Osmium isotope excursion in the central Panthalassa during the Toarcian Oceanic Anoxic Event: Relationships between Karoo-Ferrar volcanism and climatic-biologic changes

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The Toarcian Oceanic Anoxic Event (T-OAE) represents one of the most severe paleo-environmental turbulences in the Mesozoic. The volcanic activities in the Karoo-Ferrar Large Igneous Provinces (LIPs) have been considered as the most fundamental trigger for the Toarcian perturbation, although the connection between the Karoo-Ferrar LIPs and the T-OAE remains unclear. Consequently, the debate on the influence of large volcanic activities on the global environmental changes is still controversial. Radiogenic Os isotopes of sedimentary rocks are useful for estimating the influx from both ancient basaltic magmatism and continental weathering, making this tracer suitable for understanding the cause of T-OAE. Because of the lack of detailed Os isotopes across the T-OAE, the relationship between biotic crisis, anoxia, and the volcanism in the central Panthalassa is still ambiguous. To clarify the relationship between the Karoo-Ferrar LIPs and their turbulences to the global environmental changes across the T-OAE, we determined the Re and Os concentrations, seawater  $^{187}$ Os $/^{188}$ Os values, and organic carbon isotopes in Plinsbachian to Toarcian deep-sea cherts from the Inuyama area, southwest Japan. Unlike shallow marine regions, two bedded black chert intervals (T-OAE1 and T-OAE2 in stratigraphic ascending order) were recognized in the central Panthalassa. The rock powder was spiked with <sup>190</sup>Os and <sup>185</sup>Re prior to acid decomposition. The sample was digested by a mixture of CrO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> in a sealed Carius tube at 240 °C for more than 48 h. Subsequently, Os was separated by solvent extraction using CCl<sub>4</sub> and back-extracted from CCl<sub>4</sub> into HBr, followed by the final purification using the micro-distillation method. The Os isotopes were determined by N-TIMS at Tokyo Tech. The solution remaining after the CCl, extraction was transferred to a Teflon vessel, in which Cr<sup>6+</sup> was completely reduced to Cr<sup>3+</sup> by ethanol to avoid the disturbance of Re separation with ion exchange chromatography. Subsequently, Re was purified by passing the sample solution through an anion exchange resin. The Re isotopes was determined using a quadrupole-type ICP-MS at Tokyo Tech. The Os and Re concentrations were determined by the isotope dilution method. The Re and Os abundances in 27 chert samples across T-OAE intervals varied from 0.006 to 213.1 ng/g, and from 2.0 to 2078 pg/g, respectively. The initial <sup>187</sup>Os/<sup>188</sup>Os ratios in the samples decreased from the Plinsbachian to the Toarcian, and reached the minimum value of 0.11 at the onset of T-OAE1. Afterward, the seawater <sup>187</sup>Os/<sup>188</sup>Os values increased to 0.56 towards the end of T-OAE1, and decrease down to 0.24 at the interval between T-OAE1 and T-OAE2. During the T-OAE2, the seawater <sup>187</sup>Os/<sup>188</sup>Os values abruptly increased up to 1.22. Our seawater <sup>187</sup>Os/<sup>188</sup>Os values varied preceding the variation of organic carbon isotopes, most likely reflecting the difference of residence time between Os (20 kyr) and organic carbon (75-100 kyr). From these observations, we propose the following scenario for the perturbation in the T-OAE intervals. The Karoo-Ferrar volcanic activities induced an anoxic condition, which resulted in unradiogenic <sup>187</sup>Os/<sup>188</sup>Os in seawater followed by negative  $\delta^{13}C_{\text{org}}$  ratios before the T-OAE intervals. The Karoo-Ferrar volcanism released significant amount of  ${\rm CO_2}$ , which triggered the global warming and enhanced the magnitude of continental weathering during both T-OAE intervals. Subsequent gradual increases of Os isotopes likely reflect their aftermaths. To conclude, the Karro-Ferrar volcanism played an important role for induing anoxic condition and global warming during Toarcian in the central Panthalassa.

Keywords: Toarcian Oceanic Anoxic Event , central Panthalassa, bedded chert, osmium isotope, organic carbon isotope, Karoo-Ferrar volcanism