論文の内容の要旨

Reconstruction of marine organic matter content in the sediments and deep-water redox condition variability of the Japan Sea during the Quaternary using high-resolution XRF core scanner

（XRF コアスキャナーを用いた日本海第四紀の堆積物中の海洋起源有機物量と底層の酸化還元状態の復元）

氏名　関　有沙

In order to extract paleooceanographic and paleoclimatic information such as surface productivity and deep-water circulation, marine organic matter content and deep-water redox conditions are commonly reconstructed using marine sediments. In recent days, XRF core scanner is intensively used as a useful equipment to measure element variability in sediment by non-destructive, high-speed, and high spatial resolution measurement (Rothwell and Croudace, 2015a). However, in contrast to their easiness of measurement, quantitative analysis method of XRF core scanner measurement results has not been established well, and many studies use XRF core scanner measurement as a qualitative method (Rothwell and Croudace, 2015b). Therefore, in spite of usefulness of XRF core scanner, no quantitative study to reconstruct marine organic carbon in sediment and deep-water redox conditions of the past using XRF core scanner were existed. In this study, new method to estimate marine organic matter content and deep-water redox condition in high-resolution using XRF core scanner is established, and marine organic matter content and deep-water redox condition of the Japan Sea is reconstructed during the Quaternary.

The Japan Sea is a semi-closed marginal sea located in the northwest Pacific. Because of its deep average depth and shallow (< ~130m) and narrow straits, the Japan Sea is semi-isolated from surrounding seas. The modern Japan Sea produces its own deep-water, called the Japan Sea Proper Water (JSPW), which has high oxygen content (200 μmol/kg) compared to adjacent Northwest Pacific (~150 μmol/kg) (Gamo et al., 2014). The hemipelagic sediment of the Japan Sea is characterized by centimeter to decimeter scale alternations of dark and light layers. Total organic carbon contents in these dark layers are high up to 5 %, whereas that in light layers are low (generally less than 1%) during the last 200kyr (Tada et al., 1999). Moreover, deep-water redox conditions of the Japan Sea fluctuated significantly between oxic and euxinic conditions during the last 200kyr (Tada et al., 1999; Watanabe et al., 2007; Kido et al., 2007). Recently, continuous sediment records covering the entire Quaternary were recovered by IODP Expedition 346 (Tada et al., 2015a). Therefore, the Japan Sea sediments are suitable for reconstruction of marine organic carbon in sediments and deep-water redox condition, and examine possible relationship between their past variability.

Sediment cores recovered from two sites (Site U1424 and Site U1425) by IODP Expedition 346 are used in this study. Site U1424 is located off northern Honshu with the water depth of 2808m and Site U1425 is located on the Yamato Rise with the water depth of 1909m (Tada et al., 2015c; 2015d). The Quaternary sediments at both sites are approximately 100m thick, and mainly consist of clay and silty clay (Tada et al., 2015c; 2015d). Alternations of dark and light layers are observed since ~2.6 Ma, and become distinct after ~1.5 Ma (Tada et al., 2015c; 2015d). An age model was constructed at Site U1424 (Tada et al., in revision), which was projected to U1425 using correlation of dark and light layers.

An ITRAX XRF core scanner in Kochi University was used for measurement in this study. Since ITRAX used in this study was just after its installment at Kochi University in 2014 as the first ITRAX machine in Japan, I had to establish an analytical method and its settings to measure the Japan Sea sediments for this study. Since ITRAX is generally used for semi-quantitative analysis of elements (Rothwell and Croudace, 2015b), it is necessary to establish a quantitative analytical method by myself. Firstly, aging effect of X-ray tube was monitored and a correction method was established. Then, precision of ITRAX XRF measurement was evaluated, and the relationship between element peak area count and element concentration was estimated. Using the method established above, cores of Sites U1424 and U1425 were measured by ITRAX and the XRF results were calculated for the following analyses.

Br is known to concentrate in marine organic matter as organobromine compounds, while less concentrated in terrestrial organic matter (Berg and Solomon, 2016; Mayer et al., 2007; Leri et al., 2010). Based on the relationship, the method to estimate MOC (marine organic carbon) content in the sediments using Br peak area counts obtained by ITRAX XRF measurement is constructed. In order to establish the method, TOC (total organic carbon), TN (total nitrogen), and organic carbon $\delta^{13}C$ of discrete samples taken from Sites U1424 and U1425 were analyzed. Using $\delta^{13}C$ value and TOC, MOC was calculated for each sample. Then, calculated MOC were compared with Br peak area counts measured by ITRAX. Br peak area counts have high correlation with MOC content. Based on these results, method to estimate MOC content from Br peak area counts is established. Using the method, MOC content changes during the Quaternary was reconstructed for U1424 and U1425 cores with time resolution of ~50 yrs.

In order to define the criteria to distinguish redox condition from composition of elements in the sediment measured by ITRAX, concentration of element in the top 7m of U1424 cores are compared with the results of the deep-water redox condition reconstruction by previous studies (Watanabe et al., 2007; Tada et al., 1999). Based on the results of the comparison, criteria to classify the deep-water redox conditions into four classes, "Low-organic euxinic", "High-organic euxinic", "Anoxic", and "Oxic", based solely on ITRAX data are established. Using the criteria, temporal changes in deep-water redox condition are reconstructed at Sites U1424 and U1425 during the Quaternary. In order to examine the relationship between deep-water redox conditions and sea level changes, the reconstructed deep-water redox conditions are compared with sea level curves. According to the comparison, oxic condition commonly occurs during the entire Quaternary, especially during interglacial maxima. Anoxic condition and high-organic euxinic condition occurs in association with millennial-scale alternations of dark and light layers, with anoxic and high-organic euxinic condition prevailed during deposition of dark layers and oxic condition prevailed during deposition of light layers. Low-organic euxinic condition prevailed during some of the glacial maxima, when sea level was lowered to more than approximately -90m.

Finally, application of MOC estimation method and deep-water redox condition reconstruction method are demonstrated. Using above two methods, reconstructed

MOC content and deep-water redox condition were compared between cores from two different water depths. In some dark layers, vertical difference in MOC flux is corresponding to vertical difference in deep-water redox conditions. In these dark layers, MOC flux is higher at shallower site compared to deeper site and shallower site is more reductive than deeper site, which may suggest high surface productivity and OMZ (oxygen minimum zone) expansion during the periods of deposition of these dark layers. These observations are possible only by precise correlation of high-resolution MOC flux and high-resolution deep-water redox condition changes obtained by measurement of ITRAX. Thus, the method for MOC estimation using Br counts measured by ITRAX and the method for estimation of deep-water redox condition established in this study could be a strong tool for paleoceanographic studies.