholasticus-F. ventricosus* Zone (= *Ruzhencevispongus uralicus–Follicucullus scholasticus* Zone) in the Capitanian on the basis of the classic occurrence of the nominal species from the stratotype of the Capitanian in Texas (Wang and Qi, 1995; Yao and Kuwahara, 1999; Kuwahara et al., 2007), and place the G–LB at the base of the overlying *Follicucullus charveti–Albaillella yamakitai* Zone. In contrast, Xia et al. (2005), to which Kakuwa (2008) referred, constrain the *Follicucullus scholasticus–F. porrectus* Zone into the Wordian (Middle Guadalupian), and put the G–LB at the top of the *F. falx–Foremanhelena triangular* Zone above the *F. charbeti* Zone. Under such circumstances, the placement of the G–LB by radiolarians definitely needs a reliable zonation and correlation in much higher resolution and accuracy.

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