学位論文（要約）

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）

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Abstract

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 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.

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1. Introduction

1.1 Importance of organic matter content estimation for reconstruction of deep-water redox condition

The deep-water redox conditions have strong relationship with degradation of organic matter. Oxygen is usually supplied from the surface of the ocean to the deep-water via deep-water production, and is used for organic matter decomposition in the deep-water by the following reaction.

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \quad (1.1)$$

If the deep-water circulation ceased, oxygen content of the deep-water becomes decreased, and deep-water redox conditions become more reductive. As deep-water redox conditions become more reductive, reaction of organic matter decomposition changed in the order described below (Stigliani, 1988; The geochemical society of Japan, 2012).

$$CH_2O + NO_3^- \rightarrow N_2 + CO_2 \quad (1.2)$$

$$CH_2O + MnO_2 \rightarrow Mn^{2+} + CO_2 \quad (1.3)$$

$$CH_2O + Fe(OH)_3 \rightarrow Fe^{2+} + CO_2 \quad (1.4)$$

$$CH_2O + SO_4^{2-} \rightarrow H_2S + CO_2 \quad (1.5)$$

Among these five reactions, the equation 1.1 occurs under the most oxidative condition, and the equation 1.5 occurs under the most reductive condition.

When oxygen is present in the seawater and reaction of equation 1.1 occurs, the redox condition is called "oxic". When oxygen content becomes zero, reaction of equation 1.1 ceases and reaction of equations 1.2 to 1.4 occurs in the order. The redox condition under the occurrence of equations 1.2 to 1.4 is called "anoxic". When deep-water redox condition becomes further reductive, reaction of equation 1.5 occurs and H_2S is released into the seawater. This redox condition is called "euxinic" or "sulfidic". Since the term "anoxic" means the condition without dissolved oxygen, the term "anoxic" also includes "euxinic" or "sulfidic" condition. Among "anoxic" condition, if H_2S is not existed in the seawater, the redox condition is called "non-euxinic anoxic" or "non-sulfidic anoxic".

Reconstruction of deep-water redox condition from sediments provides useful information about past oceanic environment. Many proxies are used to reconstruct deep-water redox conditions from sediments. Some proxies

used the relationship between redox condition and reaction of organic matter degradation, as well as resulted chemical evidence remained in the sediment. One of such proxies is S/C ratio in the sediment, which is used to distinguish redox conditions between oxic and euxinic environment (Berner and Raiswell, 1983).

In normal marine environment where deep-water is oxic, pyrite is formed in sulfate reduction zone within the sediment in the near shore to hemipelagic sediments (Berner and Raiswell, 1983). In sulfate reduction zone, organic matter is oxidized by sulfate ion, and produced H_2S is used to form pyrite. Since organic matter in the sediments is composed of various organic molecules with wide range of reactivity to sulfate ion, some proportion of organic matter remained after sulfate ion is ultimately consumed (Berner and Raiswell, 1983). Therefore, if surface productivity is high, and a large amount of organic matter deposited into the sediment, both organic matter content and pyrite content remained high in the sediment (Berner and Raiswell, 1983). In contrast, both organic matter and pyrite contents are low when initial deposition of organic matter is low (Berner and Raiswell, 1983). Observed S_{pyrite} /C_{org} ratio (S_{pyrite}: sulfur exist as pyrite, C_{org}: organic carbon) in the sediments deposited under normal marine environment is around 0.36, because, as described above, pyrite formation is considered to be controlled by organic matter content initially deposited into the sediment (Berner and Raiswell, 1983). Whereas S_{pyrite} /C_{org} ratio becomes higher than 0.36 in euxinic deep-water conditions (Berner and Raiswell, 1983), because additional pyrite formation occurred within the euxinic water column (Muramoto et al., 1991).

Thus, for the use of parameters such as S/C ratio, estimation of organic carbon content is important. Organic carbon content is usually measured as TOC (total organic carbon) on discrete samples, on which pre-treatment is necessary to remove carbonate carbon. Since reactivity of organic matter is different in terrestrial and marine organic matter (Fig. 1.1), reactivity of organic matter in sediments could be affected by mixing ratio of terrestrial and marine organic matter in sediments which contain significant amount of terrestrial organic matter such as hemipelagic sediments. In such cases, S/C

ratio could be affected by reactivity changes of organic matter caused by changes of mixing ratio of terrestrial and marine organic matter. Therefore, to use S/C ratio correctly for deep-water redox reconstruction, it is preferred to reconstruct marine organic carbon content and terrestrial organic carbon content separately.

1.2 XRF core scanner for high-resolution measurement

In recent decades, XRF core scanners are intensively used for analysis of sediment cores, in many academic fields including peloceanographic studies (Rothwell and Croudace, 2015a). The advantages of XRF core scanner are non-destructive, high-speed, and high-resolution measurement.

In previous studies, measurement results of XRF core scanners often expressed as down core profiles of element peak area count calculated from XRF spectra (see chapter 3 for detail), not concentration of element in sediments (Rothwell and Croudace, 2015b and references therein). The reason is, since XRF core scanner is non-destructive method which can analyze half rounded cores or u-channels directly, the result is easily affected by surface condition or water content of the sample (Croudace et al., 2006; Kido et al., 2006; Weltje and Tjallingii, 2008; Weltje et al. 2015). Therefore, compared to simple and easy manner of measurement, data processing is more complicated in case of XRF core scanner. Some studies make efforts to construct calibration equation from peak area counts to concentration of elements, but generally, XRF core scanner measurements are used as a qualitative method.

The ITRAX XRF core scanner is one of the most popular and highly used XRF core scanner manufactured and sold by COX Analytical Systems (Croudace et al., 2006; Rothwell and Croudace, 2015a). Owing to flat beam technics developed for ITRAX core scanner, it has advantages for high-resolution measurement with the highest resolution of 0.2mm, compared to other XRF core scanner. Since XRF measurement of ITRAX is conducted under usual atmospheric environment, elements lighter than Al cannot be measured by ITRAX because absorption effect of XRF by air is more significant for lighter elements.

1.3 Relationship between organic matter and Br in the sediment

Although organic matter content in sediments is important for many paleooceanographic studies, organic matter or organic carbon cannot be measured by XRF core scanners because of absorption effect of the air.

So, Ziegler et al. (2008) proposed a new method to estimate TOC (Total Organic Carbon) content of marine sediment from Br counts measured by XRF core scanner, because Br is contained in organic matter as organobromine compounds in marine sediment (Leri et al., 2010). Br concentration in seawater is higher than the earth crust (The geochemical society of Japan, 2012), and Br concentration in organic matter is higher than seawater (Berg and Solomon, 2016; Mayer et al., 2007; Leri et al., 2010; Masuzawa et al., 1988). Thus, Br concentration in organic matter is far higher than concentration in detrital materials in marine sediment. Therefore, Br in sediments could be used as a proxy for organic matter in the sediment.

Moreover, Br content in organic matter is higher in marine organic matter than in terrestrial organic matter (Fig. 1.1; Berg and Solomon, 2016). Reported average Br / TOC molar ratio for marine organic matter is 0.9 - 1.8 $\times 10^{-3}$, while that for terrestrial organic matter is 0.06 - 0.3 $\times 10^{-3}$ (Berg and Solomon, 2016; Mayer et al., 2007; Leri et al., 2010). Ziegler et al. (2008) suggested the possibility to estimate MOC (Marine Organic Carbon) content from Br counts by removing samples where $\delta^{13}C$ values are less than -20‰ (typical value for marine organic carbon) to improve correlation between Br counts and TOC contents in Arabian Sea sediments. However, this possibility has not been evaluated.

1.4 Quaternary climate variability

1.4.1 Glacial-Interglacial cycle

The Quaternary is characterized by glacial-interglacial cycles, and consequent oscillations of sea level. Sea-level oscillations during the Quaternary have been mainly reconstructed using benthic foraminifer $\delta^{18}O$, because it mainly records seawater $\delta^{18}O$, which is influenced by global ice

volume (Lisiecki and Raymo, 2005). Compiled benthic foraminifer $\delta^{18}O$ curve for the last 5.3 Myr, called "LR04" stack (Fig. 1.2; Lisiecki and Raymo, 2005) is most widely used as an ice volume proxy in paleoceanographic studies. However, benthic foraminifer $\delta^{18}O$ is affected not only by seawater $\delta^{18}O$ but also by deep-water temperature. Since Mg/Ca ratio of foraminifer is used as a proxy of paleo-temperature, Elderfield et al. (2012) calculate seawater $\delta^{18}O$ from benthic foraminifer $\delta^{18}O$ and Mg/Ca ratio, and obtain seawater $\delta^{18}O$ record during the last 1.5 Myr. Both records show clear oscillations in association with glacial-interglacial cycles, with occasionally different amplitude for each cycle (for example, MIS23-22, Elderfield et al., 2012).

The dominant periodicity of the cycle is 41 kyr before 1.2 Ma, and ~100 kyr after 0.7Ma (Fig. 1.2). The transition period between 1.2 and 0.7 Ma is called mid-Pleistocene transition (MPT). Amplitude of the glacial-interglacial cycles also increased after Mid-Brunhes event (MBE).

Antarctic ice core record revealed that Antarctic temperature, atmospheric CO_2 and CH_4 were fluctuated in association with glacial-interglacial cycle during the last 800 kyr (Jouzel et al., 2007; Lüthi et al., 2008; Loulergue et al., 2008). The amplitude of temperature anomaly fluctuation, which is reconstructed from δD, is around 15°C, and the pattern shows excellent agreement with LR04 benthic $\delta^{18}O$ curve (Jouzel et al., 2007). Amplitude of CO_2 fluctuation during the last 800 kyr is around 100ppm, with 170 - 200 ppm in glacial maxima and 240 - 280 ppm in interglacial maxima (Lüthi et al., 2008). Therefore, sea level, temperature and CO_2 oscillate together in association with glacial-interglacial cycles.

1.4.2 Millennial-scale climate variability

Large amplitude abrupt climate changes of centennial to millennial time scales called Dansgaard-Oeschger (DO) cycles were recognized during the last glacial period, which was originally found in Greenland ice core $\delta^{18}O$ record (Dansgaard et al., 1993). Similar signals were also found in Antarctic ice core record (Jouzel et al., 2007). Climatic changes in association with DO cycles were also reported from marine core records (e.g., Tada et al., 1999; Tada, 2004; Hodell et al., 2013) and stalagmite $\delta^{18}O$ records (e.g., Cheng et

al., 2016) from the northern hemisphere. Millennial-scale climate variability in these records is usually superimposed on glacial-interglacial cycle. Although the mechanism of millennial-scale changes in association with DO cycles is proposed as caused by on and off of deep-water formation in north Atlantic, ultimate driving force and propagation mechanism is not well understood.

Tada (2004) proposed that westerly jet meandering could be responsible for the teleconnection of DO cycle signals between north Atlantic and the East Asia. Since northward and southward shift of westerly jet axis in association with DO cycle is reported both from the North America (Asmerom et al., 2010) and the East Asia (Nagashima et al., 2011), it is a reasonable mechanism to connect climate variability in the northern hemisphere (Nagashima and Tada, 2012). Since northward and southward shifts of westerly jet also influence the pattern of East Asian Summer Monsoon (EASM) precipitation by changing the position of Meiyu front, the northern limit of EASM precipitation (Chiang et al., 2015), it is likely that westerly jet linked DO cycle in North Atlantic and EASM (Tada, 2012).

1.5 Deep-water redox condition in the Japan Sea

The Japan Sea is a semi-closed marginal sea located on the western margin of the northwestern Pacific. Since the Japan Sea is connected to other seas only with shallow and narrow straits (<130m depth), paleoceanographic condition of the sea is easily influenced by sea level oscillations. Today, dissolved oxygen in the deep water of the Japan Sea is higher (>200 μmol kg^{-1}) compared to the adjacent northwestern Pacific (~150 μmol kg^{-1}) (Gamo et al., 2014), because the Japan Sea has its own deep water, called the Japan Sea Proper Water (JSPW), which ventilates deeper part of the sea with highly oxygenated water with short residence time of 100-300 years (Gamo et al., 2001; 2014).

However, Tada et al. (1999) revealed that deep-water redox condition in the Japan Sea oscillated dramatically from oxic to euxinic during the last 200kyr. Based on S/C ratio of the sediments, they suggest that euxinic condition prevailed in the deeper part of the Japan Sea during the sea level

lowstand in the Last Glacial Maximum (LGM). On the other hand, oxygen isotope record of planktonic foraminifera suggests that surface water salinity in the sea also decreased during the same period due to excess precipitation over evaporation and fresh water inflow from surrounding rivers (Oba et al., 1991; Matsui et al., 1998). From these observation, the sea is interpreted to have been stratified during the LGM due to development of lower salinity surface water that prevents formation of dense deep-water (high salinity and cold water) and lead to formation of euxinic deep-water (Tada et al., 1999). Such euxinic condition is reported not only from the LGM, but also during other glacial maxima such as MIS 6, 10, and 12, when sea level dropped to below -90m (Tada et al., 1999; Kido et al., 2007). Thus, sea level has significant influence on the redox conditions of the deep-water of the Japan Sea.

Oscillations of deep-water redox condition in the Japan Sea occurred not only on glacial-interglacial scale driven by sea level changes, but also on millennial scale (Tada et al., 1999). Quaternary hemipelagic sediment of the Japan Sea is characterized by alternation of distinct dark and light layers, which reflect changes in surface productivity and deep-water redox condition (Tada et al., 1999). Tada et al. (1999) suggested that centimeter to decimeter scale alternation of dark and light layers deposited during the intermediate sea level (-90m - -20m) periods reflected changes in EASM intensity rather than direct sea-level changes. They considered that surface ocean salinity and productivity in the Japan Sea had significant influence on formation of these millennial scale alternations of dark and light layers (Tada et al., 1999).

1.6 Objective of this study

In this study, new method to reconstruct marine organic carbon content and deep-water redox condition from high-resolution XRF core scanner measurement of sediment core is established in order to reconstruct high-resolution temporal changes in organic matter content in the sediment and deep-water redox condition of the Japan Sea during Quaternary (Fig. 1.3).

The Quaternary hemipelagic sediments of the Japan Sea were used because of following three main reasons. First, deep-water redox condition of the sea has been dramatically oscillated with large amplitude. Second, organic carbon content of the sediment has large amplitude fluctuation up to 5% in association with alternations of dark and light layers (Tada et al., 1999). Third, Quaternary hemipelagic sediments from the Japan Sea were recovered during IODP Expedition 346 in 2013, and continuous sediment record could be obtained from recovered sediments at multiple sites (Tada et al., 2015a, Irino et al., submitted). Moreover, correlation of dark layers among sediments recovered from IODP sites (Tada et al., in revision) enable to correlate measurement results of XRF core scanner between different sites. Also, the Japan Sea experienced little tectonic movement, and geography has not been changed during the Quaternary, especially during the last 1.7 Ma (Itaki et al., 2016). Details of the oceanographic settings and studied cores are described in chapter 2.

To accomplish objective of this study, long sequence (~100m) of sediments should be analyzed with the resolution shorter than millennial time scale that corresponds to alternation of dark and light layers. Alternations of dark and light layers in the Japan Sea sediments are in centimeter to decimeter scale, so more than 10,000 points should be measured in order to characterize each layer. Therefore, XRF core scanner (ITRAX) (Croudace et al., 2006) is used in this study for fast and high-resolution measurement. Since ITRAX is usually used for semi-quantitative studies (Rothwell and Croudace, 2015b), quantitative capability is examined and analytical method is established in chapter 3.

Although organic matter content is necessary to reconstruct redox conditions, organic matter and organic carbon content cannot be directly measured by ITRAX XRF core scanner. Therefore, Br is used as a proxy to reconstruct marine organic carbon content. First, relationship between marine organic carbon content and Br was examined using discrete samples, and then, marine organic carbon content is reconstructed using Br in chapter 4.

In previous studies, redox conditions in the Japan Sea have been

reconstructed only for the last 640kyr, mainly for the last 200kyr (Fig. 1.2; Tada et al., 1999; Watanabe et al., 2007; Kido et al., 2007). For these periods, relationship between deep-water redox condition and amplitude of sea-level change has been suggested (Kido et al., 2007). To further examine the relationship between sea-level changes and variability of deep-water redox conditions in the Japan Sea, I reconstruct deep-water redox condition changes in the Japan Sea that extends back to MPT, before when amplitude of sea-level changes were smaller than that for the last 640kyr (Fig. 1.2; Lisiecki and Raymo, 2005; Elderfield et al., 2012), the period in which previous studies existed, which was described in chapter 5.

The usefulness of organic matter estimation method developed in chapter 4 and deep-water redox reconstruction method developed in chapter 5 are demonstrated in chapter 6.

Fig. 1.1 Difference of organic matter features between marine derived organic matter and terrestrial derived organic matter

Fig. 1.2 LR04 benthic $\delta^{18}O$ stack (Lisiecki and Raymo, 2005) and main events related to periodicity of the cycle. The periods of deep-water redox reconstruction by previous studies (Tada et al., 1999; Watanabe et al., 2007; Kido et al., 2007) and this study are also shown.

Fig. 1.3 Outline and structure of this study

2. Oceanographic setting & studied core

2.1 Oceanographic settings

2.1.1 Oceanographic setting of the Japan Sea

The Japan Sea is a semi-closed marginal sea located in the northwest margin of the Pacific Ocean. The sea is connected with surrounding seas with four shallow channels, the Tsushima Strait (sill depth ~130 m), the Tsugaru Strait (sill depth ~130 m), the Soya Strait (sill depth ~55 m), and the Mamiya (Tatar) Strait (sill depth ~15 m) (Fig. 2.1). The average depth of the Japan Sea is more than 1600 m, with maximum depth of more than 3700 m (National Astronomical Observatory of Japan, 2016). The Japan Sea is composed of three basins, Japan Basin (~3800m), Yamato Basin (~3000m), and Tsushima (Ulleung) Basin (~2600m), respectively, divided by the Yamato Rise (Gamo, 2016; Fig. 2.1).

At present, the Tsushima Warm Current (TWC) is the only current flowing into the Japan Sea through the Tsushima Strait. The TWC is composed of two components, the Kuroshio Warm Current (KWC) and the Taiwan Warm Current (TWWC). The TWC originated from the KWC is flowing into the Japan Sea through the southern channel of the Tsushima Strait, whereas TWC originated from TWWC is flowing into the Japan Sea through the northern channel of the Tsushima Strait. TWWC flows from the South China Sea into the East China Sea (ECS), then flowing northeastward on the ECS shelf where it is mixed with river water supplied from the continent to become lower in salinity and higher in nutrient compared to the KWC flowing northeastward in the Okinawa Trough. Therefore, surface water salinity in the Japan Sea is easily influenced by salinity of the TWWC, which is affected by fresh water flux from the continent (Yanagi et al., 2002), and relative contribution between the TWWC and the KWC to the influx into the Japan Sea. The TWC originated from the KWC and flowing into the Japan Sea through the southern channel of the Tsushima Strait is flowing along the coast of Honshu Island, and flowing out to the northwestern Pacific through the Tsugaru Strait (Hase et al., 1999; Ito et al., 2014). This current is called the first branch of the TWC (TWC-1 in Fig. 2.1). The TWC originated from the TWWC and flowing into the Japan Sea through the

northern channel of the Tsushima Strait is separated into the second branch of the TWC (TWC-2 in Fig. 2.1) and the third branch of the TWC (TWC-3 in Fig. 2.1) (Ito et al., 2014). The TWC-2 is flowing along the continental shelf edge (Ito et al., 2014; Fig. 2.1). The TWC-3 is flowing along the east coast of the Korean Peninsula and deflected to the east at around 40°N (Ito et al., 2014; Fig. 2.1). Observational study shows the TWC-1 is highly stable throughout the year, while the TWC-2 has seasonal variability (Hase et al., 1999; Ito et al., 2014).

The modern Japan Sea produces its own deep-water called the Japan Sea Proper Water (JSPW), which is characterized by low potential temperature of 0 - 1 °C and high oxygen content throughout the deeper (>200m) part of the Japan Sea (Gamo, 2016). Dissolved oxygen level in the Japan Sea deep water is more than 200 μmol/kg in all three basins, and this value is higher than the Northwestern Pacific at the same latitude (~150 μmol kg^{-1}) (Gamo et al., 2014). Potential temperature in the sea deeper than 2000 - 2500m is uniform in all three basin with < 0.001°C fluctuations, suggesting vertical convection in the deep-water (Gamo and Horibe, 1983; Gamo et al., 2014). Current flowing along the eastern margin of the Japan Sea is cooled by Winter Monsoon wind and formed the JSPW especially in the area off Vladivostok where strong Winter Monsoon wind from the northwest is focused because of topographic effect of a mountain gap.

Since the sill depths of the modern straits are shallow (<130m) and tectonic influences are minimal, the situation should have been changed in response to sea level changes during the Quaternary. During the Last Glacial Maximum (LGM) when sea level dropped to around -120m, surface water inflow from the Tsushima Strait dramatically decreased and the sea become a closed system, and the surface water salinity in the sea also decreased due to the excess precipitation plus fresh water inflow from surrounding rivers over evaporation (Matsui et al., 1998). Consequently, the sea became stratified because production of the dense deep-water (high salinity and cold water) stopped, leading to deep-water to become euxinic (Tada et al., 1999).

The Japan Sea is also characterized by its low nutrient content (Yanagi,

2002, Tada, 2012). In the modern Japan Sea, phosphorus content in the JSPW is low (2.3μM), and residence time of phosphorus and nitrogen is short (2.2 years and 1.6 years in the upper 200m of the Japan Sea, respectively) (Yanagi, 2002, Tada, 2012). Phosphorous budget in the Japan Sea revealed that phosphorus input from the ECS through Tsushima Strait is by far the dominant source of phosphorus to the Japan Sea (Yanagi, 2002). However, 90% of phosphorus flowing into the sea via the Tsushima Strait is flowing out from the Tsugaru Strait in the modern Japan Sea, because the subsurface water, which has higher nutrient content than the surface water, is flowing out from the Tsugaru Strait, whose sill depth (~130m) is deeper than thermocline (Tada, 2012). Thus, nutrient budget in the Japan Sea is thought to have been affected significantly by sea level changes (Tada, 2012).

2.1.2 Oceanographic setting of the studied sites

In summer of 2013, Integrated Ocean Drilling Program (IODP) Expedition 346 "Asian monsoon" drilled hemipelagic sediments at seven sites in the Japan Sea (Tada et al., 2015a). Among the seven sites drilled in the Japan Sea, sediments recovered from Sites U1424 (water depth 2808m) and U1425 (water depth 1909m) are selected to observe the difference in redox conditions with the water depth, because water depth difference in the bottom-water redox condition in the Japan Sea during last 16 kyr is reported previously (Watanabe et al., 2007).

2.1.2.1 Site U1424

Site U1424 is located ~150km to the west of northern Honshu Island and ~200km to the southwest of the Tsugaru Strait (40°11.40'N, 138°13.90'E), close to the boundary of Japan Basin and Yamato Basin with the water depth of 2808 m (Fig. 2.1; Tada et al., 2015c). Site U1424 is under the influence of TWC-2 (Fig. 2.1; Tada et al., 2015c).

2.1.2.2 Site U1425

Site U1425 is located on the terrace within a graben in the middle part of the Yamato Rise (39°29.44'N, 134°26.55'E), and water depth is 1909 m (Fig. 2.1; Tada et al., 2015d). At present, Site U1425 is located under the Subpolar Front in the Japan Sea, and is under the influence of TWC-3 during the

summer (Fig. 2.1; Tada et al., 2015d).

2.2 Lithostratigraphy & Age model

2.2.1 Lithostratigraphy

2.2.1.1 Sediments recovered during IODP Exp. 346

Hemipelagic sediments of the Japan Sea are known to have distinct dark and light layers (e.g., Tada et al., 1999; Tada, 2004). During IODP Exp. 346, these dark and light layers are recovered at six sites in the Japan Sea of which water depths are deeper than 900 m (Tada et al., 2015a). Deposition of dark and light layers started at around 2.6 Ma (Million years ago) and became distinct at around 1.45 Ma (Tada et al., 2015a; Tada et al., in revision). Distinct dark layers are correlated among the six sites and their deposition was synchronous basinwide, suggesting that the Japan Sea has been acting as a single system responding to climatic / oceanographic changes throughout the Quaternary (Tada et al., 2015a; Tada et al., in revision).

At each sites, more than two holes were drilled in order to obtain continuous sequence of the sediments. Recovered cores are cut into 1.5m long sections onboard. Name of each section consists of site, hole, core number, core type (such as H, which means cores taken by advanced piston corer system), and section number (Tada et al., 2015b). For example, "U1424A-1H-1" means the first section of the first core recovered from Site U1424, Hole A. Name of discrete samples consists of site, hole, core number, core type, section number, W or A (indicating Working half or Archive half), and sampling depth interval within the section. For example, "U1424A-1H-1W 20-22cm" means discrete sample taken from depth interval from 20 cm to 22cm of working half of U1424A-1H-1. Splice intervals were defined onboard, and composite column is made of each splice interval. The depth scale of this composite column is expressed as "CCSF-D (m)" (Tada et al., 2015b). Splice intervals were further revised on shore after the cruise (Irino et al., submitted), which is employed in this study.

2.2.1.2 Lithostratigraphy of Site U1424

Three holes were drilled at Site U1424, and sediments back to 5 Ma were

recovered, which mainly consist of clay and diatom ooze, with minor component of volcaniclastic materials (Tada et al., 2015c). The recovered sediments divided into two major lithological units (Unit I and Unit II) based on Tada et al. (1994) (Tada et al., 2015c). Unit I mainly consists of clay deposited during early Pleistocene to Holocene (Tada et al., 2015c). Unit I further divided into two lithological subunits, Subunit IA and Subunit IB (Fig. 2.2). Subunit IA is characterized by decimeter-scale alternations of dark and light colored layers (Fig. 2.2; Tada et al., 2015c). Depth interval of Subunit IA on shipboard composite column is between 0 m and 47.8 m (CCSF-D) (Tada et al., 2015c). Subunit IB is identified by decreased frequency of alternations of dark and light layers and dominance of light greenish gray and light gray clay (Fig. 2.2; Tada et al., 2015c). Depth interval of Subunit IB on shipboard composite column is between 47.8 m and 70.0 m (CCSF-D) (Tada et al., 2015c). Unit II mainly consists of diatomaceous clay and diatom ooze, deposited during Pliocene to early Pleistocene (Tada et al., 2015c). Unit II further divided into Subunit IIA and Subunit IIB. Subunit IIA mainly consists of diatom-bearing and diatom-rich clay, whereas Subunit IIB is defined by consistent appearance of diatom ooze (Tada et al., 2015c). Depth interval of Subunit IIA and IIB on shipboard composite column is 70.0 - ~85 m (CCSF-D) and ~85 m - 167m, respectively (Tada et al., 2015c). In summary, Pliocene sediments (Subunit IIB) are mainly composed of diatom ooze, whereas Quaternary sediments (Subunit IA, IB, and IIA) mainly consist of clay (Tada et al., 2015c).

Splice intervals were revised after the cruise, and new depth scale for U1424 is called "U1424_CCSF-D_Patched_rev20170308 (m)" (Irino et al., submitted). Difference of shipboard depth scale (CCSF-D) and new depth scale is less than 1.5m throughout the splice (Irino et al., submitted). New depth scale is employed in this study unless otherwise noted. Thickness of the Quaternary sediment is around 90m based on the shipboard age model (Tada et al., 2015c) and ~83m (in U1424_CCSF-D_Patched_rev20170308 scale) based on the revised age model described below (Fig. 2.5; Tada et al., in revision; see also 2.2.2 in this paper). Since this site is at the same location with Ocean Drilling Program (ODP) Site 794, sediment sequence is

correlated with ODP Site 794 cores (Irino et al., submitted).

One reason to choose Site U1424 is no sediment disturbance (such as slumps) or hiatus is observed at this site (Tada et al., 2015c). In addition, color alternations of dark and light layers are distinct in this site compared to sites drilled from shallower water depth (such as Site U1426 drilled at 903m; Tada et al., 2015a; Irino et al., submitted). Another reason to choose Site U1424 is that high-precision and high-resolution age model is constructed at this site (Tada et al., in revision; see also 2.2.2 in this paper).

2.2.1.3 Lithostratigraphy of Site U1425

During previous ODP cruise, ODP Site 799, which close to IODP Site U1425, was also drilled inside the graben, and the sediments contain numerous turbidites. In order to avoid the influence of turbidites, the position of Site U1425 was selected on a terrace higher than the bottom of the graben, although slump folds are observed at two intervals (U1425D-9H-1 to 9H-2 and U1425D-10H-6; Tada et al., 2015d).

Five holes were drilled at this site, and the deepest hole was drilled to 427m below the sea floor. Sediments back to 10 Ma were recovered (Tada et al., 2015d). The recovered sediments divided into three major lithological units (Unit I, II, and III) similar to Tada et al. (1994), and further divided into six lithological subunits (Subunit IA, IB, IIA, IIB, IIIA, IIIB) (Tada et al., 2015d). Quaternary sediments used in this study are corresponding to Subunit IA, IB and upper part of Subunit IIA (Fig. 2.3). Depth intervals of Subunit IA, IB, and IIA are 0 - ~50m, ~50 - ~93 m, and ~93 - ~138m (CCSF-D), respectively (Tada et al., 2015d). In summary, Quaternary sediments mainly consist of clay and silty clay with distinct dark and light layers especially in the upper half of the sequence (Subunit IA; Fig. 2.3). Tephra layers (millimeter to decimeter scale in thickness) frequently occur throughout the sediments and represent a minor component.

Splice intervals were revised after the cruise, and new depth scale for U1425 is defined that is called "U1425_CCSF-D_Patched_rev20170309 (m)" (Irino et al., submitted). Difference of shipboard depth scale (CCSF-D) and new depth scale is less than 1.5m throughout the composite column, and less than 1m for upper 100m of the sequence (Irino et al., submitted). New depth

scale is employed in this study unless otherwise noted. Thickness of the Quaternary part of the sediments is around 100m based on the shipboard age model (Tada et al., 2015d) and ~90m based on the revised age model that will be described below (Fig. 2.6; Tada et al., in revision; see also 2.2.2 in this paper).

2.2.2 Age models

2.2.2.1 LR04 tuned age model for U1424

In the Japan Sea sediments, foraminifer shells are not continuously found from all horizons (Tada et al., 2015c; 2015d), because CCD (Carbonate Compensation Depth) in the Japan Sea was occasionally shallower than the water depths of core sites (Ujiié and Ichikura, 1973; Lee et al., 2000). Especially at Site U1424, benthic foraminifers are absent in the interval shallower than ~30m below sea floor and only occasionally present below that depth (Tada et al., 2015c). Moreover, salinity of the surface water of the Japan Sea changed dramatically in the past, and $\delta^{18}O$ of planktonic foraminifer was significantly affected by the salinity changes (Kido et al., 2007). Therefore, it is difficult to construct an age model for the hemipelagic sediments of the Japan Sea using $\delta^{18}O$ stratigraphy of foraminifer shells, which is commonly used for marine sediment.

It is known that GRA (Gamma Ray Attenuation) bulk density is a semiquantitative measure of the density of sediments and in case of the Japan Sea sediments, it reflects diatom content because diatoms have high intraskeletal porosity compared to detrital particles (Tada and Iijima 1983). In the Japan Sea, diatom abundance has been changing in association with glacial-interglacial cycles (Tada et al., 1999), because it is controlled by nutrient flux from the Tsushima Strait, which is modulated by sea-level changes.

Using this relationship, Tada et al. (in revision) constructed "LR04 tuned Age model" for U1424 by tuning GRA of U1424 composite section to LR04 $\delta^{18}O$ stack (Lisiecki and Raymo, 2005). First, they constructed a tephra and magnetostratigraphy based age model to constrain the age-depth relationship (Tada et al., in revision). Then, they further tuned the age model

by correlating GRA maxima with $\delta^{18}O$ maxima of LR04 $\delta^{18}O$ stack to construct LR04 tuned age model covering the entire Quaternary (Tada et al., in revision). Since their age model has higher resolution and reliability covering the entire Quaternary compared to the shipboard age model, this LR04 tuned age model is employed in this study.

2.2.2.2 Stratigraphic correlation of Sites U1424 and U1425 and projection of U1424 age model to U1425

Since dark and light layers are deposited synchronously throughout the deeper part of the Japan Sea, LR04 tuned age model of Site U1424 could be projected to other sites using these layers as key tie points. Therefore, in order to project LR04 tuned age model of Site U1424 to the other sites, stratigraphic correlation among the six sites drilled during IODP Expedition 346 including Sites U1424 and U1425 are conducted for the stratigraphic interval corresponding to the period from 0 to 1.5 Ma. (Tada et al., in revision). They use bottom of distinct dark layers as correlation tie points, because bioturbation effect is minimal at the dark layer bottom (Watanabe et al., 2007).

Using their method, I added correlation tie points for the time interval from 0 to 1.5 Ma in order to make higher resolution age model for Site U1425 (Table 2.1; Fig. 2.4). Also, I extended the correlation of Sites U1424 and U1425 for the stratigraphic interval corresponding to the period from 1.5 to 3 Ma. In addition to published 64 tie points (Tada et al., in revision), 24 new tie points at dark layer bottoms are used for correlation in this study (Table 2.1). Using these tie points, LR04 tuned age at Site U1424 is projected to Site U1425 (Table 2.2). Age depth relationship for Site U1425 is shown in Fig. 2.6.

Tephra layers are used to crosscheck the validity of correlation because tephra layers are the most reliable time markers for correlation. Fourteen tephra layers are correlated between U1424 and U1425 in the time interval from 0 to 3 Ma (Nagahashi and Satoguchi, personal communication; Fig. 2.4). Ages of each tephra layer bottom are calculated independently using U1424 LR04 tuned age model (Fig. 2.5) and U1425 age model projected from U1424 (Fig. 2.6). The age difference of corresponding tephra layers calculated from

two age models is less than 6kyr. Therefore, stratigraphic correlation of the two sites is reliable, and LR04 tuned age model is correctly projected to U1425 from U1424.

Fig. 2.1 A map of the Japan Sea with two studied Sites (Sites U1424 and U1425). Main surface currents and name of basins and straits are also indicated. (Modified after Tada et al., 2015a)

Fig. 2.2 Enhanced photograph of composite column and lithological unit for upper 100m of Site U1424. See text for unit details.

Fig. 2.3 Enhanced photograph of composite column and lithological unit for upper 100m of Site U1425. See text for unit details.

Fig. 2.4 Dark layer correlation between Site U1425 and Site U1424. Enhanced photograph, section name, color (L* reconstructed from RGB data, Irino et al., submitted) obtained from two Sites are shown for comparison. Red check marks show tephra horizon. Blue and black lines: dark layer bottoms correlated by Tada et al. (in revision). Green lines: dark layer bottoms correlated in this study. Red lines: tephra layers correlated between two sites (Nagahashi and Satoguchi, personal communication). Dark layer numbers are also shown. 0 - 0.12 Ma.

Fig. 2.4 continued. 0.1 - 0.22 Ma.

Fig. 2.4 continued. 0.2 - 0.32 Ma.

Red x mark on L* graph indicates dark color reflecting surface disturbance (crack at section boundary), not dark layer.

Fig. 2.4 continued. 0.3 - 0.42 Ma.

Fig. 2.4 continued. 0.4 - 0.52 Ma.

Fig. 2.4 continued. 0.5 - 0.62 Ma.

Fig. 2.4 continued. 0.6 - 0.72 Ma.

Fig. 2.4 continued. 0.7 - 0.9 Ma.

Red x mark on L* graph indicates dark color reflecting surface disturbance (crack at section boundary), not dark layer.

Fig. 2.4 continued. 0.85 - 1.03 Ma.

Red x marks on L* graph indicate dark color reflecting surface disturbance (cracks at section boundary), not dark layers.

Fig. 2.4 continued. 1 - 1.17 Ma.

Red x mark on L* graph indicates dark color reflecting surface disturbance (crack at section boundary), not dark layer.

Fig. 2.4 continued. 1.15 - 1.4 Ma.

Red x marks on L* graph indicate dark color reflecting surface disturbance (cracks at section boundary), not dark layers.

Fig. 2.4 continued. 1.31 - 1.5 Ma.

Red x marks on L* graph indicate dark color reflecting surface disturbance (cracks at section boundary), not dark layers.

Fig. 2.5 Age-Depth relationship for Site U1424. See Table 2.2 for age tie points. Subunits are also shown.

Fig. 2.6 Age-Depth relationship for Site U1425. See Table 2.2 for age tie points. Subunits are also shown.

Table 2.1 List of correlation tie point between Sites U1424 and U1425 in the time interval from 0 to 3 Ma.

Dark layer No.	U1424 Position	U1424 CCSF-D_ Patched_ rev20170308 (m)	U1425 Position	U1425 CCSF-D_ Patched_ rev20170309 (m)
0-1*	U1424A-1H-1 69cm	0.69	U1425D-1H-1 67cm	0.67
1-1*	U1424A-1H-1 121cm	1.21	U1425D-1H-2 25cm	1.75
1-1-2	U1424C-1H-2 78cm	1.45	U1425D-1H-2 58cm	2.08
1-2*	U1424A-1H-2 24cm	1.71	U1425D-1H-2 80cm	2.30
1-3*	U1424A-1H-2 76cm	2.16	U1425D-1H-2 116cm	2.66
1-4*	U1424A-1H-2 102cm	2.42	U1425D-1H-2 149cm	2.99
1-4-2	U1424A-1H-3 27.5cm	3.18	U1425B-1H-3 109.5cm	4.10
1-4-3	U1424A-1H-3 43.5cm	3.34	U1425B-1H-3 135cm	4.35
1-5*	U1424A-1H-3 84cm	3.74	U1425B-1H-4 35cm	4.85
1-5-2	U1424A-1H-3 109cm	3.99	U1425B-1H-4 64cm	5.14
1-6*	U1424A-1H-4 45cm	4.85	U1425B-1H-5 22cm	6.22
1-6-2	U1424A-1H-4 104cm	5.44	U1425B-1H-5 80cm	6.80
1-6-3	U1424B-2H-1 99cm	5.74	U1425B-1H-5 106cm	7.06
2-1*	U1424B-2H-1 132cm	6.07	U1425B-1H-6 22cm	7.72
2-2*	U1424B-2H-2 32cm	6.57	U1425D-2H-2 52cm	8.38
2-2-2	U1424B-2H-2 41cm	6.66	U1425D-2H-2 61cm	8.47
2-2-3	U1424B-2H-2 67cm	6.92	U1425D-2H-2 91cm	8.77
2-3*	U1424B-2H-2 100cm	7.25	U1425D-2H-2 130cm	9.16
2-4*	U1424B-2H-3 9cm	7.84	U1425D-2H-3 45cm	9.81
2-4-2	U1424B-2H-3 32cm	8.07	U1425D-2H-3 73cm	10.09
2-5*	U1424B-2H-3 76cm	8.51	U1425D-2H-3 118.5cm	10.55
2-5-2	U1424B-2H-3 130.5cm	9.06	U1425D-2H-4 27cm	11.13
2-6*	U1424B-2H-4 22cm	9.47	U1425D-2H-4 67cm	11.53
2-6-2	U1424B-2H-4 39cm	9.64	U1425D-2H-4 92cm	11.78
2-7*	U1424B-2H-4 58.5cm	9.84	U1425D-2H-4 113cm	11.99
2-8*	U1424B-2H-4 107cm	10.32	U1425D-2H-5 9.5cm	12.46
3-1*	U1424B-2H-5 13.5cm	10.89	U1425D-2H-5 63.5cm	13.00
3-1-2	U1424B-2H-5 54.5cm	11.30	U1425D-2H-5 111cm	13.47
3-1-3	U1424B-2H-5 83.5cm	11.59	U1425D-2H-5 141.5cm	13.78
3-2*	U1424B-2H-5 112cm	11.87	U1425D-2H-6 27cm	14.13
3-2-2	U1424B-2H-5 144cm	12.19	U1425D-2H-6 62cm	14.48
3-2-3	U1424B-2H-6 11.5cm	12.38	U1425D-2H-6 80.5cm	14.67
3-2-4	U1424B-2H-6 25cm	12.51	U1425D-2H-6 98cm	14.84
3-3*	U1424B-2H-6 50cm	12.76	U1425D-2H-6 123cm	15.09
4-1*	U1424A-2H-5 38.5cm	13.86	U1425B-2H-5 85cm	16.21
4-1-2	U1424A-2H-5 79cm	14.26	U1425B-2H-5 132cm	16.68
4-1-3	U1424A-2H-5 116cm	14.63	U1425B-2H-6 29.5cm	17.15
4-1-4	U1424A-2H-5 143.5cm	14.91	U1425B-2H-6 61cm	17.47
4-2*	U1424A-2H-6 9cm	15.06	U1425B-2H-6 80cm	17.66
4-2-2	U1424A-2H-6 22cm	15.19	U1425B-2H-6 100.5cm	17.86

(Table 2.1 continued)

Dark layer No.	U1424 Position	U1424 CCSF-D_ Patched_ rev20170308 (m)	U1425 Position	U1425 CCSF-D_ Patched_ rev20170309 (m)
5-1*	U1424B-3H-2 68cm	16.74	U1425D-3H-3 140cm	19.99
5-1-2	U1424B-3H-2 82cm	16.88	U1425D-3H-4 2cm	20.11
5-2*	U1424B-3H-2 107cm	17.13	U1425D-3H-4 34cm	20.43
5-2-2	U1424B-3H-2 123cm	17.29	U1425D-3H-4 66cm	20.75
5-2-3	U1424B-3H-3 13.5cm	17.70	U1425D-3H-4 131cm	21.40
5-2-4	U1424B-3H-3 21cm	17.77	U1425D-3H-4 142cm	21.51
5-3*	U1424B-3H-3 38cm	17.94	U1425D-3H-5 12cm	21.71
5-4*	U1424B-3H-4 30cm	19.36	U1425B-3H-3 47cm	23.35
6-1*	U1424A-3H-2 22cm	19.82	U1425B-3H-3 73.5cm	23.62
6-1-2	U1424A-3H-2 45cm	20.05	U1425B-3H-3 109cm	23.97
6-1-3	U1424A-3H-2 55cm	20.15	U1425B-3H-3 122cm	24.10
6-2*	U1424A-3H-2 72cm	20.32	U1425B-3H-3 142cm	24.30
6-2-2	U1424A-3H-2 141cm	21.01	U1425B-3H-4 74cm	25.12
6-3*	U1424A-3H-3 25.5cm	21.35	U1425B-3H-4 108cm	25.46
6-3-2	U1424A-3H-3 51cm	21.61	U1425B-3H-4 126cm	25.64
6-4*	U1424A-3H-3 84cm	21.94	U1425B-3H-5 8cm	25.96
7-1*	U1424A-3H-4 120cm	23.80	U1425D-4H-2 23cm	28.46
7-1-2	U1424A-3H-4 145cm	24.05	U1425D-4H-2 51cm	28.74
7-1-3	U1424A-3H-5 17.5cm	24.27	U1425D-4H-2 82.5cm	29.05
7-2*	U1424A-3H-5 27cm	24.37	U1425D-4H-2 95cm	29.18
7-2-2	U1424A-3H-5 43cm	24.53	U1425D-4H-2 114cm	29.37
7-3*	U1424A-3H-5 132cm	25.42	U1425D-4H-3 35cm	30.08
8-1*	U1424B-4H-1 122cm	26.04	U1425D-4H-3 119cm	30.92
8-2*	U1424B-4H-2 43.5cm	26.75	U1425D-4H-4 74cm	31.97
8-2-2	U1424B-4H-2 67cm	26.99	U1425D-4H-4 99cm	32.22
8-3*	U1424B-4H-2 87.5cm	27.19	U1425D-4H-4 122.5cm	32.45
9-1*	U1424B-4H-3 15cm	27.97	U1425D-4H-5 48cm	33.21
9-2*	U1424B-4H-3 106cm	28.88	U1425D-4H-5 147cm	34.20
9-3*	U1424B-4H-4 88cm	30.20	U1425D-4H-6 118cm	35.41
10-1*	U1424B-4H-4 127.5cm	30.59	U1425B-4H-5 16cm	36.26
10-2*	U1424A-4H-2 64.5cm	31.15	U1425B-4H-5 91cm	37.01
10-3*	U1424A-4H-2 103cm	31.53	U1425B-4H-5 125cm	37.35
10-3-2	U1424A-4H-2 146cm	31.96	U1425B-4H-6 37cm	37.97
11-1*	U1424A-4H-3 22cm	32.22	U1425B-4H-6 56.5cm	38.16
11-1-2	U1424B-4H-6 24cm	32.55	U1425B-4H-6 85cm	38.45
11-2*	U1424B-4H-6 52cm	32.83	U1425B-4H-6 105cm	38.65
12-1*	U1424A-4H-4 73cm	34.21	U1425D-5H-2 138cm	39.94
12-2*	U1424A-4H-4 119cm	34.67	U1425D-5H-3 39cm	40.45
13-1*	U1424A-4H-5 29cm	35.27	U1425D-5H-3 109cm	41.15
13-2*	U1424A-4H-5 48cm	35.46	U1425D-5H-3 131.5cm	41.37
13-2-2	U1424A-4H-5 58cm	35.56	U1425D-5H-3 144cm	41.50
13-3*	U1424C-4H-5 68cm	35.81	U1425D-5H-4 19cm	41.75

(Table 2.1 continued)

Dark layer No.	U1424 Position	U1424 CCSF-D_ Patched_ rev20170308 (m)	U1425 Position	U1425 CCSF-D_ Patched_ rev20170309 (m)
14-1*	U1424B-5H-2 84cm	36.73	U1425D-5H-4 106cm	42.62
14-2*	U1424B-5H-2 108cm	36.97	U1425D-5H-4 145cm	43.01
14-3*	U1424A-4H-7 7cm	38.23	U1425D-5H-5 88cm	43.94
14-3-2	U1424B-5H-3 102cm	38.44	U1425D-5H-5 120.5cm	44.26
15-1*	U1424B-5H-3 116.5cm	38.59	U1425D-5H-5 136cm	44.42
15-2*	U1424B-5H-4 24cm	39.16	U1425D-5H-6 41.5cm	44.97
16-1*	U1424B-5H-4 69.5cm	39.62	U1425D-5H-6 83cm	45.39
16-2*	U1424B-5H-4 108cm	40.00	U1425D-5H-6 133cm	45.89
16-3*	U1424B-5H-5 65.5cm	41.08	U1425B-5H-5 141cm	47.41
17-1*	U1424A-5H-2 23.5cm	41.39	U1425B-5H-6 48.5cm	47.98
17-2*	U1424A-5H-2 131.5cm	42.47	U1425D-6H-2 101cm	49.46
18-1*	U1424A-5H-3 49cm	43.15	U1425D-6H-3 12cm	50.06
18-2*	U1424C-5H-3 79cm	44.00	U1425D-6H-3 86cm	50.80
18-2-2	U1424C-5H-3 91cm	44.12	U1425D-6H-3 97cm	50.91
18-2-3	U1424C-5H-3 100cm	44.21	U1425D-6H-3 106cm	51.00
18-2-4	U1424C-5H-3 123cm	44.44	U1425D-6H-3 132.5cm	51.27
19-1*	U1424A-5H-4 8cm	44.65	U1425D-6H-3 149cm	51.43
19-2*	U1424A-5H-4 80cm	45.37	U1425D-6H-4 49cm	51.93
20-1*	U1424B-6H-2 2cm	47.23	U1425B-6H-2 119cm	53.88
21-1*	U1424B-6H-2 25cm	47.54	U1425B-6H-2 142cm	54.11
21-2*	U1424B-6H-2 132.5cm	48.61	U1425B-6H-3 61cm	54.80
21-2-2	U1424B-6H-2 145cm	48.74	U1425B-6H-3 74cm	54.93
FF	U1424B-6H-4 10.5cm	50.39	U1425B-6H-4 99cm	56.68
GG'	U1424B-6H-5 109cm	52.88	U1425B-6H-5 125cm	58.44
GG″	U1424B-6H-6 42cm	53.71	U1425B-6H-6 45cm	59.14
HH	U1424A-6H-5 128cm	57.50	U1425D-7H-3 64cm	61.62
II	U1424B-7H-4 27cm	61.05	U1425D-7H-6 33.5cm	65.82
II'	U1424B-7H-5 16.5cm	62.45	U1425B-7H-5 25cm	67.52
JJ	U1424B-7H-6 32cm	64.10	U1425B-7H-6 13cm	68.90
KK	U1424A-7H-4 39cm	65.17	U1425B-7H-6 112cm	69.89
LL	U1424A-7H-5 2cm	66.30	U1425D-8H-2 140cm	70.70
MM	U1424A-7H-5 135cm	67.63	U1425D-8H-4 47cm	72.34
NN	U1424A-7H-6 98.5cm	68.77	U1425D-8H-5 6cm	73.44
OO	U1424B-8H-2 142.5cm	69.54	U1425D-8H-5 66cm	74.04
PP	U1424B-8H-3 136cm	70.97	U1425B-8H-3 33cm	75.25
QQ	U1424B-8H-4 112cm	72.23	U1425B-8H-4 28cm	76.70
RR	U1424B-8H-5 79cm	73.40	U1425E-9H-3 142cm	77.61
SS	U1424A-8H-5 52cm	75.79	U1425B-8H-7 16cm	81.34
TT	U1424B-9H-2 48.5cm	78.64	U1425D-9H-4 117cm	83.00
UU	U1424B-9H-3 139cm	81.04	U1425B-9H-3 116cm	86.66
VV	U1424B-9H-4 68cm	81.83	U1425B-9H-4 38cm	87.38
WW	U1424B-9H-5 34cm	83.36	U1425D-10H-2 139cm	89.30
XX	U1424A-9H-4 39cm	84.71	U1425D-10H-4 15cm	91.06
YY	U1424A-9H-5 65cm	86.60	U1425D-10H-6 103cm	94.12
ZZ	U1424A-9H-6 112cm	88.57	U1425B-10H-6 39cm	96.69
AAA	U1424B-10H-3 56cm	90.39	U1425D-11H-3 138.5cm	98.79

* Defined by Tada et al. (in revision)

Dark layer numbers are tentative, and will be changed by future work.

Table 2.2 List of correlation tie point between Sites U1424 and U1425 and estimated ages based on projection of LR04 tuned age model at Site U1424.

Dark layer No.	U1424 LR04 tuned Age (Ma)	U1424 CCSF-D_ Patched_ rev20170308 (m)	U1425 CCSF-D_ Patched_ rev20170309 (m)
0-1*	0.013	0.69	0.67
1-1*	0.024	1.21	1.75
1-1-2	0.030	1.45	2.08
1-2*	0.036	1.71	2.30
1-3*	0.047	2.16	2.66
1-4*	0.053	2.42	2.99
1-4-2	0.071	3.18	4.10
1-4-3	0.075	3.34	4.35
1-5*	0.084	3.74	4.85
1-5-2	0.090	3.99	5.14
1-6*	0.110	4.85	6.22
1-6-2	0.123	5.44	6.80
1-6-3	0.130	5.74	7.06
2-1*	0.141	6.07	7.72
2-2*	0.161	6.57	8.38
2-2-2	0.163	6.66	8.47
2-2-3	0.169	6.92	8.77
2-3*	0.177	7.25	9.16
2-4*	0.191	7.84	9.81
2-4-2	0.196	8.07	10.09
2-5*	0.207	8.51	10.55
2-5-2	0.220	9.06	11.13
2-6*	0.228	9.47	11.53
2-6-2	0.231	9.64	11.78
2-7*	0.234	9.84	11.99
2-8*	0.243	10.32	12.46
3-1*	0.258	10.89	13.00
3-1-2	0.271	11.30	13.47
3-1-3	0.280	11.59	13.78
3-2*	0.288	11.87	14.13
3-2-2	0.296	12.19	14.48
3-2-3	0.302	12.38	14.67
3-2-4	0.306	12.51	14.84
3-3*	0.313	12.76	15.09
4-1*	0.344	13.86	16.21
4-1-2	0.358	14.26	16.68
4-1-3	0.371	14.63	17.15
4-1-4	0.381	14.91	17.47
4-2*	0.386	15.06	17.66
4-2-2	0.391	15.19	17.86

(Table 2.2 continued)

Dark layer No.	U1424 LR04 tuned Age (Ma)	U1424 CCSF-D_ Patched_ rev20170308 (m)	U1425 CCSF-D_ Patched_ rev20170309 (m)
5-1*	0.444	16.74	19.99
5-1-2	0.449	16.88	20.11
5-2*	0.457	17.13	20.43
5-2-2	0.462	17.29	20.75
5-2-3	0.475	17.70	21.40
5-2-4	0.477	17.77	21.51
5-3*	0.483	17.94	21.71
5-4*	0.529	19.36	23.35
6-1*	0.544	19.82	23.62
6-1-2	0.553	20.05	23.97
6-1-3	0.556	20.15	24.10
6-2*	0.563	20.32	24.30
6-2-2	0.586	21.01	25.12
6-3*	0.595	21.35	25.46
6-3-2	0.601	21.61	25.64
6-4*	0.610	21.94	25.96
7-1*	0.661	23.80	28.46
7-1-2	0.669	24.05	28.74
7-1-3	0.676	24.27	29.05
7-2*	0.678	24.37	29.18
7-2-2	0.683	24.53	29.37
7-3*	0.710	25.42	30.08
8-1*	0.733	26.04	30.92
8-2*	0.760	26.75	31.97
8-2-2	0.767	26.99	32.22
8-3*	0.774	27.19	32.45
9-1*	0.800	27.97	33.21
9-2*	0.827	28.88	34.20
9-3*	0.868	30.20	35.41
10-1*	0.882	30.59	36.26
10-2*	0.906	31.15	37.01
10-3*	0.922	31.53	37.35
10-3-2	0.930	31.96	37.97
11-1*	0.935	32.22	38.16
11-1-2	0.941	32.55	38.45
11-2*	0.946	32.83	38.65
12-1*	0.974	34.21	39.94
12-2*	0.985	34.67	40.45
13-1*	1.004	35.27	41.15
13-2*	1.010	35.46	41.37
13-2-2	1.013	35.56	41.50
13-3*	1.021	35.81	41.75

(Table 2.2 continued)

Dark layer No.	U1424 LR04 tuned Age (Ma)	U1424 CCSF-D_ Patched_ rev20170308 (m)	U1425 CCSF-D_ Patched_ rev20170309 (m)
14-1*	1.049	36.73	42.62
14-2*	1.056	0.00	43.01
14-3*	1.091	38.23	43.94
14-3-2	1.097	38.44	44.26
15-1*	1.100	38.59	44.42
15-2*	1.112	39.16	44.97
16-1*	1.121	39.62	45.39
16-2*	1.139	40.00	45.89
16-3*	1.191	41.08	47.41
17-1*	1.205	41.39	47.98
17-2*	1.247	42.47	49.46
18-1*	1.265	43.15	50.06
18-2*	1.288	44.00	50.80
18-2-2	1.292	44.12	50.91
18-2-3	1.295	44.21	51.00
18-2-4	1.301	44.44	51.27
19-1*	1.308	44.65	51.43
19-2*	1.329	45.37	51.93
20-1*	1.411	47.23	53.88
21-1*	1.421	47.54	54.11
21-2*	1.455	48.61	54.80
21-2-2	1.458	48.74	54.93
FF	1.494	50.39	56.68
GG'	1.535	52.88	58.44
GG″	1.571	53.71	59.14
HH	1.699	57.50	61.62
II	1.793	61.05	65.82
II'	1.860	62.45	67.52
JJ	1.899	64.10	68.90
KK	1.941	65.17	69.89
LL	1.997	66.30	70.70
MM	2.062	67.63	72.34
NN	2.112	68.77	73.44
OO	2.147	69.54	74.04
PP	2.196	70.97	75.25
QQ	2.238	72.23	76.70
RR	2.284	73.40	77.61
SS	2.357	75.79	81.34
TT	2.461	78.64	83.00
UU	2.540	81.04	86.66
VV	2.567	81.83	87.38
WW	2.609	83.36	89.30
XX	2.654	84.71	91.06
YY	2.714	86.60	94.12
ZZ	2.755	88.57	96.69
AAA	2.792	90.39	98.79

*From Tada et al. (in revision).

Dark layer numbers are tentative, and will be changed by future work.

Ages are calculated from the LR04 tuned age model for Site U1424 (Tada et al., in revision).

3. Towards quantitative elemental measurement using ITRAX XRF core scanner

In order to reconstruct Quaternary oceanographic variability recorded in centimeter- to decimeter-scale alternations of dark and light layers in the Japan Sea sediments, ITRAX XRF core scanner is used to measure elemental variability of the sediments with high-resolution. In this Chapter, I describe an attempt to establish quantitative measurement method of major and minor elements using ITRAX XRF core scanner installed in Kochi University. The machine is newly installed in 2014 and a method for systematic and efficient measurement was established in this study. Since ITRAX is usually used for semi-quantitative analysis of elements (Rothwell and Croudace, 2015b), it is necessary to establish a quantitative analytical method by myself.

3.1 The ITRAX core scanner

ITRAX is XRF (X-ray fluorescence) core scanner manufactured and sold by COX Analytical Systems (Croudace et al., 2006). It has an advantage to measure elemental abundance in sediment cores in non-distractive manner. Optical image, radiograph image, and XRF spectrums can be obtained simultaneously from the same core. Flat beam technics developed for ITRAX core scanner enable us to obtain high-resolution radiograph and XRF measurement with the highest resolution of 0.2mm, which is same as the X-ray beam width (Croudace et al., 2006). Long (up to 180cm) and thick (up to 12cm diameter) samples such as half-round core and U-channel samples could be measured directly with ITRAX (Croudace et al., 2006). Owing to high intensity X-ray beam, measurement time of ITRAX is short for XRF analysis compared to other XRF core scanner.

Conventionally, WD-XRF (wavelength-dispersive X-ray fluorescence), which needs time-consuming sample preparation (Croudace et al., 2006), is used to analyze element composition of discrete sediment samples. For conventional XRF analysis, samples are dried and grinded, then pressed to make pellets or fused to make glass beads. On the other hand, ITRAX is ED-XRF (energy-dispersive X-ray fluorescence), which have an advantage of

short measurement time, but usually result in less quantitative compare to WD-XRF. In addition, since ITRAX adopts non-destructive analytical method, it is more easily affected by particle size, porosity and water content variations (Croudace et al., 2006; Kido et al., 2006). Also, because ITRAX is focused on high spatial resolution measurement, excitation volume of the XRF measurement is small, which resulted in smaller counts for XRF spectra. Therefore, advantages of ITRAX, non-destructive, speedy and high-resolution measurement, are counterbalanced by disadvantages such as less quality (higher measurement error and lower precision) of XRF data compared to conventional WD-XRF method. In order to compare ITRAX XRF results and WD-XRF results, as an example, samples taken from same Mediterranean sediment core (archive half for ITRAX measurement and discrete samples for WD-XRF measurement) are measured (Croudace et al., 2006). Although results from two measurements do not have exact constant relationship, they show similar down core variation patterns of element concentrations (Croudace et al., 2006). Therefore, ITRAX is usually used for semi-quantitative elemental composition analysis to obtain, for example, down core element profiles.

Some of previous studies focused on quality improvement of XRF data obtained by ITRAX (Weltje and Tjallingii, 2008; Weltje et al. 2015; Ohlendorf et al., 2015). ITRAX have three generations, prototype, second generation, and third generation. The prototype ITRAX output data is integral of peak area for each element calculated from XRF spectra, but data output system is improved in second-generation ITRAX, in which peak area could be calculated to quantity of element concentrations (Croudace et al., 2006). The calculated element concentrations show down core variation pattern similar to that based on WD-XRF results, but the two data do not have exact one to one relationship (Croudace et al., 2006). In order to solve this problem, log-ratio calibration model is proposed (Weltje and Tjallingii, 2008; Weltje et al. 2015). Log-ratio calibration has an advantage over the linear calibration because theoretically, log-ratio of peak area counts has linier relationship with log-ratio of concentrations, even when matrix effect and specimen effect (measurement geometry and specimen homogeneity) existed (Weltje and

Tjallingii, 2008; Weltje et al., 2015). By further developing this method, Weltje et al. (2015) proposed multivariate calibration algorithm using log ratios. Using data obtained from marine sediment core, they also demonstrated the concentration calculated using multivariate method has higher correlation with concentration measured by conventional method (WD-XRF and ICP-AES), compared to concentration calculated by calibration equation obtained by linear correlation (Weltje et al., 2015). Although their method could improve correlation and thus quality of analytical results, number of replicate XRF scanning and large number of measurement of discrete sample for various elements including replicate measurement is necessary for the method (Weltje et al., 2015). Therefore, more practically, many studies use peak area counts as semi-quantitative method.

Ohlendorf et al. (2015) shows aging effect of X-ray tube causes significant decrease of intensity of XRF spectra and peak area counts of each element calculated from XRF spectra. They pointed out that the aging effect might lead to misinterpretation of down core variation of element concentration, especially when the entire period of ITRAX measurement is long. However, correction method of this effect is not well established (Ohlendorf et al., 2015) because long sediment cores are rarely measured in previous studies (Rothwell and Croudace, 2015a and reference therein).

In this study, ITRAX installed in Center for Advanced Marine Core Research, Kochi University is used. The ITRAX was installed in the autumn of 2014, and I started ITRAX measurement for this study from the summer of 2015. Since ITRAX is generally used for a semi-quantitative analysis, and the ITRAX in Kochi University is the only machine installed in Japan, no technical knowledge existed to conduct quantitative analysis. In addition, approaches for quantitative analysis is rare in previous studies (Weltje and Tjallingii, 2008; Weltje et al. 2015; Ohlendorf et al., 2015). In order to ensure data quality for this study, I collected basic data about measurement settings, X-ray tube aging effect, and measurement precision of the ITRAX with the help of a technical person in Center for Advanced Marine Core Research, Kochi University. The results of the basic tests (test

measurements in order to obtain basic data to decide measurement settings, and standard sample measurement to obtain basic data for X-ray tube aging effect, measurement precision, and quantitative capability) are summarized in following sections, and quality of ITRAX measurement results will be improved using the basic test results.

3.2 ITRAX measurement procedure and settings

3.2.1 Materials used in this chapter

Archive-half of cores recovered during IODP Exp. 346 were used for ITRAX measurement (see chapter 2 in this paper for sample detail). To define measurement settings in 3.2.3 of this paper, three archive halves (U1425D-1H-2A, U1425B-1H-4A, and U1425B-1H-5A) were used for test measurements.

In order to monitor aging effect (3.3 in this paper) and measurement precision (3.4 in this paper) of ITRAX in Kochi University, standards made from the Japan Sea sediment are measured. "The Japan Sea sediment standard samples" were made from the Japan Sea sediments of four characteristic lithofacies, and named "light-layer", "dark-layer", "calcareous", and "siliceous" (Karasuda, personal communication). Each sample was dried, homogenized and pressed to make a pellet (Karasuda, personal communication). General homogeneity of pressed standards in cm-scale was checked prior to this study by measuring three different areas of each standard using ITRAX, and all four standards are well homogenized in cm-scale (Kurokawa, personal communication).

Reference glass provided by COX Analytical Systems as standard ITRAX accessory to monitor ITRAX measurement condition is also used for basic analytical test.

In 3.5 in this paper, seven commercially available sediment standard reference materials were measured by ITRAX to estimate element concentration from peak area counts calculated from XRF spectra (Table 3.1). These standard reference materials were provided as fine powder, and pressed to make pellets before measurement. Pressed power is 20 tons. The Br concentrations of the Japan Sea sediments are high (up to more than 100

ppm), thus concentrations of Br in commercially available standard reference materials (up to 60 ppm) are not high enough to cover the concentration range of Br suitable for the Japan Sea sediments. So, I prepared additional reference materials by adding KBr to JG-1 (standard reference material that contains only small amount of Br (0.068ppm, Table 3.1)) to construct calibration curve for Br up to 500 ppm. To make KBr added standard reference materials, commercially available small (a few millimeter in diameter) KBr crystals were crushed by multi-beads shocker (Yasui kikai) to make powder. Then, crushed KBr powder was mixed with JG-1 powder using multi-beads shocker, and pressed to make pellets.

3.2.2 ITRAX basic measurement procedure

The surface of an archive-half core was scraped using plastic card to make the surface flat and smooth just before measurement. As surface condition could affect ITRAX measurement, sediment surface was carefully observed before measurement, and any crack or roughness was described. Sediment surface was covered with thin plastic film provided by COX Analytical Systems as standard accessory for ITRAX, to prevent sediment surface from desiccation. This thin film was not used for dried material, for example, reference glass and pressed pellet. Although ITRAX operation detail is basically same as is described in Croudace et al. (2006), measurement procedure is briefly summarized as below.

Firstly, ITRAX obtain optical image of the core surface and measure surface smoothness using laser triangulation system (Croudace et al., 2006). Measured surface smoothness is used to fit XRF detector close to the sediment surface during XRF measurement that will be conducted later. Then, after semi-automated tunings (about radiograph X-ray energy and peak area calculation parameter from XRF spectra, details are not shown) are finished, user sets the measurement interval, step size, measurement time and number of elements used for peak area count calibration from XRF spectra (detail will be described later). After that, radiographic image is taken and then XRF spectrum from 1.0 to 18.0 keV (Fig. 3.1) is obtained. After the measurement, the software automatically calculates peak area

counts of each element (for elements set by user before measurement) from the XRF spectrum (Fig. 3.1).

3.2.3 Define ITRAX measurement settings for this study

For all XRF measurement by ITRAX used in this study, Mo X-ray tubes were used under the settings of 30kV and 55mA energy. As described above, the user have to set step size and measurement time for XRF analysis, and elements to be calculated from XRF spectra before the measurement. To set most suitable step size for this study, I conducted test measurements using four step sizes, 0.2mm, 1mm, 2mm, and 5mm. To illustrate the difference of four setting, Fig. 3.2 shows results of Br measurements for the interval U1425D-1H-2A 60 - 120cm as an example. Br is concentrated in dark layers (Fig. 3.2; see also chapter 4 in this paper for interpretation). For example, sharp Br difference across the dark and light layer boundary around 1160mm is detected clearly by 0.2mm, 1mm and 2mm step size measurement, but not clear in 5mm step size measurement (Fig. 3.2). Therefore, the step size resolution of 5mm is not fine enough for detecting sharp elemental gradient observed at the boundary of dark and light layers. Thus, 5mm step size is not enough to characterize distinct dark and light layers of the Japan Sea sediments and 0.2mm, 1mm, or 2mm step size is suitable for this study (Fig. 3.2).

Four measurement times, 4s, 10s, 20s, 100s were also tested to define optimum measurement time. The results of 4s measurement and 10s measurement are shown in Fig 3.3. XRF spectra of 4s measurement sometimes show 0 count and background show odd shape that looks different from typical background shape of XRF spectra at around 3 keV (Fig. 3.3a). Also, XRF spectra of 4s measurement is not smooth enough for elemental peak calculation compared to 10s measurement (Fig. 3.3). Results of 20s and 100s measurement show smoother XRF spectra, but difference from 10s measurement is not large compare to 4s measurement. From these results, 4s measurement time is too short to obtain enough XRF counts, and 10s, 20s, 100s measurement time is suitable for this study (Fig. 3.3).

Thus, step size of 0.2mm, 1mm, or 2mm and measurement time of 10s, 20s,

or 100s is suitable for this study (Fig. 3.2 and 3.3). To minimize measurement time under the constraint of high enough data quality to characterize distinct dark and light layers of the Japan Sea sediment, measurement condition of "2mm step size" and "10s measurement time" was selected.

Based on the results of test measurements, I selected 27 elements for default peak area calculation from XRF spectra (Fig. 3.1). Basically, elements which are included in default settings of ITRAX software and also detectable in XRF spectra obtained from the Japan Sea sediment ware selected. Among 27 elements selected, 21 elements satisfied above two conditions, and 6 elements (P, As, Ba, Ta, W, Pb) only satisfied one of two requirements. P and Ba are included in default settings of ITRAX software, but peaks are not obvious in XRF spectra probably because intensity is small and large peak is existed close to the peak (Fig. 3.1). As, Ta, W, and Pb are not included in default settings of ITRAX software, but their peaks are obviously detectable in the XRF spectra (Fig. 3.1). In addition, Ba and Pb were reported as detectable elements in marine sediments by ITRAX according to the ITRAX machine development and review literatures (Croudace et al., 2006; Rothwell and Croudace, 2015b). Therefore, 27 elements (Al, Si, P, S, Cl, Ar, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Br, Rb, Sr, Y, Zr, Ba, Ta, W, Pb) at least satisfied one of two requirements were selected in this study.

3.3 Aging effect of an X-ray tube

3.3.1 X-ray tube aging

Intensity of XRF spectra, and thus peak area value of each element, is basically proportional to the concentration of each element. However, it also depends on the intensity of X-ray beam generated by an X-ray tube. It is reported that X-ray beam intensity gradually decreases and peak area value of each element also decreases with the aging of an X-ray tube (Nakai, 2005; Ohrendorf et al., 2015). This aging effect is significant when measurement period ranges long time. For example, many sediment cores covering a long sedimentary sequence are analyzed, or measurement period is separated

into several intervals. However, little attention has been paid on the aging effect of an X-ray tube in previous studies mainly because analysis of long (>100m) sediment sequence is rare. Ohlendorf et al. (2015) reported the aging effect of an X-ray tube in case of an ITRAX core scanner. To monitor aging effect, they measured a reference glass of known composition after each core run. They reported that heavier elements (Sr, Zr) are more affected by aging effect compared to lighter elements (Si, Ca, Fe). They also reported that Mo coh (coh= coherent scatter at the same energy as the tube anode radiation by Rayleigh scattering) and Mo inc (inc= incoherent scatter at a lower energy than the tube anode radiation by Compton scattering) is decreased by the ratios similar to those of heavier elements (Ohrendorf et al., 2015). Based on these observations, they proposed that aging effect of heavier elements (Sr, Zr) could be canceled by dividing element peak area by Mo coh or Mo inc peak area. For lighter elements (Si, Ca, Fe), they proposed to use element ratios with comparable atomic numbers of which aging effect is similar (e.g., Si/Ti ratio, sometimes interpreted as a proxy of biogenic silica content; Rothwell and Croudace, 2015b) in order to cancel the aging effect (Ohrendorf et al., 2015).

In this study, I correct aging effect because measurement period is long up to a half year for one site. Also, in the previous study, aging effect is reported for only five elements (Si, Ca, Fe, Sr, Zr; Ohrendorf et al., 2015), which are not enough in this study in which other elements also will be discussed.

3.3.2 Monitoring aging effect

Aging effect of a Mo X-ray tube was monitored by measuring the Japan Sea sediment standard samples at time intervals of a week to a few months (Table 3.2). U1425 cores (85 sections, 120.5m in total) were measured using the first X-ray tube (Table 3.4). The first Mo X-ray tube was lasted for 5663 hours in total. The second Mo X-ray tube was installed just before measurement of U1424 cores (102 sections, 144.0m in total; Table 3.3), and used for other studies until summer of 2017.

Pressed pellets of the Japan Sea sediment standard samples of 2cm in diameter were measured by ITRAX at 0.2mm interval, for 15 lines, with 32s

measurement time. The measurement was repeated five times. All the results for each standard are averaged and standard deviations are calculated. Since all the results of four Japan Sea standard samples show the same decreasing trend caused by X-ray tube aging effect (Mitake, personal communication), and light-layer standards are measured most frequently, results of light-layer measurement (Table 3.2) is shown in this chapter. The results of the light-layer measurement are shown in Fig. 3.4. In Fig. 3.4, peak area counts of each elements plus standard deviation are plotted against operating time of X-ray tubes. Aging effects of 27 elements plus Mo inc and Mo coh are monitored (Fig. 3.4).

In Fig. 3.4, some elements show different trend from the other elements as X-ray tube ages. In case of W, an increase in W counts is observed with the increase in X-ray tube operating time (Fig. 3.4z). The filament inside an X-ray tube is composed of W, and it is known that W is gradually evaporated and coated inside an X-ray tube, and W peak area in XRF spectra increases as X-ray tube ages (Nakai, 2005; Ohrendorf et al., 2015). Therefore, the increase in W counts resulted from another effect of tube aging, showing that aging effect is not simply the decrease in X-ray intensity as tube aging. Ta counts also shows a trend similar to that of W counts (Fig. 3.4y and 3.4z). This is possibly because Ta peak is overlapped with W inc (Compton scattering) peak. Thus, Ta counts could be contaminated with W inc count due to W coating effect inside an X-ray tube (Fig. 3.4y). It is also reported that Cr is sometimes observed as an impure line of X-ray spectra radiated from X-ray tube (Nakai, 2005). Fig. 3.4k shows Cr counts decreases with the increase in tube age in case of the 1st Mo X-ray tube reflecting the decrease in X-ray intensity due to the aging effect of an X-ray tube. On the other hand, Cr counts increases with the increase in tube age in the 2nd Mo X-ray tube. This indicates an impure line of Cr is observed only in the 2nd X-ray tube (Fig. 3.4k). Ar counts is also increasing only in the 2nd Mo X-ray tube (Fig. 3.4f). An impure line of Ar has not been reported in the literature, thus reason of Ar counts increase is not clear. However, Ar counts mainly reflects Ar in the air between a sample surface and a XRF detector, thus Ar counts do not reflect element variability in the sediments. Therefore, aging effect of

Ar is not important because Ar counts are not used to interpret element variability in sediment cores. Therefore, W, Ta, Cr and Ar counts are not used for discussion in this study.

For the other elements and Mo coh and Mo inc, counts are decreasing with time as a result of decreasing X-ray intensity due to the X-ray tube aging (Fig. 3.4). Since the age of the second Mo X-ray tube was still relatively young at the time when I finished measurement, the aging effect is not significant especially in lighter elements for the second Mo X-ray tube (Fig. 3.4).

Consequently, measurement results of the first Mo X-ray tube are used for evaluating the aging effect in this chapter. Fig. 3.5 shows the percentage of decrease in counts during 1st X-ray tube lifetime for 17 elements, of which standard deviation is less than 10%. The percentages of decreases in counts for each element are calculated by the counts at the end of X-ray tube lifetime (5636 hours) divided by the counts near the beginning of the tube installation (661 hours). Fig. 3.5a shows a result of the percentage of decrease in counts during lifetime versus atomic number for 17 elements. Overall trend especially for lighter elements is similar to the trend previously reported by Ohrendorf et al. (2015), although the percentages are shifted to higher value (Fig. 3.5a). The reason for this difference may have arose from the difference in X-ray tube lifetime or the tube voltage used. Alternatively, X-ray tube intensity already had decreased within the first 661 hours of the measurement. For heavier elements, the percentages of decrease in counts do not have good correlation with atomic number (Fig. 3.5a).

To further examine the reason why the percentages of decrease in counts do not have good correlation with atomic number, percentages of decrease in counts are plotted against energy of the main peak of each element on XRF spectra (Fig. 3.5b). For three elements (Rb, Sr, Zr) examined in this study, both K line and L line are observed in the XRF spectra. Thus, the decreasing percentages of counts for these three elements are affected by both K line and L line. In other words, decreasing percentages of counts for these three elements are sum of K line decreasing percentages and L line decreasing

percentages. For these three elements, calculated decreasing percentage of counts are plotted for two energies, K line energy and L line energy (Fig. 3.5b). Fig. 3.5b shows percentages of decrease in counts are decreasing with the increase of energy. Using the trend of black plots obtained from elements which only K line or L line was observed, elements for which both K line and L line were observed (Rb, Sr, Zr) show mean value percentage estimated from K line's energy and L line's energy (Fig. 3.5b). For example, percentages of decrease in counts of Rb is estimated as around 70% for Rb K-line energy (13.3 keV), and estimated as around 50% for Rb L-line energy (1.7 keV; Fig. 3.5b). Based on these results, I found that the difference in percentages of decrease in counts during Mo X-ray tube lifetime is depending on energy, not atomic number as was suggested in previous study (Ohlendorf et al., 2015).

3.3.3 Correction of aging effect

Ohrendorf et al. (2015) proposed that the peak area counts of an element divided by Mo coh counts is an effective way to correct for the aging effect for heavier elements. So, I calculated element/Mo coh ratios of light-layer results and compare it with X-ray tube operation time to see for which elements this method is applicable (Fig. 3.6). Mo coh is used because it is proposed as reflecting X-ray beam intensity, whereas Mo inc is also affected by other factors such as water content, organic matter content, and porosity of sediment (Ohrendolf et al., 2015). Fig. 3.6 shows results of light-layer measurement, where each element counts are divided by Mo coh counts. Aging effect on Br, Rb and Sr is cancelled by dividing by Mo coh counts within analytical error, but aging effect on other elements remains (Fig. 3.6). The reason is that percentage of decrease in counts during tube lifetime for Mo coh is 55±1%, which is close to the value of Br (52±3%), Rb (59±4%), and Sr (59±3%), whereas the value is more than 60% for the other elements (Fig. 3.5). Therefore, Br / Mo coh ratio, Rb / Mo coh ratio, Sr / Mo coh ratio could be used for correction of aging effects, however, this method can not be applicable for the other elements (Fig. 3.6).

Another method for correcting aging effect is monitoring the decreasing rate of an element counts by measuring the standard samples, and correct

aging effect of samples using monitored decreasing rate for each element. From the results shown in Fig 3.4, the decreasing rate of an element counts by aging effect at each tube operating time can be calculated for each element. Using the calculated results, aging effect on the measured element counts for each sample can be corrected.

In this paper, aging effect is corrected using the monitored decreasing rate of counts for each element calculated from light-layer results, because the method divided by Mo coh is applicable to only a few elements. In the early stage of 2nd Mo X-ray tube lifetime, five times standard measurements during 5664 to 6287 hours (equal to 1 to 624 hour of 2nd Mo X-ray tube lifetime; Table 3.2) show relatively small variability, and results of five measurement are the same within analytical errors for most of the elements (Fig. 3.4). Therefore, in this paper, I use the average of the five measurements conducted during this period (1 to 624 hour of 2nd Mo X-ray tube lifetime; Table 3.2) as the initial counts obtained by new X-ray tube that are not affected by aging effect. Since all U1424 cores were measured during this period (Table 3.3), aging effect should be negligible for U1424 cores. On the other hand, U1425 cores were measured during five different periods (1394 - 1444 hour, 1674 - 2026 hour, 2888 - 2957 hour, 3676 - 3951 hour, and 4016 - 4060 hour of 1st X-ray tube lifetime; Table 3.4). Between 661 and 2980 hour, no measurement was conducted for the Japan Sea sediment standard samples (Table 3.2; Fig. 3.4). Since reference glass measurements conducted by staffs of Kochi University during this period show relatively constant decreasing rate of counts (Yagyu, personal communication), I use linear regression of counts versus tube operation time between 661 and 2980 hour, which include three of five measurement intervals of U1425 cores (Table 3.4). Since measurement results of the Japan Sea sediment standard samples between 3667 and 4009 hour is constant within errors, average of these the Japan Sea sediment standard samples measurement results are used to correct for aging effects for the other two measurement intervals of U1425 cores (3676 - 3951 hour, and 4016 - 4060 hour; Table 3.4). For calculations to correct for aging effect, light-layer standard measurement results are used for all elements except Ca and Sr, because monitored aging effect is the same

for four Japan Sea standards (Mitake, personal communication) and light-layer is measured most frequently. For Ca and Sr, measurement results of calcareous standard are used for correction of aging effect because their analytical errors are large in light-layer measurement due to low contents of these elements, whereas the errors are small in calcareous standard (Fig. 3.7).

3.4 Evaluation of ITRAX measurement precision from repeated measurement

To evaluate analytical error of ITRAX measurement, repeated measurement of the Japan Sea standard samples, which were also used for aging effect monitoring, was conducted using ITRAX. Fifteen areas (each area is 0.2mm × 8mm, equal to X-ray beam size) on each standard sample were measured five times (Fig. 3.8). Although homogeneity of standard samples in cm-scale was checked prior to this study (Kurokawa, personal communication), I further checked homogeneity in 0.2mm scale, by comparing measurement results of 15 different areas on the same standard sample (Fig. 3.8), because fine scale homogeneity could affect variability of the analytical result of repeated measurement. From the results, I found there were element count variations up to several times of count difference depends on each area in the same standard sample in 0.2mm scale. Thus, in order to evaluate precision of ITRAX repeated measurements which not affected by sample inhomogeneity, measurement was repeated five times for each of the 15 areas and the results of five times repeated measurements were averaged for each area. Therefore, results from 15 areas are treated separately, and averaged five times repeated measurement results for each area is not affected by sample inhomogeneity. The five times repeated measurements were conducted eleven times (Feb. 3rd, 12th, 16th, 29th, Mar. 8th, 14th, 21st, Aug. 23rd, 24th, Sep. 13th, 20th in 2016) for four Japan Sea standard samples.

Fig. 3.9 shows the results of repeated measurements of four standard samples described above. In Fig. 3.9, average (horizontal axis) and standard deviation (vertical axis) of peak area counts of five times repeated

measurements that are 165 (15 areas measured at different eleven days) in total for each standard sample are plotted. Total average of "peak area average (horizontal axis)" and "standard deviation (vertical axis)" of 165 measurements for each standard sample is also shown in Fig. 3.9. Due to X-ray tube aging effect, averaged counts of 165 measurements are separated into two clusters for some elements (Si, Cl, K, Ca, Ti, Mn, Fe, Ni, Zn, Br, Rb, Sr, Zr, W, Mo inc, and Mo coh). One cluster is composed of the data measured by 1st Mo X-ray tube when it was close to its tube lifetime (Feb. 3rd, 12th, 16th, 29th, Mar. 8th, 14th, 21st, and Aug. 23rd in 2016, when tube operating time was 3667 to 5636 hours) and other cluster is composed of the data measured by 2nd Mo X-ray tube when X-ray tube was relatively new (Aug. 24th, Sep. 13th, 20th in 2016, when tube operating time is 1 hour to 624 hour). The results are separated into four clusters in case of W (Fig. 3.9z).

Theoretically, standard deviation of the peak area counts of elements obtained by ITRAX XRF measurement can be described as follows (Croudace et al., 2006; Nakai, 2005).

standard deviation = $\sqrt{N}$

N: measured peak area counts

Although Croudace et al. (2006) suggests to use this theoretical value for measurement precision of the ITRAX, they also propose other potential error sources such as surface condition of samples. In XRF measurements, experimentally, the measurement is reliable if its measured standard deviation is roughly less than $2*\sqrt{N}$ (Nakai, 2005). To check this reliability, theoretical line (standard deviation (vertical axis) = $\sqrt{N}$, $2\sqrt{N}$, and $3\sqrt{N}$, N = peak area counts (horizontal axis)) were drawn in Fig. 3.9 for comparison. For most of the elements, averages are plotted below $2\sqrt{N}$ line. However, for elements whose peak area counts are small (<500 counts) (P, V, Cu, Ga As, Y, Ba, Ta, Pb), standard deviations are larger than $2\sqrt{N}$ (Fig. 3.9). Exception is Zr, which has larger peak area counts compared to above nine elements, but its standard deviation is larger than $2\sqrt{N}$ (Fig. 3.9w). Further study is necessary to check their precision for these ten elements when larger counts are obtained in the measurement. For Si (Fig. 3.9b), Cl (Fig. 3.9e), and K (Fig. 3.9g), average of standard deviation is as small as theoretical value, $\sqrt{N}$.

From the five times repeated measurement results shown in Fig. 3.9, I conclude standard deviation of peak area count is different depend on elements.

In this study, I define standard deviation for each element as follows.

$\sigma = \alpha_{element}\sqrt{N}$

σ: standard deviation of peak area count, $\alpha_{element}$: factor specific to each element, N: measured peak area counts

$\alpha_{element}$ was calculated for each element based on the following procedure. First, average count and standard deviation are calculated for five times repeated measurements for each area. Then, standard deviation is divided by square root of averaged counts for each five times repeated measurement to calculate factor "a ($a = \sigma / \sqrt{N}$ for each repeated measurement (165 times in all), $\alpha_{element}$ = average of a)". Then all factor "a" were averaged for each element to calculate $\alpha_{element}$ (Table 3.5). σ for each element calculated from $\alpha_{element}$ is also shown in Fig. 3.9. σ value will be used as standard deviation of peak area counts obtained by sample measurement for following chapter in this paper.

3.5 Estimation of element concentration

To estimate element concentration from peak area counts measured by ITRAX, pressed standard reference materials and KBr added standard reference materials (see 3.2.1 in this chapter and Table 3.1 for detail) were measured by ITRAX using the same settings as for the measurement of the Japan Sea standard samples described in section 3.4 (Fig. 3.8). Each of fifteen areas were measured five times, all results (15 × 5 = 75 results) were averaged, and standard deviations of 75 results were calculated for each standard reference materials and KBr added standard reference materials to obtain a calibration curve for each element. Average counts and standard deviation measured by ITRAX for standard reference materials are shown in Fig. 3.10. Calibration line for each element calculated from these results is also shown in Fig. 3.10. Among 27 elements measured by ITRAX, Cr, W, Ta are excluded from discussion because impure lines of these elements from X-ray tube are also contributed to the peak area counts of these elements. Ar

is also excluded because there is no standard reference material with certificated value of Ar. Among the other 23 elements, correlation coefficient (r^2) is more than 0.9 for 16 elements, whereas r^2 is less than 0.9 for seven elements (Al, Cl, Zn, Ga, Sr, Zr, Pb) mainly due to small counts or high variability of plotted data (Fig. 3.10). Therefore, relationship between counts and concentration is confirmed for these 16 elements (Si, P, S, K, Ca, Ti, V, Mn, Fe, Ni, Cu, As, Br, Rb, Y, Ba) within concentration range which standard reference materials are covered (Fig. 3.10). Linear relationship between peak area counts and concentrations for these elements may suggest difference of matrix between seven standard reference materials (marine sediment, lake sediment, river sediment, and granodiorite; see Table 3.1 for detail) is negligible.

The average counts and standard deviation measured by ITRAX for KBr added standard reference materials are shown in Fig. 3.11. Since Br counts of each 15 area in same pressed standard sometimes have large difference, it turned out that the KBr added standard reference materials were not homogenized enough. Because of this inhomogeneity, the standard deviations of Br counts are large (Fig. 3.11). However, slope of the regression line is the same as that for standard reference materials, and a clear linear relationship is observed between counts and concentration of Br (Fig. 3.11).

Peak area counts of light elements are easily affected by water content of sediments and thin water film between the sediment surface and plastic wrap, because low energy fluorescence is easily absorbed by water (e. g., Kido et al., 2006; 2007). Standard reference materials are prepared in the form of pressed dry powder, whereas core samples measured in this study are in wet condition with 40-75 wt. % of interstitial water (Tada et al., 2015c, 2015d). To check water absorption effect, element concentrations of discrete samples obtained from U1425 cores were measured by conventional XRF method (Kurokawa, personal communication), and the results are compared with ITRAX results of U1425 cores from exactly the same intervals as those of samples analyzed by conventional XRF method. The results of comparison for elements Ca, Ti and Fe revealed the difference between calibration curves obtained for dry samples (constructed based on comparison between

ITRAX measurement of pressed standard reference materials and their certificated concentration values) and those for wet samples (constructed based on comparison between ITRAX measurement of wet U1425 cores and conventional XRF measurement of discrete samples from U1425 cores) (Fig. 3.12). The difference may come from absorption of X-ray fluorescence by interstitial water of core samples, or by thin water film formed between the sediment surface and plastic wrap, or plastic wrap itself (Kido et al., 2006). Further analysis is necessary to specify the reason of this difference, and also to observe difference of dry and wet conditions for other elements. Therefore, ITRAX measurement results of U1424 and U1425 cores in this study is expressed as peak area counts, and relationship between peak area counts and concentration of element will be taken into account in discussion of this study.

3.6 Summary

In this Chapter, method of ITRAX measurement, their precision and potential for quantitative analysis were discussed. First, ITRAX settings for core measurement were defined from test measurements as 2mm step size, 10s measurement time, and 27 elements to be calculated from XRF spectra. Since aging effect of X-ray tube should be taken into account in case of long-term measurement, aging effect of X-ray tube was monitored and correction method for the aging effect was established. For Br, Rb and Sr, aging effects can be cancelled by dividing peak area counts of each element by Mo coh counts (Fig. 3.6). However, this method cannot be applied to other elements. Another way to make correction for aging effect is using decay curves. In this study, decay curves were obtained by measuring the Japan Sea standard samples (Fig. 3.4), and used for correcting X-ray tube aging effect for U1425 core measurement results, which are also used in the following chapter of this paper. Precision of the ITRAX XRF measurement (10s measurement time) is estimated from five repeated measurements of the Japan Sea sediment standard samples, and standard deviation of ITRAX measurement is calculated for each elements (Fig. 3.9, Table 3.5). Standard reference materials were used to establish calibration equation for each

element to estimate their concentrations from peak area counts. Calibration equations for 16 elements are established for dry sediment (Fig. 3.10). However, in case of wet sediments, XRF absorption effect by water is not negligible especially for light elements (Fig. 3.12). Therefore, in this study, results of core measurement by ITRAX are presented as peak area counts, and relationships between peak area counts and element concentrations will be taken into account in discussion of following chapters.

Fig. 3.1 XRF spectrum of U1425D-1H-2A taken during test measurement. Black line: Sum spectrum from 737 spectra measured from U1425D-1H-2A (2mm, 10s). Red line: result of peak fitting used for peak area calculation. Green line: background. Main peak for 27 selected elements in this study is shown by arrows.

Fig. 3.2 Results of Br counts of U1425D-1H-2A 60-120cm measured by ITRAX in four different settings. (a) 0.2mm step size, 4s measurement time, (b) 1mm step size, 20s measurement time, (c) 2mm step size, 10s measurement time, (d) 5mm step size, 100s measurement time. Photograph of measured interval (color contrast is enhanced) is also shown.

Fig. 3.3 XRF spectrum of U1425D-1H-2A 63cm with measurement time 4s (a) and 10s (b). Black line: XRF spectrum measured from U1425D-1H-2A 63cm. Red line: peak fitting for peak area calculation. Green line: background.

Fig. 3.4 Aging effect monitored using light-layer (the Japan Sea sediment standard, see text for detail). (a) Al, (b) Si, (c) P, (d) S, (e) Cl, and (f) Ar. Blue: measured by first Mo X-ray tube, used for total 5663 hours. Orange: Measured by second Mo X-ray tube.

Fig. 3.4 continued. (g) K, (h) Ca, (i) Ti, (j) V, (k) Cr, (l) Mn

Fig. 3.4 continued. (m) Fe, (n) Ni, (o) Cu, (p) Zn, (q) Ga, (r) As

Fig. 3.4 continued. (s) Br, (t) Rb, (u) Sr, (v) Y, (w) Zr, (x) Ba

Fig. 3.4 continued. (y) Ta, (z) W, (aa) Pb, (bb) Mo inc, (cc) Mo coh

Fig. 3.5 Percentage of counts at the end of 1st Mo X-ray tube lifetime (5636 hours) divided by counts at the early stage of lifetime (661 hours) versus a) atomic number, and (b) energy of X-ray fluorescence. Black: elements only K line or L line is observed from light-layer measured in this study. Green: elements both K line and L line of fluorescence observed from light-layer measurement in this study (Rb, Sr, Zr). Red: data obtained from reference glass measurement (Ohlendorf et al., 2015).

Fig. 3.6 Element counts divided by Mo coh counts using light-layer (the Japan Sea sediment standard) measurement results. (a) Al / Mo coh, (b) Si / Mo coh, (c) P / Mo coh, (d) S / Mo coh, (e) Cl / Mo coh, (f) K / Mo coh. Blue: measured by first Mo X-ray tube, used for total 5663 hours. Orange: measured by second Mo X-ray tube.

Fig. 3.6 continued. (g) Ca / Mo coh, (h) Ti / Mo coh, (i) V / Mo coh, (j) Mn / Mo coh, (k) Fe / Mo coh, (l) Ni / Mo coh

Fig. 3.6 continued. (m) Cu / Mo coh, (n) Zn / Mo coh, (o) Ga / Mo coh, (p) As / Mo coh, (q) Br / Mo coh, (r) Rb / Mo coh

Fig. 3.6 continued. (s) Sr / Mo coh, (t) Y / Mo coh, (u) Zr / Mo coh, (v) Ba / Mo coh, (w) Pb / Mo coh, (x) Mo inc / Mo coh

Fig. 3.7 Aging effect monitored using calcareous (the Japan Sea sediment standard, see text for detail) measurement results. (a) Ca, (b) Sr. Blue: measured by first Mo X-ray tube, used for total 5663 hours. Orange: measured by second Mo X-ray tube.

Fig. 3.8 Schematic diagram of measurement area of the Japan Sea standard samples. As an example, photo of the Japan Sea standard sample (light-layer) is also shown.

Fig. 3.9 Standard deviations and average peak area counts of five times repeated measurements of four Japan Sea standard samples. Horizontal axis is average of peak area counts from five times repeated measurement for each 0.2mm × 8mm area. Average of each standard is also shown (see text for detail). STD: standard deviation. Ave.: Average. Theoretical standard deviation (σ) line is also shown (see text for detail). (a) Al, (b) Si, (c) P, (d) S, (e) Cl (f) Ar.

Fig 3.9 continued. (g) K, (h) Ca, (i) Ti, (j) V, (k) Cr, (l) Mn

Fig. 3.9 continued. (m) Fe, (n) Ni, (o) Cu, (p) Zn, (q) Ga, (r) As.

Fig. 3.9 continued. (s) Br, (t) Rb, (u) Sr, (v) Y, (w) Zr, (x) Ba

Fig. 3.9 continued. (y) Ta, (z) W, (aa) Pb, (bb) Mo inc, (cc) Mo coh

Fig. 3.10 Calibration line for concentration of each element obtained from standard reference materials measurement. (a) Al, (b) Si, (c) P, (d) S, (e) Cl (f) K.

Fig 3.10 continued. (g) Ca, (h) Ti, (i) V, (j) Mn, (k) Fe, (l) Ni.

Fig. 3.10 continued. (m) Cu, (n) Zn, (o) Ga, (p) As, (q) Br, (r) Rb.

Fig. 3.10 continued. (s) Sr, (t) Y, (u) Zr, (v) Ba, (w) Pb.

Fig. 3.11 Measured peak are counts and a regression line for KBr added standard reference materials (black). Results of standard reference materials (same as Fig. 3.10q) are also shown (green).

(a)

(b)

(c)

Fig. 3.12 Comparison of regression lines for three elements obtained from measurement of dry samples (green; pressed dry powder of standard reference material) and wet samples (orange; wet core samples of U1425 cores, element concentration defined by conventional XRF measurement). (a) Ca (b) Ti (c) Fe.

		JMS-1		JMS-2		JLk-1	JSd-1	JSd-3	MESS-4		JG-1
Material		marine sediment		marine sediment		Lake sediment	River sediment	River sediment	marine sediment		granodiorite
Samples from		Tokyo Bay		South Pacific		Lake Biwa	Ibaraki prefecture	Ibaraki prefecture	–		Gunma prefecture
Provided by		AIST		AIST		AIST	AIST	AIST	NRC		AIST
Data from		Terashima et al. (2002)		Terashima et al. (2002)		Imai et al. (1996)	Imai et al. (1996)	Imai et al. (1996)	Cirtification		Imai et al. (1995)
Al	%	8.37 ±	0.06	7.50 ±	0.05	8.85	7.75	5.24	7.91 ±	0.2	7.54
Si	%	25.12 ±	0.10	19.53 ±	0.09	26.72	31.11	35.53	27.8 ±	2	33.8
P	%	0.08 ±	0.00	0.55 ±	0.01	0.09	0.05	0.04	0.104 ±	0.016	0.043
S	%	1.32 ±	0.04	0.29 ±	0.02	0.1052	0.0068	0.0399	0.158 ±	0.02	0.00109
Cl	%	2.69 ±	0.03	4.05 ±	0.02		0.00675	0.0039	1.31 ±	0.44	0.00581
K	%	1.86 ±	0.03	2.24 ±	0.02	2.33	1.81	1.64	2.38 ±	0.1	3.3
Ca	%	1.52 ±	0.03	3.34 ±	0.04	0.49	2.17	0.40	1.31 ±	0.06	1.57
Ti	%	0.42 ±	0.01	0.84 ±	0.01	0.40	0.39	0.24	0.384 ±	0.022	0.16
V	μg/g	127 ±	2	183 ±	3	117	76	70.4	216 ±	8	25.2
Mn	%	0.08 ±	0.00	1.75 ±	0.02	0.21	0.07	0.11	0.0298 ±	0.0014	0.049
Fe	%	4.83 ±	0.03	7.67 ±	0.06	4.85	3.54	3.06	3.79 ±	0.16	1.52
Ni	μg/g	53 ±	2	311 ±	3	35	7.04	19.6	42.8 ±	1.6	7.47
Cu	μg/g	88 ±	2	447 ±	2	62.9	22	426	32.9 ±	1.8	2.52
Zn	μg/g	264 ±	3	166 ±	2	152	96.5	136	147 ±	6	41.1
Ga	μg/g					21.4	17.2	13.5	18		17.8
As	μg/g	18 ±	1	35 ±	1	26.8	2.42	252	21.7 ±	2.8	0.33
Br	μg/g					8.7	1.65	3.9	60		0.068
Rb	μg/g	88 ±	2	65 ±	1	147	67.4	285	180		182
Sr	μg/g	154 ±	2	454 ±	4	67.5	340	58.7	132 ±	8	184
Y	μg/g	24.3 ±	0.8	254 ±	4	40	14.8	14.9	20		30.6
Zr	μg/g	132 ±	3	220 ±	3	137	132	124	96		111
Ba	μg/g	307 ±	3	1856 ±	16	574	520	462	920		466
Pb	μg/g	49 ±	2	88 ±	2	43.7	12.9	82.1	21.5 ±	1.2	25.4

Table 3.1 List of standard reference materials used for this study

Table 3.2 Date of light-layer (the Japan Sea sediment standard) measurement by ITRAX and operating time of Mo X-ray tube

Date	time (hour)	X-ray tube	operating time for each tube (hour)
2015/3/11	661	1st Mo X-ray tube	661
2015/11/28	2980	1st Mo X-ray tube	2980
2015/12/3	3112	1st Mo X-ray tube	3112
2015/12/11	3292	1st Mo X-ray tube	3292
2016/2/3	3667	1st Mo X-ray tube	3667
2016/2/12	3877	1st Mo X-ray tube	3877
2016/2/16	3963	1st Mo X-ray tube	3963
2016/2/29	4009	1st Mo X-ray tube	4009
2016/8/23	5636	1st Mo X-ray tube	5636
2016/8/24	5664	2nd Mo X-ray tube	1
2016/9/2	5856	2nd Mo X-ray tube	193
2016/9/8	5998	2nd Mo X-ray tube	335
2016/9/13	6121	2nd Mo X-ray tube	458
2016/9/20	6287	2nd Mo X-ray tube	624
2016/10/25	7104	2nd Mo X-ray tube	1441
2016/11/15	7594	2nd Mo X-ray tube	1931
2016/11/21	7735	2nd Mo X-ray tube	2072
2016/12/2	7986	2nd Mo X-ray tube	2323
2016/12/6	8080	2nd Mo X-ray tube	2417

Table 3.3 Date of measurement for U1424 cores by ITRAX and operating time of Mo X-ray tube

Start Date	End Date	Start time (hour)	End time (hour)
2016/8/27	2016/9/19	5736	6273

Table 3.4 Date of measurement for U1425 cores by ITRAX and operating time of Mo X-ray tube

Start Date	End Date	Start time (hour)	End time (hour)
2015/8/30	2015/9/1	1394	1444
2015/9/12	2015/10/2	1674	2026
2015/11/24	2015/11/27	2888	2957
2016/2/3	2016/2/15	3676	3951
2016/2/29	2016/3/2	4016	4060

Table 3.5 Calculated precision of ITRAX XRF measurement.

$\sigma = \alpha_{element}\sqrt{N}$, where σ: standard deviation, $\alpha_{element}$: factor depend on each element, N: measured peak area counts (see text for detail). Maximum and minimum of observed average peak area counts during repeated measurement described in 3.4 is also shown.

	α element	average peak area counts maximum	average peak area counts minimum
Al	1.6	226	79
Si	1.0	1852	619
P *1	2.5	51	0
S	1.3	591	136
Cl	1.0	1735	620
Ar	1.3	346	145
K	1.0	6099	3042
Ca	1.1	131579	1243
Ti	1.2	4254	898
V	2.7	283	4
Cr	1.9	441	15
Mn	1.4	1774	429
Fe	1.2	205273	37191
Ni	2.0	586	163
Cu	2.9	511	151

	α element	average peak area counts maximum	average peak area counts minimum
Zn	1.8	1618	474
Ga	3.7	488	31
As *2	7.2	378	0
Br	2.1	3725	414
Rb	3.2	2847	333
Sr	1.7	16708	1129
Y	4.8	492	48
Zr	2.9	1785	451
Ba	2.3	392	30
Ta *1	2.4	605	0
W	1.5	1783	49
Pb *3	6.2	286	0
Mo inc	2.0	47001	13351
Mo coh	1.6	13809	5772

*1 $\alpha_{element}$ was calculated from measurement results of light-layer, dark-layer, and siliceous standard samples. Calcareous standard sample was excluded because no counts were detected during some measurement of calcareous standard sample.

*2 $\alpha_{element}$ was calculated from measurement results of dark-layer and siliceous standard samples, because no counts were detected during some measurement of light-layer and calcareous standard sample.

*3 $\alpha_{element}$ was calculated from measurement results of light-layer and calcareous standard samples, because no counts were detected during some measurement of dark-layer and siliceous standard sample.

第４章
本章については、５年以内に雑誌等で刊行予定のため、非公開。

第５章
本章については、５年以内に雑誌等で刊行予定のため、非公開。

6. General Discussion

In this chapter, usefulness of the method of MOC estimation using Br counts measured by ITRAX, which is established in chapter 4, and the method to reconstruct deep-water redox conditions, which is established in chapter 5 will be demonstrated.

Firstly, to demonstrate usefulness of MOC estimation using Br counts measured by ITRAX, which is established in chapter 4, variations of MOC in Site U1425 (water depth 1909m) and Site U1424 (water depth 2808m) are compared. Fig. 6.1 shows temporal variations of MOC reconstructed from Br peak area counts obtained by ITRAX for Sites U1424 and U1425 (see also subsection 2.2.2 in this paper for age model of the sediments). During the entire Quaternary, MOC contents are comparable for both sites in most of the time interval (Fig. 6.1). Since sedimentation rates at two sites during the Quaternary are approximately the same within ~10% difference (see also subsection 2.2.2 in this paper), comparison of MOC contents between the two sites can be regarded as comparison of MOC burial fluxes. Since most of marine organic matter are produced within the surface water and decomposed during settling and in near surface sediments, comparable MOC burial fluxes at the two sites suggest that labile marine organic matter was mostly decomposed above ~1900m water depth.

Whereas in several intervals, for example, dark layers around 0.05Ma, 0.08Ma, 0.22Ma, 0.53Ma, and 1.33Ma, MOC content at Site U1425 is more than 0.5% higher than that at Site U1424 (Fig. 6.1). This could be interpreted that marine organic matter was decomposed within the water column between ~1900m and ~2800m water depth or marine organic matter decomposition within near surface sediments was faster at the deeper site (U1424) than shallower site (U1425). Among above five intervals, deep-water redox conditions at both sites were anoxic in the dark layers at around 0.05Ma and 0.08Ma (Fig. 5.6). On the other hand, deep-water redox condition at Site U1425 is high-organic euxinic, and condition at Site U1424 is anoxic in the dark layers at around 0.22Ma, 0.53Ma, and 1.33Ma (Fig. 5.6). This difference in deep-water redox condition indicates that the shallower site (~1900m) is more reductive than the deeper site (~2800m) during

deposition of these three dark layers. Age of these three layers are corresponding to the period of intermediate to slightly high sea-level during MIS 7, 13, and 41. Although age controlling points are relatively sparse (Fig. 5.6, Tada et al., in revision), which lead to uncertainly in age estimation of each dark layer, roughly estimated eustatic sea levels from sea-level curve (Fig. 5.6; Elderfield et al., 2012) for dark layers at around 0.22Ma, 0.53Ma, and 1.33Ma are around -30m, -50m, and 0m, respectively, with uncertainty around 30m (Fig. 5.6).

Tada et al. (1999) proposed a hypothesis that centimeter to decimeter scale alternation of dark and light layer deposited during intermediate sea level (-90m - -20m) periods reflected changes in EASM intensity through changes in nutrient concentrations and salinity of the Tsushima Warm Current (TWC). When EASM became stronger, nutrient flux into the Japan Sea increased, and salinity of TWC decreased. High nutrient flux leads to high surface productivity, and oxygen minimum zone (OMZ) may have enhanced because great amount of oxygen are consumed to decompose organic matter settling from the surface water. Decreased salinity may lead to reduction of deep-water formation in the Japan Sea, which may partly contribute to lack of oxygen around OMZ.

This expected oceanic condition is similar to what I observed in the dark layers around 0.22Ma, 0.53Ma, and 1.33Ma. In these layers, high MOC contents suggest high productivity on the surface. Marine organic matters were suggested to be decomposed not only above ~1900m water depth, but also between ~1900m and ~2800m, which suggests large amount of organic matter were settled down within the water column. The shallower sites (~1900m) were more reductive compared to deeper sites (~2800m), and both sites show at least anoxic condition. Although the estimation has high uncertainty, sea level is intermediate to slightly high in these periods, which may comparable to sea-level estimation of enhanced OMZ environment by Tada et al. (1999). The characteristic features of three dark layers described above (high MOC content at both sites, higher MOC at shallower site, and more reductive condition in shallower site) are similar to what expected by Tada et al. (1999). Therefore, the results of this study provide the first

evidence of euxinic condition caused by intensification of OMZ hypothesized by Tada et al. (1999).

However, there is a possibility that environment of the two sites was different in these periods, because Site U1424 is under the influence of TWC-2 whereas Site U1425 is under the influence of TWC-3 (see Fig. 2.1 and section 2.1 in this paper for detail). Alternatively, since Site U1425 is located under the Subpolar Front (Tada et al., 2015c), Subpolar Front moving southwards and Site U1425 became under the influence of cold current in these periods with Site U1424 remained under the influence of warm current. To check this possibility of different environment at two sites, MOC content of two sites are further compared with another site, IODP Site U1426. Site U1426 is located at 37°2.00'N, 134°48.00'E under the influence of TWC-2 (Tada et al., 2015e). Since water depth of Site U1426 is 903m, sedimentation rate of sediments from Site U1426 is approximately three times higher than Site U1424 and U1425 (Tada et al., in revision). To compare with Sites U1424 and U1425, correlation tie points were newly identified in this study for Sites U1426 during the last 0.5 Myr in addition to the published points (Tada et al., in revision), using the same procedure described in subsection 2.2.2 in this paper (Table 6.1). Using tie points listed in Table 6.1, a high-resolution age model of Site U1426 is constructed for the last 0.5 Myr.

U1426 cores were measured by ITRAX and aging effect of X-ray tubes was corrected using the same method with U1424 and U1425 cores (Mitake, personal communication; see chapter 3 for detail of the method). MOC contents of U1426 cores were calculated from Br peak area counts using the same method with other two cores (see chapter4 for detail). Fig. 6.2 shows comparison of reconstructed MOC from three sites during the last 0.5 Myr. Although sedimentation rate of Site U1426 is approximately three times higher than the other two sites, MOC content is comparable at the three sites (Fig. 6.2). In dark layers deposited around 0.05Ma and 0.08Ma, MOC contents at Site U1426 are comparable to those at Site U1425. In dark layer deposited around 0.22Ma, MOC content at Site U1426 is lower than that at Site U1425 and higher than that at U1424. Since MOC contents are comparable between Sites U1426 and U1425 during most of the time of the

last 0.5Myr and the situation is same during deposition of dark layer around 0.05Ma and 0.08Ma (Fig. 6.2), the possibility of occurrence of different environment only for Site U1425 during deposition of dark layer around 0.05Ma and 0.08Ma is unlikely. Although Sites U1426 and U1424 are under the influence of TWC-2, whereas Site U1425 is under the influence of TWC-3 and located under Subpolar Front, it could be said oceanic environment (surface productivity and redox conditions) was similar at all three sites, at least during the deposition of the dark layers around 0.05 and 0.08Ma when MOC contents are comparable between Sites U1426 and U1425. Therefore, difference in MOC content (nearly equal to MOC flux) and deep-water redox condition between Sites U1424 and U1425 possibly reflects vertical difference as described in the first half of this chapter.

Above discussions become possible for the first time thanks to high-resolution MOC record and deep-water redox condition record obtained by ITRAX using the methods established in this study. 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.

Fig. 6.1 MOC variability reconstructed from Br peak area counts obtained by ITRAX during Quaternary at Sites U1424 (Red) and U1425 (Black). Red triangle shows correlation tie point between Sites U1424 and U1425 (Table 2.2).

0 - 0.5 Ma.

Fig. 6.1 continued. 0.5 - 1 Ma.

Fig. 6.1 continued. 1 - 1.5 Ma.

Fig. 6.1 continued. 1.5 - 2 Ma.

Fig. 6.1 continued. 2 - 2.5 Ma.

Fig. 6.1 continued. 2.5 - 3 Ma.

Fig. 6.2 MOC variability reconstructed from Br peak area counts obtained by ITRAX during 0 - 0.5 Ma at Sites U1424 (Red), U1425 (Black), and U1426 (Purple). Red triangle shows correlation tie point between Sites U1424, U1425, and U1426 (Table 2.1 and Table 6.1).

Table 6.1 List of correlation tie point of U1426 for correlation with Sites U1424 and U1425 in the time interval from 0 to 0.53 Ma.
Estimated ages based on projection of LR04 tuned age model at Site U1424 (Tada et al., in revision) is also shown.

Dark layer No.	U1424 LR04 tuned Age (Ma)	U1426 Position	U1426 CCSF-D_ Patched_rev 20150519 (m)
0-1*	0.013	U1426C-1H-2 75cm	2.25
1-1*	0.024	U1426C-1H-3 63cm	3.63
1-1-2	0.030	U1426A-2H-1 97.5cm	4.18
1-2*	0.036	U1426C-1H-4 12.5cm	4.69
1-3*	0.047	U1426A-2H-2 93.5cm	5.62
1-4*	0.053	U1426A-2H-3 25cm	6.43
1-4-2	0.071	U1426A-2H-4 68.5cm	8.37
1-4-3	0.075	U1426A-2H-4 113cm	8.81
1-5*	0.084	U1426A-2H-5 64.5cm	9.83
1-5-2	0.090	U1426A-2H-5 144cm	10.62
1-6*	0.110	U1426C-2H-5 27cm	13.00
1-6-2	0.123	U1426C-2H-6 88cm	15.11
1-6-3	0.130	U1426A-3H-2 129cm	15.89
2-1*	0.141	U1426A-3H-3 74cm	16.84
2-2*	0.161	U1426A-3H-4 46cm	18.06
2-2-2	0.163	U1426A-3H-4 73cm	18.33
2-2-3	0.169	U1426A-3H-4 132cm	18.92
2-3*	0.177	U1426A-3H-5 88cm	19.98
2-4*	0.191	U1426A-3H-6 73cm	21.36
2-4-2	0.196	U1426C-3H-4 15cm	22.02
2-5*	0.207	U1426C-3H-4 79cm	22.66
2-5-2	0.220	U1426C-3H-5 31cm	23.68
2-6*	0.228	U1426C-3H-5 148.5cm	24.85
2-6-2	0.231	U1426A-4H-2 29.5cm	25.20
2-7*	0.234	U1426A-4H-2 75cm	25.65
2-8*	0.243	U1426A-4H-3 80cm	27.09
3-1*	0.258	U1426A-4H-4 32.5cm	28.03
3-1-2	0.271	U1426A-4H-5 7cm	29.01
3-1-3	0.280	U1426A-4H-5 59cm	29.53
3-2*	0.288	U1426A-4H-5 137cm	30.31
3-2-2	0.296	U1426A-4H-6 85cm	31.20
3-2-3	0.302	U1426A-4H-6 125.5cm	31.61
3-2-4	0.306	U1426C-5H-2 53cm	32.01
3-3*	0.313	U1426C-5H-2 120cm	32.68
4-1*	0.344	U1426C-5H-5 16cm	35.82
4-1-2	0.358	U1426C-5H-5 121.5cm	36.88
4-1-3	0.371	U1426C-5H-6 69cm	37.81
4-1-4	0.381	U1426D-5H-3 1cm	38.59
4-2*	0.386	U1426D-5H-3 38cm	38.96
4-2-2	0.391	U1426D-5H-3 79cm	39.37
5-1*	0.444	U1426D-5H-6 107cm	43.67
5-1-2	0.449	U1426D-5H-6 134cm	43.94
5-2*	0.457	U1426D-5H-7 23cm	44.33
5-2-2	0.462	U1426D-5H-7 55cm	44.65
5-2-3	0.475	U1426C-6H-5 14cm	45.74
5-2-4	0.477	U1426C-6H-5 41cm	46.01
5-3*	0.483	U1426C-6H-5 73cm	46.33
5-4*	0.529	U1426A-6H-6 72cm	50.96

*From Tada et al. (in revision).

7. Summary and Conclusions

In this paper, the method to reconstruct marine organic carbon content in the sediments, and the method to reconstruct past deep-sea redox condition using the result of ITRAX XRF core scanner measurement of the hemipelagic sediments is established. These methods are successfully applied to the Quaternary hemipelagic sediments of the Japan Sea.

In chapter 2, the details on the Quaternary hemipelagic sediments of the Japan Sea used in this study are summarized. The Japan Sea hemipelagic sediments are used because deep-sea redox condition of the Japan Sea fluctuated in a wide range from oxic to euxinic repeatedly in the past. Also, organic carbon content of the Japan Sea hemipelagic sediment have high variability up to 5% TOC. Furthermore, long-term continuous sediment records with high-resolution age model are available for the Quaternary hemipelagic sediments of the Japan Sea obtained by IODP Exp. 346.

In chapter 3, in order to establish the methods to reconstruct MOC content and deep-water redox condition by ITRAX measurement, capability of ITRAX for quantitative measurement is evaluated by some basic tests in the beginning. Firstly, XRF measurement settings suitable for the Japan Sea sediments are explored. Then, a method to correct for X-ray tube aging effect on the peak area count of each element is established. Finally, precision of ITRAX XRF measurement is evaluated for each element, and the relationship between element peak area count and element concentration is estimated. Based on these results, ITRAX measurement results in following chapters are corrected.

In chapter 4, the method to estimate MOC (marine organic carbon) content in the sediments using Br peak area counts obtained by ITRAX XRF measurement is constructed. TOC, TN, and $\delta^{13}C$ of discrete samples taken from Sites U1424 and U1425 were measured to calculate MOC content from TOC content and $\delta^{13}C$. Calculated MOC are 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.

In chapter 5, a method to reconstruct deep-sea redox conditions only from

ITRAX XRF measurement results was established. Based on Br counts, S counts, and Fe/Ti ratios measured by ITRAX, deep-sea redox conditions are classified into four categories (oxic, anoxic, high-organic euxinic, low-organic euxinic).

Finally, using these methods, MOC content and deep-water redox conditions are reconstructed for the Japan Sea hemipelagic sediment cores obtained from two different water depths in chapters 4, 5, and 6. Comparison of two cores enables us to examine vertical similarity or difference in MOC content in sediments and vertical similarity or difference in deep-water redox condition within the water column of the sea, which provide useful information to discuss about past oceanographic environmental changes.

The results presented in this study could be regarded as a case study at this stage, but has a high potential for wide application in the future studies, because deep-water redox conditions of the Japan Sea fluctuated wide range from oxic to euxinic repeatedly, and parameters introduced in this study are modification of conventional proxies widely used in previous studies. Using the methods established in this study, high-speed, high-resolution XRF measurement by ITRAX enables us to obtain long-term, high-resolution record of past changes in deep-sea redox conditions and MOC content in the sediments from multi sites within a short time period.

8. Future Prospective

Although deep-water redox conditions are successfully reconstructed using element composition of the sediment measured by ITRAX, its application to cores from two sites with water depths of ~2000m and ~3000m are not enough to discuss vertical distribution of redox conditions within the water column and examine the exact cause of changes in redox condition, because deep-water redox conditions are similar between two sites during most of the time. "High-organic euxinic" condition is interpreted as reflecting euxinic condition prevailed within the water column, probably caused by high productivity that resulted in expansion and intensification of OMZ. Although some layers described in chapter 6 suggest expansion and/or intensification of OMZ during the period when "high-organic euxinic" conditions are existed at Site U1425, there is little strong evidence that euxinic condition was prevailed at the depth of OMZ. Watanabe et al. (2007) reconstructed vertical distribution of redox conditions during last 160 kyr, using cores obtained from a deep depth (2885m) and shallow depths (932m and 800m), and reveal that there is significant difference in redox conditions, which were reconstructed from lamina preservation, between deep and shallow depths. Based on their results, it is expected that deep-water redox condition reconstructed from cores obtained at shallow depth (<1000m) show more difference with deep site (Site U1424, ~3000m) compared to Site U1425 (~2000m), which have difference in deep-water redox conditions in only several intervals described in chapter 5 and 6. Thus, reconstruction of redox condition using cores recovered from shallow depths (<1000m) is necessary to obtain significant evidence about the cause of euxinic conditions in the water column.

"Low-organic euxinic" condition is identified based on high S and low Br (and thus MOC) contents, and this is characteristic of the layers deposited under stratified euxinic conditions inferred from euxinic deep-water condition and low salinity surface water. Although stratified oceanic condition is strongly suggested during sea-level low-stands at MIS 2, 6, 10, 12, 16, 18, 20, 22 when "low-organic euxinic" layers are identified based on elemental composition measured by ITRAX in this study, no surface water

salinity reconstruction is available for the periods older than MIS 6. Since sea-level is decreased to approximately more than -90m during these periods, "low-organic euxinic" layers are not identified for Site U1425 (~2000m) during MIS 18, 20, and 22 when sea level decrease are not significant compared to MIS 2, 6, 10, 12, and 16 based on LR04 curve (Lisiecki and Raymo, 2005). However, sea-level reconstruction by Elderfield et al. (2012) indicates significant sea-level decrease during MIS 20 and 22. Although it is confirmed that sea-level changes has significant effect for stratified oceanic condition of the Japan Sea, importance of amplitude or duration of sea-level decrease are still uncertain. Therefore, further study to reconstruct surface water salinity from oxygen isotope of planktonic foraminifer could provide more strong evidence for stratified ocean in these periods, and provide clues to examine influence of different amplitude or duration of sea-level decrease in each glacial maximum.

Millennial-scale variability of redox conditions are reconstructed throughout the last 1.5 Myr and compared with global sea-level curves. The result suggests that millennial-scale variability of deep-water redox condition in the Japan Sea tends to have been distinct during intermediate sea level periods when alternations of distinct dark and light layers occurred. Since vertical differences in redox conditions are sometimes observed from reconstructed redox condition in U1424 and U1425, comparison of deep-water redox condition is only possible for correlated dark layers between two sites. Therefore, higher resolution age model will enable me to compare each millennial scale redox condition between different water depths, which provide information to examine vertical structure of water column.

Finally, using the methods established in this study, MOC content and deep-water redox condition are simultaneously reconstructed from element composition of sediments measured by ITRAX. This method could be applied to sediments from other oceans, and could contribute to reveal past oceanographic variability (organic matter decomposition, ocean circulation etc.), as demonstrated in chapter 6. The methods established in this study have high potential of applicability owing to advantages of high-speed,

high-resolution, semi-quantitative measurement by ITRAX.

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