



The Sea of Japan and Its Unique Chemistry Revealed by Time-Series Observations over the Last 30 Years

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Abstract Chemical tracers in seawater, as well as physical parameters such as temperature and salinity, have been measured to better characterize the dynamics of water convection and its spatiotemporal changes in the Sea of Japan (also called the Japan Sea), a semi-closed, hyperoxic marginal sea (maximum depth: ~3,800 m) in the northwestern corner of the Pacific Ocean. Repeated conductivity, temperature, and depth (CTD) observations and measurements of dissolved oxygen, for more than 30 years, have confirmed that the bottom layer of the Japan Sea, with a thickness of ~1 km below the boundary at a depth of ~2,500 m, is characterized by vertical homogeneity with fluctuations of potential temperature and dissolved oxygen of $<0.001^{\circ}\text{C}$ and $<0.5 \mu\text{mol kg}^{-1}$, respectively. The timescale of the abyssal circulation in the Japan Sea has been estimated to be 100–300 years, using ^{14}C and other chemical tracers. Stable isotope analyses for dissolved He, O_2 and CH_4 have given us information on their unique geochemical cycles in the Japan Sea. Profiles of the short-lived radioisotope ^{222}Rn just above the sea bottom have brought new insights into the short-term lateral water movement with a timescale of several days in the Japan Sea bottom water. It is of special concern that the gradual deoxygenation and warming of the bottom water over the last 30 years have resulted in an ~10% decrease in dissolved oxygen and ~0.04°C increase in potential temperature, suggesting a change of the deep convection system in the Japan Sea. The temporal changes in the vertical profiles of tritium from 1984 to 1998 have suggested a shift of the abyssal circulation pattern from a “total (overall) convection mode” to a “shallow (partial) convection mode”. It is likely that the global warming since the last century has hindered the formation of dense surface seawater and its ability to sink down to the bottom, isolating the bottom layer from the deep convection loop that is indispensable as the source of cold and oxygen-rich water. However, the decreasing trend of bottom dissolved oxygen between 1977 and 2010 was not monotonous; rather, it was interrupted by an occasional break in the winter of 2000–2001, when severely cold weather may have resulted in especially dense surface water to sink down to the bottom layer for its ventilation.

Keywords: Sea of Japan, Chemical tracers, Global warming, Time-series data, Oceanography.

1. Introduction

The Sea of Japan (also called the Japan Sea) is a semi-closed marginal sea in the northwestern Pacific Ocean, surrounded by the Japanese Archipelago and Far Eastern Eurasia (Fig. 1). Paleomagnetic, chronological, sedimentological and geochemical studies have elucidated that the Japanese Archipelago was pulled apart from the easternmost Eurasian Continent to produce the Japan Sea ~20 Myr ago, followed by two rapid land rotation processes: an anti-clockwise rotation of the northeast Japan Arc and a clockwise rotation of the southwest Japan Arc (e.g., Otofujii *et al.*, 1985; Tamaki *et al.*, 1992; Baba *et al.*, 2007). Since then, the Japan Sea and

the Japanese Archipelago have been suffering and sharing various environmental events, changing their features and interactions (e.g., Tada, 1994).

The area of the Japan Sea is $1.013 \times 10^6 \text{ km}^2$, which is ~0.3% of that of the world's oceans. Sverdrup *et al.* (1942), in their famous textbook “The Oceans”, pointed out the comparability of the Japan Sea with the Arctic, Norwegian, and Labrador Seas in surface water circulation. The geography of the Japan Sea is characterized by its marked isolation in bathymetry. As shown in Fig. 1, four passages, the Tsushima, Tsugaru, Soya, and Tatar (Mamiya) straits, connect the Japan Sea with the neighboring seas (the north-

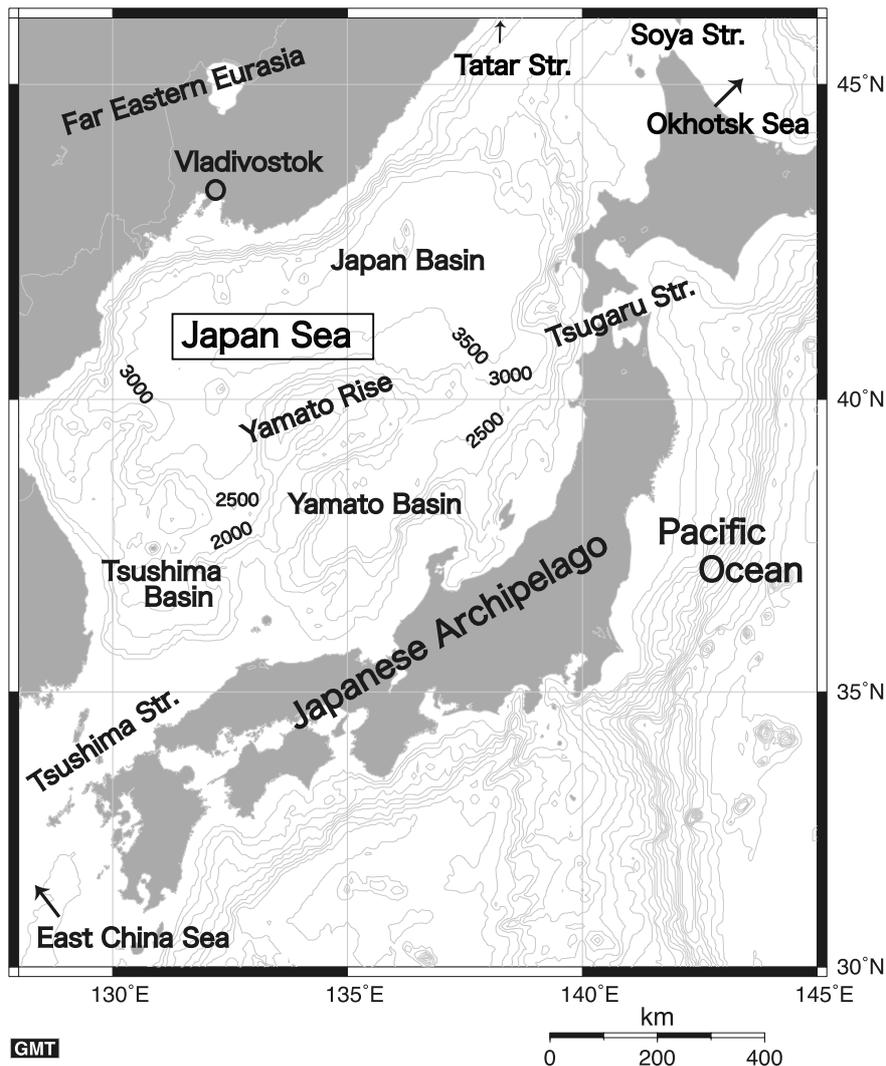


Fig. 1. The major geography of the Japan Sea.

western Pacific Ocean, the Okhotsk Sea, and the East China Sea). All of the sill depths of these passages (~ 20 m, ~ 50 m, ~ 130 m and ~ 130 m for the Tatar, Soya, Tsugaru and Tsushima Straits, respectively) are much shallower than the mean depth (1,667 m) and the greatest depth ($\sim 3,800$ m) of the Japan Sea. Such land-locked bathymetry gives a closed feature or independency to the deeper layer of the Japan Sea than the maximum sill depth.

In contrast, there is no restriction for surface currents to enter the Japan Sea. Through the Tsushima Strait, a branch of the Kuroshio Current (Fig. 2) flows into the Japan Sea, supplying warm, saline and nutrient-poor surface seawater, while another warm current, the Taiwan Current, also flows into the Japan Sea, providing less saline but nutrient-rich surface water. Such a combined flow system, which is generally called the Tsushima Current, has played an important role in controlling the climate of the Japanese Islands, the primary production and the deep convection in the Japan Sea.

The pioneering works by Suda (1932) and Uda (1934) on the water column properties of the Japan Sea revealed that the deep water below the thermocline is extremely uniform

as inferred from the distributions of physicochemical parameters: potential temperature, salinity, and dissolved oxygen. Below ~ 500 m depth in the Japan Sea, the potential temperature, salinity and dissolved oxygen are in significantly narrow ranges, between 0.0°C and 0.6°C , between 34.06 and 34.08, and between 200 and $230 \mu\text{mol kg}^{-1}$, respectively. Due to this homogeneity, the waters below the thermocline have been given the generic name “the water-mass proper to the Japan Sea” or “the Japan Sea Proper Water” (Uda, 1934; Yasui *et al.*, 1967). Worthington (1981) regarded the Japan Sea Proper Water as a single water mass because of its very narrow temperature and salinity ranges.

This paper summarizes the recent geochemical studies of the Japan Sea, particularly the investigations of chemical tracers in the Japan Sea Proper Water. Not only spatial but also temporal variations observed in chemical tracer distributions will be discussed in association with recent global climate changes.



Fig. 2. Surface currents around the Japanese Archipelago. (Courtesy of T. Senjyu, Kyushu University.)

2. General Geography and Oceanography of the Japan Sea

The semi-closed bathymetric feature of the Japan Sea allows no inflow or outflow of deep and bottom waters between the Japan Sea and the surrounding seas. The origin of the Japan Sea Proper Water (abbreviated as “JSPW” hereafter) must therefore be somewhere within the Japan Sea itself. The JSPW shows a high dissolved oxygen content ($>200 \mu\text{mol kg}^{-1}$) even in the deepest water down to $>3,500 \text{ m}$, whereas the deep water in the northwestern Pacific Ocean at a similar latitude and depth contains oxygen with a concentration as low as $\sim 150 \mu\text{mol kg}^{-1}$ (Fig. 3). Talley *et al.* (2006) highlighted this peculiar feature of the Japan Sea by comparing it with the whole of the Pacific Ocean in a horizontal O_2 distribution map at $1,000 \text{ m}$ depth. Such a hyperoxic character of the JSPW, together with its low potential temperature, indicates active water convection between the surface and deep layers in the Japan Sea.

The deep convection or thermohaline circulation in the Japan Sea has been believed to be driven by the formation and sinking of dense (low-temperature and high-salinity) surface seawater in northern areas of the Japan Sea during severe winter seasons (Suda, 1932; Uda, 1934; Yasui *et al.*, 1967; Nitani, 1972; Moriyasu, 1972; Gamo and Horibe, 1983; Gamo *et al.*, 1986; Sudo, 1986). Excessive cooling and brine rejection due to ice formation in the surface water, which is accelerated by a saline water supply from the Tsushima Current, should promote the formation of dense surface seawater in winter seasons. The Japan Sea is often called “a miniature ocean” because of this independent deep convection system (or conveyor belt), driven by the high-density surface water sinking in a manner similar to that of

the global conveyor belt that originates in the northern Atlantic (Broecker, 1990).

During the ice ages in the Quaternary, however, the global fall of the sea level by $\sim 100 \text{ m}$ must have nearly closed the Tsushima Strait to retard or cease the intrusion of the Tsushima Current into the Japan Sea. The resulting lower salinity of surface water should have reduced or halted the deep convection in the Japan Sea, bringing anoxic conditions to the JSPW (e.g., Oba *et al.*, 1991; Tada, 1994). After the Last Glacial Maximum, the rising sea level revived the flow of the Tsushima Current $\sim 8,000$ years ago. Such environmental changes in the Japan Sea are thought to have also inflicted major changes in the climatic conditions of the Japanese Islands.

The Japan Sea has three deep basins (Fig. 1): the Japan Basin (the northern part), Yamato Basin (the southeastern part), and Tsushima Basin (the southwestern part), accompanied by a topographic high (Yamato Rise) in the center of the sea. The sinking of high-density surface seawater could occur in northern areas of the Japan Sea to transport oxygen-rich surface water to deep and bottom layers of the Japan Basin, and then to the Yamato and Tsushima Basins by southward bottom currents. Such an abyssal circulation pattern in the JSPW is qualitatively reflected in the distribution of dissolved oxygen in bottom waters (depth $[D] > 2,000 \text{ m}$) as shown in Fig. 4 (Gamo, 2011), which was drawn using the bottom O_2 distribution in the whole of the Japan Sea measured in 1969 (Ohwada and Tanioka, 1970; Japan Meteorological Agency, 1971). The circulation pattern in Fig. 4 is in good harmony with that obtained by direct current meter observations in the Japan Sea (figure 12 in Senjyu *et al.*, 2005a).

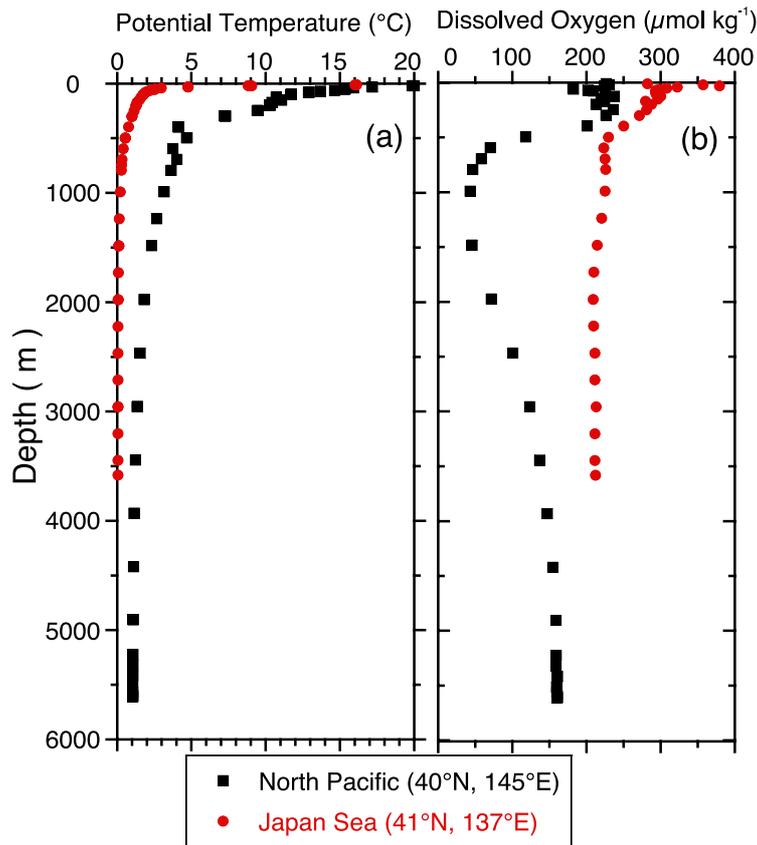


Fig. 3. Comparison of potential temperature profiles (a) and those of dissolved oxygen (b) between the Japan Sea (41°N, 137°E) and the northwest Pacific Ocean (40°N, 145°E). Data were obtained during the R/V *Hakuho Maru* KH-98-3 cruise.

3. Research Cruises and Hydrographic Observations

Full-dress cruises for geochemical studies in the Japan Sea have been conducted since 1977, accumulating data on chemical tracers in the three basins. Table 1 is a list of the research cruises, for which three vessels were used: *Hakuho Maru (the 1st and the 2nd)* and *Tansei Maru the 2nd*. The *Hakuho-Marun the 1st* (3,200 tonnage, max. 32 scientists) was built in 1967; the *Hakuho-Marun the 2nd* (3,991 tonnage, max. 35 scientists) was built in 1989, and the *Tansei-Marun the 2nd* (610 tonnage, max. 12 scientists) was built in 1982 by the Ocean Research Institute, University of Tokyo. These vessels are well-equipped with onboard facilities and laboratories for the purpose of pursuing basic and multidisciplinary oceanographic work in collaboration with domestic and foreign researchers in various marine sciences. R/V *Hakuho Marun the 2nd* and R/V *Tansei Marun the 2nd* were transferred from the University of Tokyo to the Japan Agency for Marine-Earth Science and Technology (JAMSTEC) in 2004. R/V *Tansei Marun the 2nd* was retired in January 2013.

Seawater samples for chemical analyses were usually taken using Niskin-type samplers with various volumes (between 2.5-L and 23-L). A large-volume water sampling system designed to take 250-L seawater samples (Horibe and Tsubota, 1977) was also used in the years 1977 to 1984 to obtain ~200 L of seawater for measuring the β activity of radiocarbon (^{14}C) in seawater (Östlund *et al.*, 1974; Gamo

et al., 1987). A CTD-rosette water sampling system with 12-L Niskin bottles (General Oceanics, Miami, FL) was introduced on board the R/V *Hakuho-Marun the 1st* and *Tansei-Marun the 2nd* at the beginning of the 1990s.

4. Water Mass Structure and Timescale of Abyssal Circulation

The Russian Navy began systematic observations on water temperature, density and currents in the Japan Sea in 1857 (e.g. Danchenkov *et al.*, 2006), and the results were summarized as monographs (Shrenk, 1870, 1874), identifying two major surface currents in the Japan Sea (the Tsushima Current and the Liman Current). Basin-scale oceanographic surveys, including those for deep waters, by Japanese researchers date from the 1930s (e.g. Suda, 1932; Uda, 1934). The physicochemical parameters of seawater have been measured for characterizing the JSPW and its deep convection pattern. Nitani (1972) published a leading review of the studies conducted between 1928 and 1971, summarizing observational data on the deep and bottom waters of the Japan Sea. He discussed water convection mechanisms, spatiotemporal variability of the deep and bottom water characteristics, and the bottom water formation mechanism, using a reliable dataset of potential temperature, salinity and dissolved oxygen values. Nitani (1972) first pointed out that the JSPW has layered structures: Deep Water ($D = 500$ to 1,000 m), Upper Bottom Water (1,000 to 2,000 m), and Lower Bottom Water

Table 1. List of the research cruises of R/V *Hakuho Maru* and *Tansei Maru* related to this study.

Year (Month)	Cruise Name	Eastern Japan Basin		Yamato Basin		Tsushima Basin		Research vessel	Chief scientist
		Stn. No.	Location	Stn. No.	Location	Stn. No.	Location		
1977 (Sep–Oct)	KH-77-3	PE18	41°20'N, 137°21'E	PE14	37°44'N, 135°12'E	PE24	37°18'N, 131°20'E	<i>Hakuho-Maru (I)</i>	Yoshio Horibe
1979 (Jun–Aug)	KH-79-3	AL2	41°20'N, 137°20'E	AL3	37°45'N, 135°14'E	AL4	38°23'N, 132°49'E	<i>Hakuho-Maru (I)</i>	Yoshio Horibe
1984 (Aug–Sep)	KH-84-3	AN11	41°25'N, 138°15'E	AN16	38°17'N, 135°30'E	AN21	38°41'N, 132°48'E	<i>Hakuho-Maru (I)</i>	Hitoshi Sakai
1998 (Jul–Aug)	KH-98-3	CM12	41°22'N, 137°20'E	CM20	37°44'N, 135°14'E	—	—	<i>Hakuho-Maru (II)</i>	Yoshiyuki Nozaki
2001 (Sep–Oct)	KT-01-15	3	41°21'N, 137°20'E	—	—	—	—	<i>Tansei-Maru (II)</i>	Jing Zhang
2003 (July)	KT-03-9	5	41°21'N, 137°20'E	8	37°44'N, 135°14'E	—	—	<i>Tansei-Maru (II)</i>	Jing Zhang
2005 (May)	KT-05-11	6	41°21'N, 137°20'E	2B	37°45'N, 135°14'E	—	—	<i>Tansei-Maru (II)</i>	Toshitaka Gamo
2007 (Sep–Oct)	KT-07-24	15	41°21'N, 137°20'E	10	38°00'N, 135°36'E	8	37°04'N, 130°57'E	<i>Tansei-Maru (II)</i>	Toshitaka Gamo
2010 (Jun–Jul)	KH-10-2	CR2	41°21'N, 137°20'E	CR66	37°45'N, 135°14'E	—	—	<i>Hakuho-Maru (II)</i>	Jing Zhang

The locations of the stations in the three basins are shown.

(2,000 m to the bottom).

The KH-77-3 cruise of R/V *Hakuho Maru* (Horibe, 1981) was the first to conduct geochemical research in the Japan Sea. State-of-the-art technology, including a highly precise CTD-sensor instrument (Neil Brown Mark III), was applied for water column surveys down to the bottom at four stations, revealing the existence of a clear boundary (or the benthic front) at 2,000–2,500 m depth from potential temperature profiles (Gamo and Horibe, 1983). At each of the three basins, Gamo and Horibe found a vertically homogeneous layer with a potential temperature fluctuation of $<0.001^{\circ}\text{C}$ below the benthic front. They called this water mass the Bottom Water as shown in Fig. 5, which almost corresponds to the Lower Bottom Water defined by Nitani (1972).

Gamo *et al.* (1986) made further CTD observations from the surface to the bottom, as well as seawater sampling for chemical measurements, at nine stations in the Japan Sea during the KH-84-3 cruise of R/V *Hakuho Maru* (Fig. 6). They reconfirmed the benthic front and the homogeneous bottom layers in the three basins. As for the bottom potential temperature profiles (Fig. 7), the lowest (0.036°C) and the highest (0.047°C) values were observed in the Eastern Japan Basin (stations AN-7, -11, -12, and -13) and in the Yamato Basin (AN-16), respectively, and station AN21 (Tsushima Basin) showed a value (0.037°C) similar to that in the Eastern Japan Basin. As for the bottom dissolved oxygen values, the stations in the Eastern Japan Basin and that in the Tsushima Basin showed similar values of $222.7 \mu\text{mol kg}^{-1}$ and $223.6 \mu\text{mol kg}^{-1}$, respectively, while AN-16 in the Yamato Basin showed the lowest value of $217.2 \mu\text{mol kg}^{-1}$.

The higher dissolved oxygen in the Eastern Japan Basin bottom water compared with that in the Yamato Basin suggests a southward bottom current from the Eastern Japan Basin to the Yamato Basin. Gamo *et al.* (1986) pointed out the lack of a bottom homogeneous layer in the passage zone between the Eastern Japan Basin and the Yamato Basin east of the Yamato Rise (AN-14 and -27 shown in Fig. 7), suggesting some topographic effect of the Yamato Rise to restrict the bottom water exchange between the two basins (cf. Senjyu *et al.*, 2005b).

Figure 8 is a schematic cross-section of the Japan Sea, illustrating the bottom water formation and abyssal circulation. Cooling and freezing (brine rejection) in winter due to strong East Asian monsoons could make the surface water dense enough to sink along the slope down to the bottom layer. The newly formed bottom water should have kinetic energy to induce active vertical mixing, possibly maintaining the homogeneous bottom layer (Figs. 5 and 7).

With regard to the probable formation area of the bottom water, the following two locations have been pointed out: the northernmost Japan Sea (Tatar Strait) and the northwestern Japan Sea off Vladivostok in Russia. Martin *et al.* (1992) monitored the ice coverage using daily passive microwave images, and they suggested that the northern Tatar Strait is an important bottom water formation zone, where ice growth and brine rejection are caused by severe winter storms. In contrast, the area south of Vladivostok has been suggested to be the JSPW formation zone, based on geophysical obser-

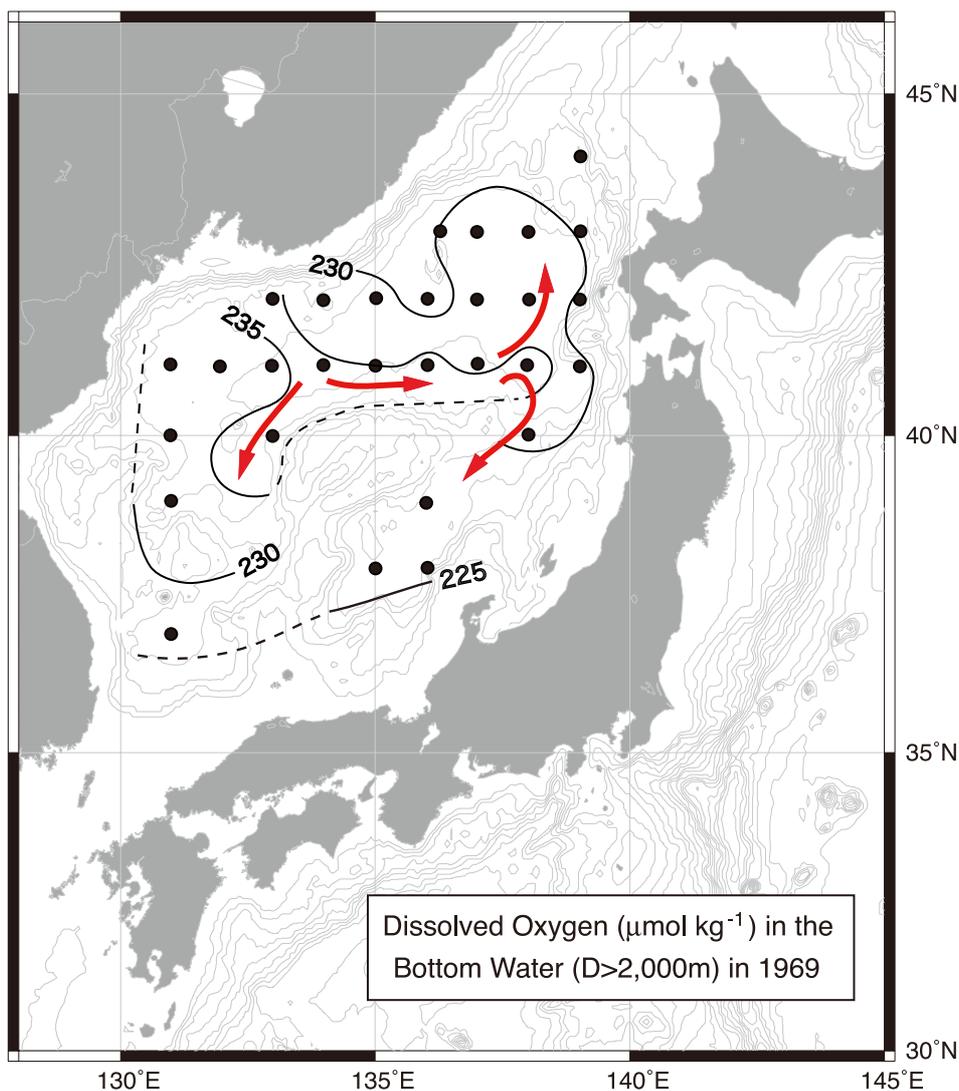


Fig. 4. Schematic patterns of bottom circulations in the Japan Sea as inferred from the contour map of bottom dissolved oxygen (autumn of 1969) below a depth of 2,000 m (Gamo, 2011). Oxygen concentrations were measured by the Japan Meteorological Agency (1971) at stations shown by filled circles. (Modified from *TrAC Trends Anal. Chem.*, 30, Gamo, T., Dissolved oxygen in the bottom water of the Sea of Japan as a sensitive alarm for global climate change, 1308–1319, Copyright 2011, with permission from Elsevier.)

vations (Sudo, 1986; Senju and Sudo, 1993, 1994; Seung and Yoon, 1995). Kawamura and Wu (1998) investigated the wintertime sea surface temperature (SST) and surface winds over the Japan Sea using satellite observation data in the winter of 1996–1997, and they found that an area with strong winds (monthly averaged value: $>9 \text{ m s}^{-1}$) was offshore of Vladivostok with a dia. of $\sim 150 \text{ km}$, north of 41°N between 132° and 134°E , which was in good coincidence with the cold SST ($\sim 0^\circ\text{C}$) zone. Kawamura and Wu suggested that the winter monsoon wind from the Eurasian continent is enhanced by the land-topographic focusing effect to supply outbreaks of dry and cold air masses, which may trigger the formation of the Japan Sea bottom water if they are strong enough.

The timescale of abyssal circulation in the Japan Sea has been estimated from the distribution of radiocarbon (^{14}C) with a half-life of 5,730 y. Gamo and Horibe (1983) took ^{14}C measurements in the Japan Sea bottom water for the first time

using 200-L seawater samples during the KH-77-3 (Horibe, 1981) and KH-79-3 cruises. They extracted total inorganic carbon from acidified seawater samples onboard the ship, converted it to C_2H_2 in the Carbon Dating Laboratory (CDL) at the University of Tokyo, and measured its β -activity with a Houtermans-Oeschger-type multi-anode anticoincidence gas proportional counter in collaboration with H. Kobayashi of CDL. Gamo and Horibe (1983) reported the $\Delta^{14}\text{C}$ value of $-74 \pm 6\text{‰}$ as the averaged value for the bottom waters of the Japan Sea in 1977–1979, applying a simple two-box model (Broecker, 1974) to the $\Delta^{14}\text{C}$ value to obtain a mean residence time of the bottom water of $300 \pm 100 \text{ y}$. According to the conventional way (Stuiver and Polach, 1977), the $\Delta^{14}\text{C}$ value is defined as: $(A_{\text{sn}}/A_{\text{abs}} - 1) \times 1000 (\text{‰})$, where A_{sn} is the ^{14}C activity of a sample normalized to its $\delta^{13}\text{C} = -25\text{‰}$ relative to the PDB standard (see Section 5.6 as to the definition of $\delta^{13}\text{C}$), and A_{abs} (absolute international standard activity) is 95% of the NBS oxalic acid activity in AD 1950 which is

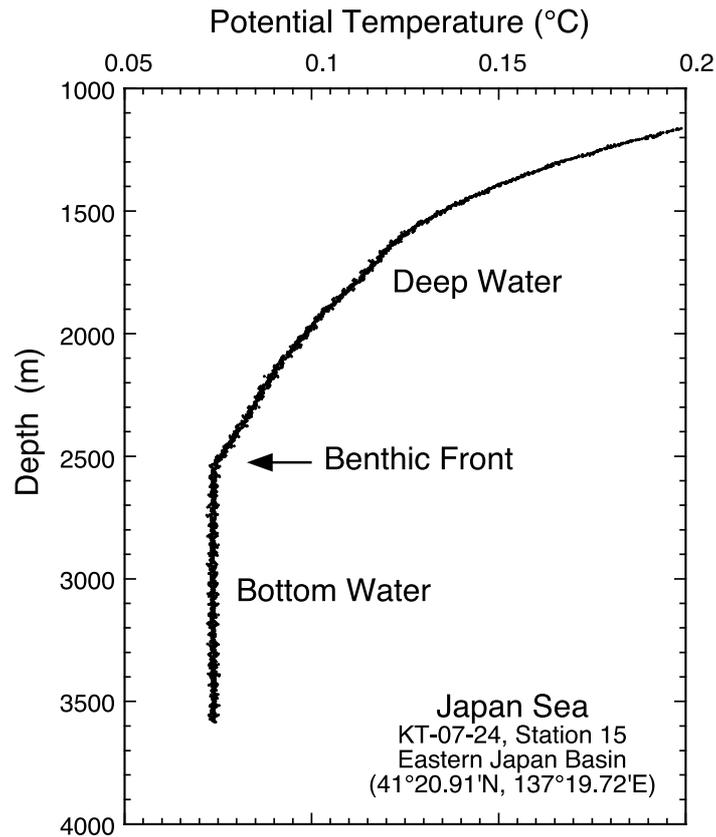


Fig. 5. A typical profile of potential temperature in the Eastern Japan Basin (41°20'N, 137°20'E) showing a boundary (benthic front) at ~2,500 m deep, below which a homogeneous bottom layer was observed. Data were obtained during the R/V *Tansei Maru* KT-07-24 cruise.

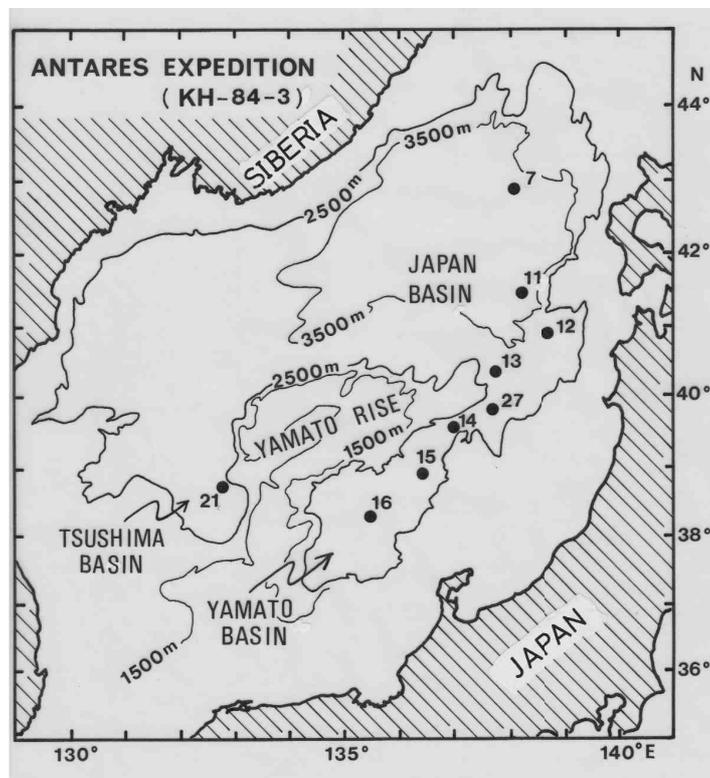


Fig. 6. Topographic map of the Japan Sea showing the location of nine stations of the R/V *Hakuho Maru* KH-84-3 cruise in 1984 (from Gamo *et al.*, 1986).

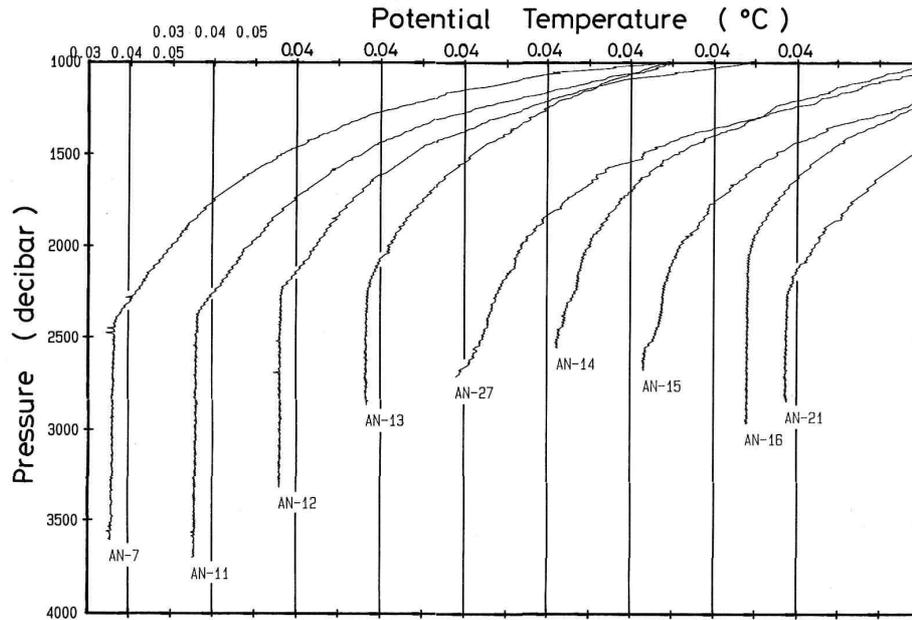


Fig. 7. Vertical profiles of potential temperature below a pressure of 1000 decibars in the Eastern Japan Basin (AN-7, -11, -12, and -13), Yamato Basin (AN-16), and Tsushima Basin (AN-21) observed in 1984. For easier comparisons among the stations, each profile is successively shifted horizontally by 0.02°C (from Gamo *et al.*, 1986).

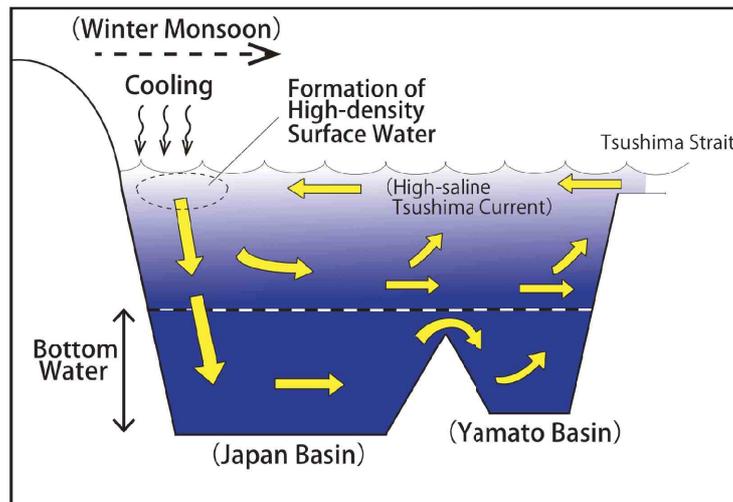


Fig. 8. A simplified vertical cross-section of the Japan Sea with a schematic flow pattern of the abyssal circulation.

normalized to $\delta^{13}\text{C} = -19\text{‰}$.

Although the above model calculation needed the preindustrial $\Delta^{14}\text{C}$ value of surface seawater to correct the effect of artificial ^{14}C due to the atmospheric bomb tests, no such data were available in the Japan Sea. Gamo and Horibe (1983) assumed the preindustrial surface $\Delta^{14}\text{C}$ value to be $-50 \pm 10\text{‰}$ by summarizing a few available pre-bomb $\Delta^{14}\text{C}$ data for the world oceans (Broecker and Li, 1970; Broecker and Peng, 1982; Broecker *et al.*, 1985), which were corrected for the Suess effect of $\sim 8\text{‰}$ between 1850 and 1950 (Broecker and Peng, 1982). It is known that the pre-bomb $\Delta^{14}\text{C}$ level of the subarctic Pacific was very low ($\sim -80\text{‰}$ or less) due to the

upwelling of old, low $\Delta^{14}\text{C}$ subsurface waters (Chen *et al.*, 1995). It should also be taken into consideration, however, that the Japan Sea surface water is strongly affected by the subtropical Tsushima warm current (Fig. 2), which may have raised the pre-bomb $\Delta^{14}\text{C}$ value of the Japan Sea surface water to a higher value, similar to the $\sim -50\text{‰}$ observed in the Temperate Zone of the Pacific (Broecker *et al.*, 1985).

Many studies have been conducted for the elucidation of the time scale of the Japan Sea abyssal circulation since Gamo and Horibe's 1983 study. Various chemical tracers have been used: radium-226 (Harada and Tsunogai, 1986), tritium (Watanabe *et al.*, 1991; Postlethwaite *et al.*, 2005), chlo-

rofluorocarbons (Tsunogai *et al.*, 1993; Riser *et al.*, 1999), rare earth elements (Hatta and Zhang, 2006), and iodine-129 (Suzuki *et al.*, 2009a, b), as well as carbon-14 (Chen *et al.*, 1995; Kumamoto *et al.*, 1998, 2008). Many of the studies gave a timescale of 100–200 years, slightly shorter than the 300 ± 100 years reported by Gamo and Horibe (1983).

It should be noted that the timescale of 100–300 years is much shorter than that of the global conveyor belt of 1000–2000 years (Broecker and Peng, 1982; Broecker *et al.*, 1988). This short timescale, together with the relatively small capacity (volume) of the Japan Sea, gives the Japan Sea a unique characteristic in that it might be much more sensitive to global environmental changes, such as global warming, compared with the open oceans.

5. Characterization of the Japan Sea by Chemical Tracers

5.1 Dissolved oxygen

Dissolved oxygen in seawater has given us much information regarding not only the physical processes of water convection but also the *in situ* biological processes, for the following two reasons: (1) the source of oxygen is only at the ocean surface where photosynthesis produces oxygen, and (2) oxygen is steadily consumed by the oxidative decomposition of organic material in seawater all through the water column. If there is no vertical convection between surface and deep waters, as in the Black Sea, the deep seawater becomes anoxic and sulfate reduction occurs to produce hydrogen sulfide (e.g., Konovalov *et al.*, 2005). The deep water of the Sulu Sea, a tropical marginal sea (max. depth: $\sim 5,000$ m) in the western Pacific, is not anoxic but it shows a considerably low oxygen concentration of $\sim 50 \mu\text{mol kg}^{-1}$, suggesting restricted vertical mixing (Gamo *et al.*, 2007). In contrast, the deep and bottom waters of the Japan Sea are super-oxic because of the existence of an independent bottom water formation mechanism as mentioned above.

The oxygen dissolved in the world's oceans has been measured over the past >100 years by the iodometric titration "Winkler method" (Winkler, 1888). The method has been modified and improved to increase its reliability and suitability for immediate analyses of dissolved oxygen in discrete seawater samples onboard a research vessel (e.g., Gamo, 2011). Carpenter (1965) proposed a whole-bottle titration method by introducing a special Erlenmeyer flask as a new oxygen bottle for both sampling and titration, in order to avoid the analytical error due to the vapor loss of iodine during the sample transfer from a sampling bottle to another titration bottle. In Japan, Horibe and Gamo (1981) adopted this idea from Carpenter to make a new oxygen bottle for the routine measurement of dissolved oxygen, which has been used onboard the R/V *Hakuho Maru* since 1977. The modified Carpenter's oxygen bottle provides oxygen data with low analytical errors of <0.1% or $\pm 0.3 \mu\text{mol kg}^{-1}$, which was based on a precise calibration using the same standard solution (CSK 0.0100 N KIO_3 solution from Wako Pure Chemical Industries, Osaka, Japan) (e.g., Gamo, 2011).

Gamo *et al.* (1986), combining the time-series bottom water O_2 data obtained during the cruises KH-77-3, KH-

79-3, and KH-84-3 with those taken in 1969 by the Japan Meteorological Agency (1971), first noticed a significant O_2 decrease in the bottom water of the Eastern Japan Basin and the Yamato Basin from 1969 to 1984 (Fig. 9). They also observed that the oxygen minimum zone had deepened and the thickness of the bottom layer had decreased since 1969 (Fig. 9). Minami *et al.* (1999) compiled the temporal data of dissolved oxygen and potential temperature from 1958 to 1996 collected by the Maizuru Marine Observatory, Japan Meteorological Agency, confirming the long-term decreasing trend of dissolved oxygen in the JSPW, together with an increasing trend of bottom potential temperature. Gamo (1999) added the KH-98-3 cruise data together with many historical data going back to 1928, and found that the oxygen decreasing trend in the Eastern Japan Basin and the Yamato Basin bottom waters can be traced back to the first half of the 20th century. Such a long-term change strongly suggests the contribution of a worldwide climate change or global warming.

At the beginning of the 21st century, four R/V *Tansei Maru* cruises (from KT-01-15 to KT-07-24) and an R/V *Hakuho Maru* KH-10-2 cruise (as shown in Table 1) were conducted to obtain time-series data more frequently in the Japan Sea, and these cruises confirmed the decreasing trend of dissolved oxygen in the bottom waters in greater detail. Figure 10(a)–(c) summarizes all of the available oxygen profiles in the three basins of the Japan Sea since 1977. It is apparent that dissolved oxygen has decreased in all three basins, with similar rates of decrease. In addition, the 1977 dissolved oxygen profiles showed definite oxygen minimum zones at 1000–1500 m depth in all of the basins, but these zones had almost, or completely, disappeared in 2007 or 2010 (Fig. 10).

The gradual decrease of dissolved oxygen in the bottom water demonstrates the imbalance between the supply of oxygen from the surface and the oxygen consumption in the bottom water for the decomposition of organic matter falling from the surface. The latter process apparently has exceeded the former one since 1977. The oxygen decrease in the bottom water is thought to have been caused by the shortage of oxygen supply from the surface, which means a weakening, or cessation, of thermohaline convection between the surface and the bottom in the Japan Sea. This point will be further discussed in Chapter 6, together with other chemical tracer data.

5.2 Tritium

Anthropogenic tritium (^3H or T, half-life: 12.3 y), which originated from the atomic bomb tests in the atmosphere in the 1960s, is a useful transient tracer to characterize the temporal changes of the deep circulation pattern in the Japan Sea. Since the supply of tritium is limited to precipitation from the atmosphere to the ocean surface where tritium exists as tritiated water (HTO), the amount of tritium in subsurface and deep waters should reflect the magnitude of surface water sinking or convection to the deep layer. Tritium profiles in the Eastern Japan Basin and the Yamato Basin were measured in 1984 (Kaji *et al.*, 1988) and 1998 (Gamo *et al.*, 2001) during the KH-84-3 cruise and the KH-98-3 cruise, re-

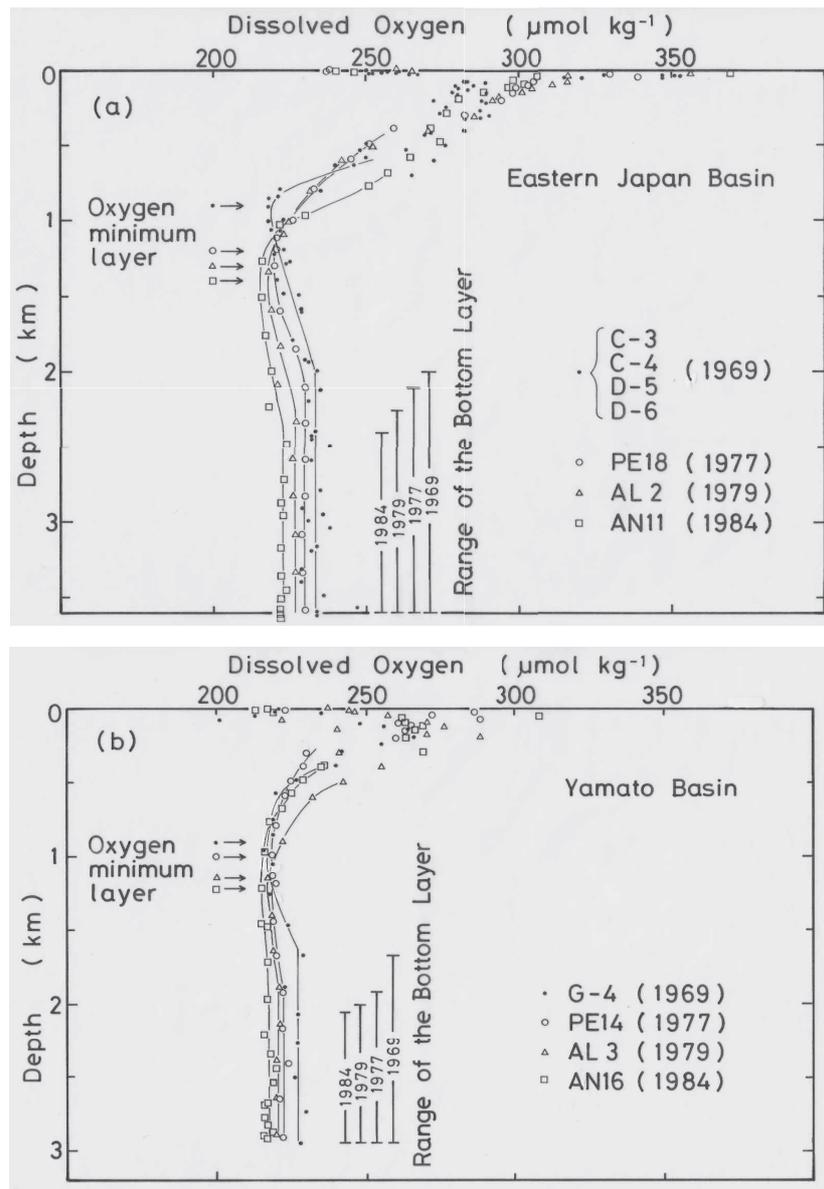


Fig. 9. Vertical profiles of dissolved oxygen in (a) the Eastern Japan Basin and (b) the Yamato Basin between 1969 and 1984, showing a temporal decrease of dissolved oxygen in both bottom waters (from Gamo *et al.*, 1986). The 1969 data are from the Japan Meteorological Agency (1971).

spectively. Figure 11 compares the tritium profiles in 1984 and 1998, with a statistical counting error ($\pm\sigma$) of 0.01 Bq L⁻¹ or less. The tritium values in 1984 are decay-corrected to those in 1998.

It is notable that the tritium concentration in the bottom water (below 2,500 m depth) showed little change between 1984 and 1998 at both locations, indicating that little tritium had entered from the surface to the bottom layer during the 14 years from 1984 to 1998. This finding demonstrates that the sinking of surface seawater to the bottom layer was very small during this 14-year period. In contrast to the bottom water, a distinct increase in the tritium level was observed at the Eastern Japan Basin in the depth range between 700 and 2,000 m (unfortunately no 1984 data in the Yamato Basin are available), as shown by the shaded area in Fig. 11(a).

The increase of tritium in the upper JSPW (700–2,000 m depth) demonstrates the existence of sinking surface seawater at this depth range. It is suspected that winter cooling in the northern Japan Sea still occurred to produce dense surface seawater, but that this surface seawater was not dense enough to sink down to the bottom layer, probably because the winter cooling was weaker than before. The tritium data in 1984 and 1998, together with the dissolved oxygen data described in Subsection 5.1, suggests that the thermohaline conveyor system of the Japan Sea was shifted sometime before 1977 from the previous mode (A) to the current mode (B) as shown in Fig. 12 (Gamo *et al.*, 2001). Mode A, or the “total (overall) convection mode”, is the normal abyssal circulation pattern in which the surface water is sufficiently cooled and sinks down to the bottom layer. In contrast, Mode

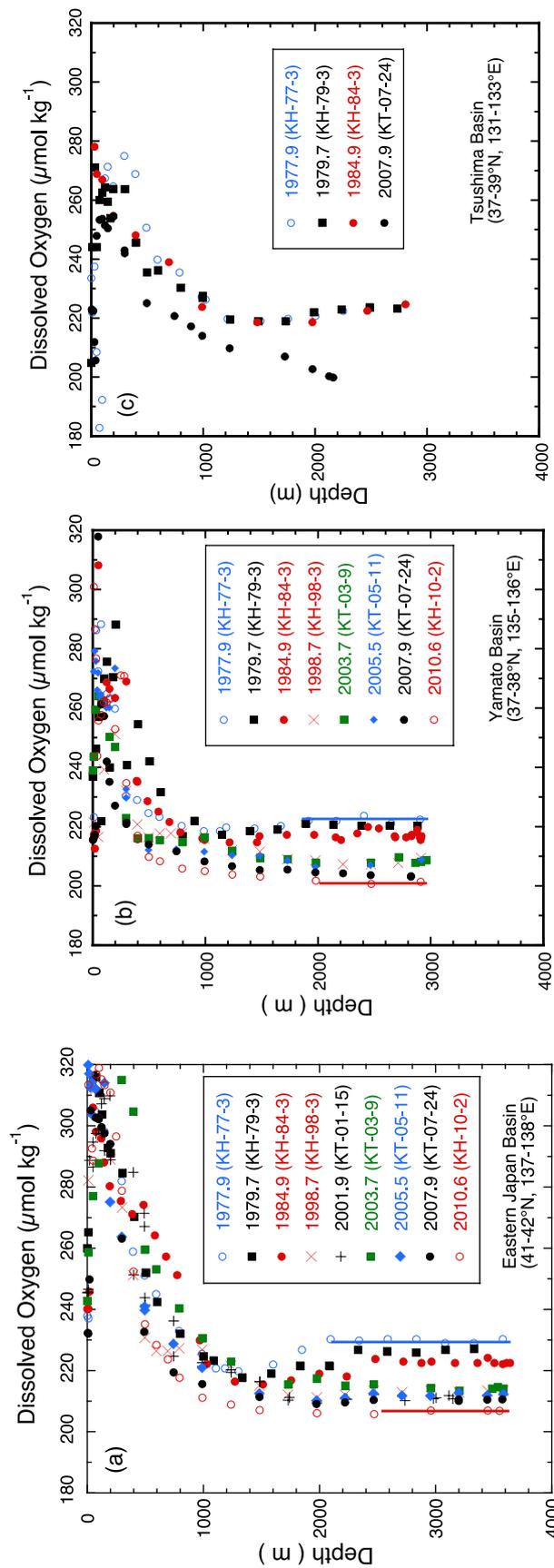


Fig. 10. Vertical profiles of dissolved oxygen in the Eastern Japan Basin from 1977 to 2010 (a), Yamato Basin from 1977 to 2010 (b), and Tsushima Basin from 1977 to 2007 (c).

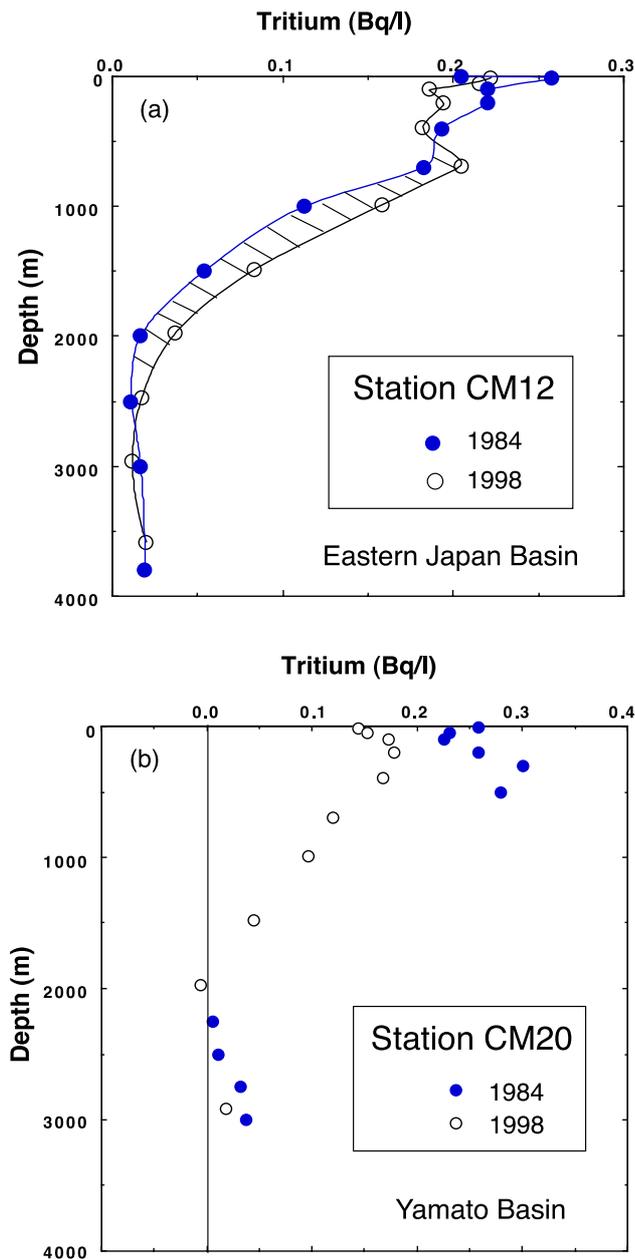


Fig. 11. Vertical profiles of tritium in 1984 and 1998 at station CM12 ($41^{\circ}21'N$, $137^{\circ}20'E$) in the Eastern Japan Basin (a) and at station CM20 ($37^{\circ}44'N$, $135^{\circ}14'E$) in the Yamato Basin (b) (from Gamo *et al.*, 2001). The values in 1984 (Kaji *et al.*, 1988) are decay-corrected to those in 1998.

B, or the “shallow (partial) convection mode”, corresponds to the present Japan Sea, in which the sinking surface water can reach only an intermediate depth shallower than 2,000 m due to its insufficient density. In Mode B, the bottom water is detached and isolated from the water convection loop.

Recent observation studies have elucidated a temporary shift from Mode B to Mode A, or a transient formation of bottom water in an extremely cold winter, which will be discussed in Chapter 6.

5.3 The $^{18}O/^{16}O$ ratio of dissolved oxygen

The stable isotopic composition ($^{18}O/^{16}O$ ratio) of dissolved O_2 provides important information on water mixing

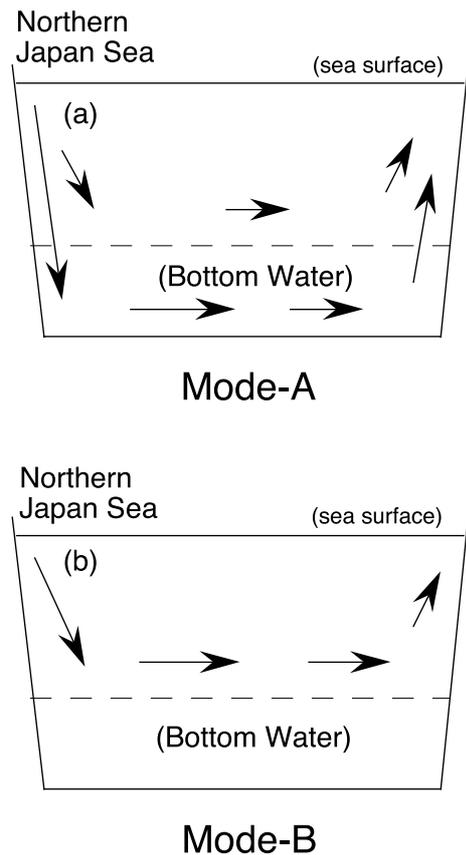


Fig. 12. Schematic images of the deep convection system of the Japan Sea: (a) normal condition (Mode-A) and (b) the present-day condition (Mode-B), where the deep convection cell is shifted upward to a depth of $\sim <2,000$ m, leaving the bottom water below the broken line in a stagnant state (from Gamo *et al.*, 2001).

processes and biological O_2 consumption (Craig and Kroopnick, 1970; Horibe and Shigehara, 1973; Kroopnick and Craig, 1976). The $^{18}O/^{16}O$ ratio is commonly expressed as $\delta^{18}O$ (‰): $([R_x/R_{std}] - 1) \times 1000$, where R_x and R_{std} represent the $^{18}O/^{16}O$ ratios of a sample and an international standard material, respectively. The $\delta^{18}O$ of dissolved O_2 is known to change during respiration because organisms consume $^{16}O_2$ preferentially to $^{18}O^{16}O$ (O_2 made up of ^{18}O and ^{16}O), increasing the $\delta^{18}O$ of the remaining dissolved O_2 . Several studies have examined the magnitude of this isotope effect in culture (Guy *et al.*, 1989; Kiddon *et al.*, 1993) and in ocean surface waters (Bender and Grande, 1987; Quay *et al.*, 1993; Hendricks *et al.*, 2004, 2005). Although studies of the isotopic composition of dissolved O_2 may greatly facilitate better estimations of dissolved O_2 consumption processes, few $\delta^{18}O$ data of dissolved O_2 in the Japan Sea are available at this time.

Nakayama *et al.* (2007) first measured the isotopic ratio ($\delta^{18}O$) of dissolved O_2 in the Eastern Japan Basin during the KT-05-11 cruise in 2005. The vertical profile of the $\delta^{18}O$ together with the O_2 concentrations are shown in Fig. 13. The O_2 concentrations were up to $\sim 10\%$ supersaturated in the surface layer (0–30 m depth) with respect to those in equilibrium with the atmosphere at the temperature and salinity of

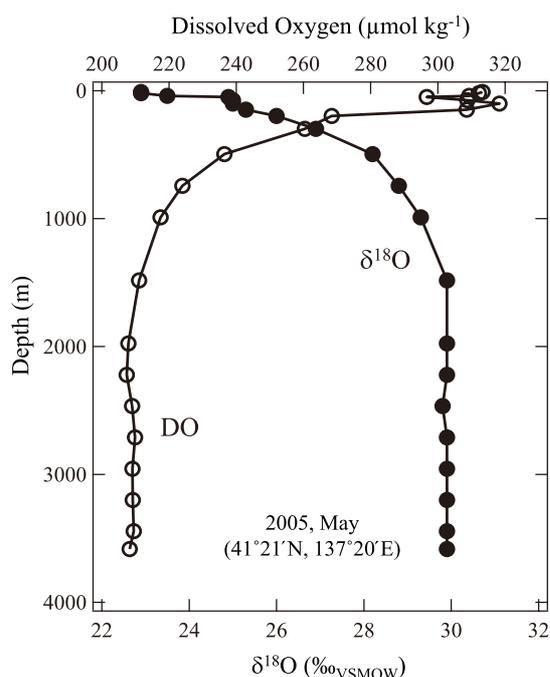


Fig. 13. Vertical profiles of dissolved O₂ (open circle symbols) and its isotopic ratio (δ¹⁸O) (closed circle symbols) measured in 2005 in the Eastern Japan Basin (41°21'N, 137°20'E) (Nakayama *et al.*, 2007).

the samples. The dissolved O₂ decreased with depth to reach a nearly constant value of ~210 μmol kg⁻¹ in the bottom water below a depth of 2500 m. The vertical profiles of O₂ concentration and its δ¹⁸O values are mirror images of each other. The isotopically lightest dissolved O₂ was observed in surface waters above 20 m depth with an average δ¹⁸O value of +22.9‰, which is lighter by +1.4‰ than the atmospheric equilibrium value of +24.3‰ at 10°C (Kroopnick and Craig, 1972). The light δ¹⁸O value in the surface layer seems to reflect that the photosynthetically produced O₂ by phytoplankton with a lower δ¹⁸O value of ~0‰ was added to the surface seawater. Below the surface layer, the δ¹⁸O increases with depth, reaching a maximum value of +29.9‰ at 1483 m depth, remaining almost constant down to the bottom (Fig. 13).

By assuming a closed system for the Japan Sea deep water, Nakayama *et al.* (2007) applied the Rayleigh distillation equation to the relationship between the observed δ¹⁸O values and the fraction of O₂ saturation, to obtain the isotope fractionation factor (α) of 0.9875 ± 0.0003 (the isotope effect = +12.5 ± 0.3‰). This isotopic fractionation factor was found to be significantly higher than those obtained in heterotrophic bacteria (α = 0.981) cultured in laboratory studies (Kiddon *et al.*, 1993) and obtained for ocean surface waters (α = 0.979) (Hendricks *et al.*, 2004, 2005). The obtained fractionation factor is nearly equal to the value of 0.987 estimated by Kroopnick and Craig (1976) for the deep Pacific waters, suggesting a similar mechanism of O₂ consumption in the deep waters between the Pacific Ocean and the Japan Sea. Although the Rayleigh distillation equation predicts that the δ¹⁸O values would increase by 0.05‰–0.06‰ per year

according to the *in situ* O₂ consumption rate of 1.2–1.4 μmol kg⁻¹ y⁻¹ and the fractionation factor of 0.9875, the linearity may be affected by small residual fractions of dissolved O₂ or by admixtures of old and young water masses. Time-series measurements of the δ¹⁸O of dissolved O₂ as well as the dissolved O₂ concentration should be continued in order to solve the above problem.

5.4 Helium isotopes

The ³He/⁴He ratio is one of the most sensitive and conservative tracers in chemical oceanography (Schlosser and Winckler, 2002) because of the primordial signature, rapid mobility and chemical inertness of the isotopes. Observed ³He excesses in seawater samples are usually reported in the δ³He notation, which is defined as an anomaly of the helium isotope ratio relative to the atmospheric standard: δ³He(‰) = ([³He/⁴He]_{seawater}/³He/⁴He]_{air} - 1) × 100. Some helium isotope data were obtained in 1986 from a station in the Eastern Japan Basin (Sano *et al.*, 1989), in 1999 from the entire region of the Japan Sea (Postlethwaite *et al.*, 2005), and in 2005 from the Eastern Japan Basin and the Yamato Basin (Takahata *et al.*, 2008). Based on these data, the helium isotopes in the Japan Sea are characterized as follows: (1) maximum δ³He values of ~8‰ (Postlethwaite *et al.*, 2005; Takahata *et al.*, 2008) are observed at mid-depth (~1000 m), which may be attributable to the decay product of the bomb-produced tritium, (2) δ³He values in deep waters are significantly smaller than those in deep Pacific waters (at 2500 m depth) ~20‰ adjacent to the Japanese archipelago, which indicates that mantle-derived helium in deep Pacific seawater cannot enter the Japan Sea, and (3) the homogeneous δ³He values of ~2‰ observed in bottom waters (Postlethwaite *et al.*, 2005; Takahata *et al.*, 2008) indicate that very little mantle helium is supplied from the bottom (Fig. 14).

Sano *et al.* (1989) first found significant excesses of ³He in the intermediate and bottom seawaters at (40°43'N, 139°01'E) in the Eastern Japan Basin. The δ³He value of ~4‰ at 1000 m depth suggested an addition of tritogenic ³He. This excess of ~4‰ is smaller than those observed by Postlethwaite *et al.* (2005) and Takahata *et al.* (2008) (6–8‰). This may be due to the differences of tritium concentration and seawater age among the three observations. Sano *et al.* also reported that the δ³He value of ~4‰ in the bottom seawater might be a signature of mantle-derived helium. Postlethwaite *et al.* (2005) discussed deep convection processes in the Japan Sea after measuring tritium and δ³He in seawater. They reported that brine rejection in the Tatar Strait, as suggested by Martin *et al.* (1992), is not currently a significant deep-water formation mechanism in the Japan Sea. Their model calculations suggested that the subduction of sea-ice melt water might be a significant ventilation mechanism for the Japan Sea Intermediate Water, based on an argon minimum at the recently ventilated salinity minimum in the Tatar Strait and western Japan Basin. Postlethwaite *et al.* (2005) also found that the Tsushima Basin shows ~1% higher δ³He values than the other regions of the Japan Sea for deep seawater at the same density, suggesting the existence of older water in the Tsushima Basin.

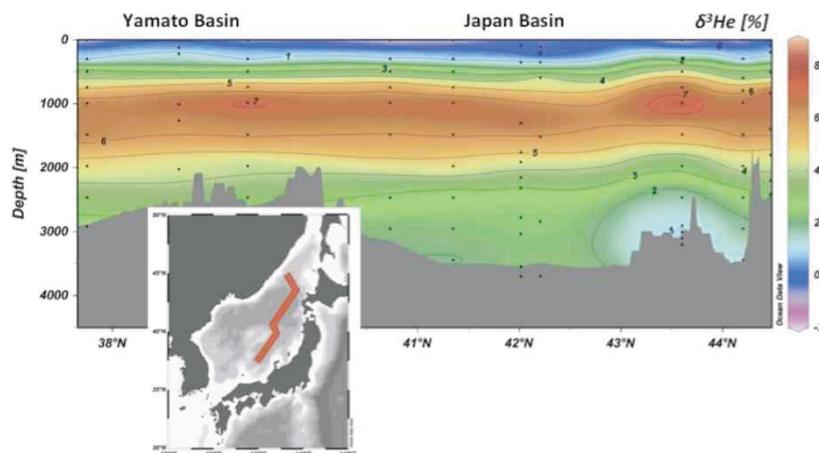


Fig. 14. Vertical distributions of $\delta^3\text{He}$ (%) along the sampling sites, along the thick red line in the inserted map. Data are from Takahata *et al.* (2008) and Postlethwaite *et al.* (2005).

Takahata *et al.* (2008) investigated the helium isotopic ratios of seawater samples collected during the KT-05-11 cruise in 2005. Figure 14 shows a contour map of $\delta^3\text{He}$ drawn using the KT-05-11 data together with data reported by Postlethwaite *et al.* (2005). The vertical profiles of the excess ^3He do not differ much among the sampling sites. The $\delta^3\text{He}$ values near the sea surface are almost 0%, and some are minus values. The $\delta^3\text{He}$ values increase downward, and maxima of about 8% are observed at mid-depth (~ 1000 m), which may be attributable to the decay product of tritium. The $\delta^3\text{He}$ decreases to $\sim 2\%$ in the bottom water. The Bottom Water in the Yamato Basin has slightly higher $\delta^3\text{He}$ values compared with the Japan Basin. The lower $\delta^3\text{He}$ values below 2500 m at a northern station ($43^\circ 36' \text{N}$, $139^\circ 18' \text{E}$) may indicate an intrusion of water mass with higher temperature, lower salinity and low $\delta^3\text{He}$ compared with other stations, which seems different from any bottom waters in other regions in the Japan Sea and may derive from the Tatar strait.

Takahata *et al.* (2008) also discussed the ^3H - ^3He ages of seawater in the Japan Sea. The ^3H - ^3He ages of about 5 to 20 years observed at depths shallower than 1000 m in the Japan Sea showed a monotonic increase with depth. There is a positive correlation between the apparent oxygen utilization and the ^3H - ^3He ages. The estimated oxygen utilization rate from the correlation in a layer between 500 m and 1000 m is about $3 \mu\text{mol kg}^{-1} \text{y}^{-1}$, which is similar to that in the eastern subtropical North Atlantic (Jenkins, 1987).

5.5 Excess ^{222}Rn

Radon-222 (^{222}Rn) is a radioactive rare gas with a half-life of 3.82 days. Dissolved ^{222}Rn in seawater is formed from its parent nuclide radium-226 (half-life, 1600 years), usually in secular radioactive equilibrium with ^{226}Ra . There is another source of ^{222}Rn from the seafloor: the emanation of ^{222}Rn derived from the sedimentary ^{226}Ra . This additional ^{222}Rn , detected only near the seafloor due to its short half-life, is called “excess ^{222}Rn ”, and its amount can be obtained by subtracting the background ^{226}Ra activity (^{222}Rn in radioactive equilibrium with ^{226}Ra) from the total ^{222}Rn activity. The excess ^{222}Rn is an ideal chemical tracer for estimating the short-

term water movement and eddy diffusion just above the sea bottom (e.g. Broecker, 1965; Chung and Craig, 1972; Chung and Kim, 1980; Gamo and Horibe, 1984).

It has been speculated that the vertical uniformity, or extremely weak stratification, of the Japan Sea bottom layer (Fig. 5) is maintained by active vertical mixing or eddy diffusion (Gamo *et al.*, 1986). In order to evaluate this speculation from a geochemical point of view, Gamo (2014) measured the excess ^{222}Rn profiles in the Japan Sea bottom water, using the same method as Gamo and Horibe (1984). The obtained excess ^{222}Rn data, together with the vertical profiles of potential temperature, are shown in Fig. 15(a, b), for the Eastern Japan Basin and the Yamato Basin, respectively. Since the bottom sediment is the only source for the excess ^{222}Rn , its vertical profile is generally expected to decrease exponentially with the distance above the bottom, and we could estimate the vertical eddy diffusivity by assuming a steady-state diffusion model (e.g., Broecker, 1965). The profiles observed in the Japan Sea, however, are completely different from the above expectation. We obtained zigzag patterns with mid-depth minima and mid-depth maxima (Fig. 15), which strongly suggest the horizontal transport of ^{222}Rn -rich waters to the excess ^{222}Rn maximum depths temporarily.

It is noteworthy that topographically induced eddies or deep horizontal currents (e.g., Takematsu *et al.*, 1999; Senjyu *et al.*, 2005a) could cause the temporal mid-depth ^{222}Rn maxima. If such lateral and short-term convections exist ubiquitously in deep basins of the Japan Sea, they may also play a role in activating vertical mixing to maintain the vertical homogeneity of the Sea’s bottom layer. Although the Japan Sea bottom water is vertically too uniform to extract any information on the fine structures of bottom water dynamics from physicochemical tracers, such as potential temperature and dissolved oxygen, the excess ^{222}Rn profiles clearly evidence short-term heterogeneity of the Japan Sea bottom water, thanks to the short half-life of ^{222}Rn .

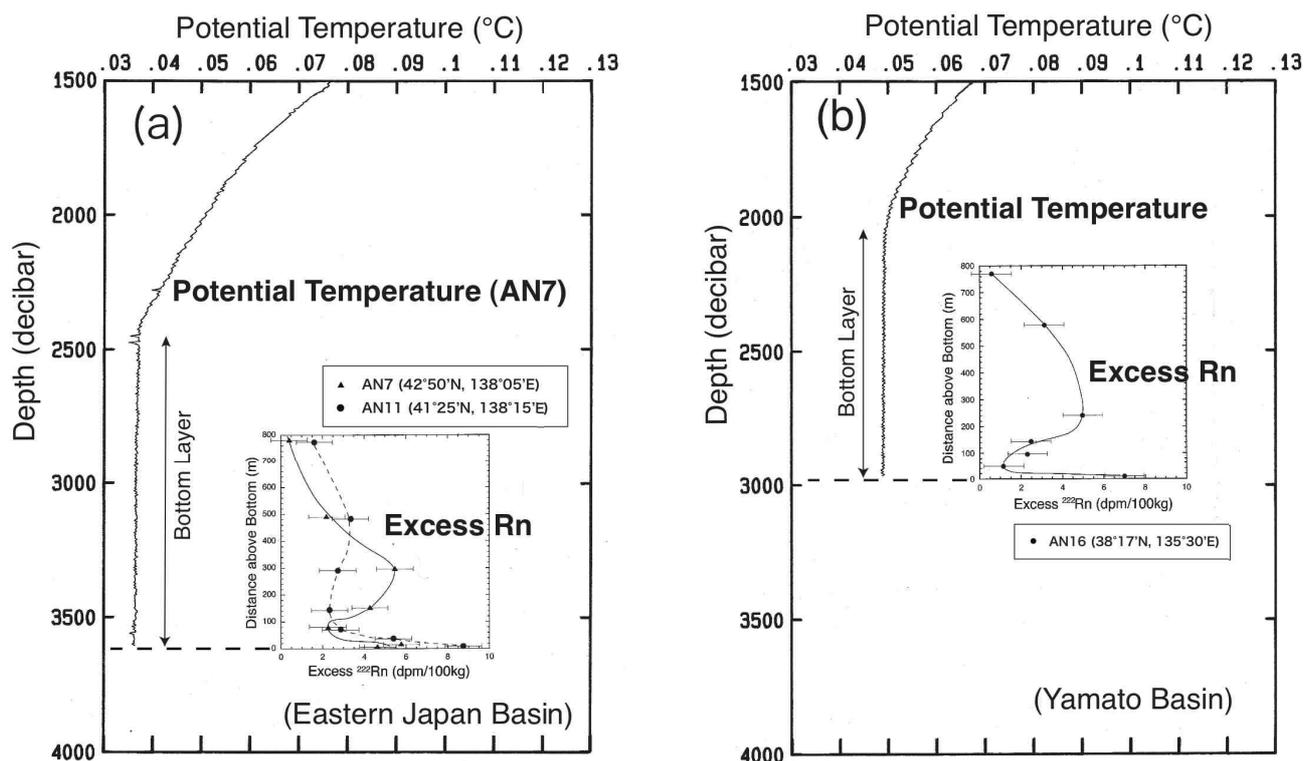


Fig. 15. Vertical profiles of excess ^{222}Rn and potential temperature above the bottom at two stations (AN7 and AN11) in the Eastern Japan Basin (a), and that (AN16) in the Yamato Basin (b). (Reprinted from *Prog. Oceanogr.*, 121, Gamo, T., Excess ^{222}Rn profiles in the bottom layer of the Japan Sea and their implication for bottom water dynamics, 94–97, Copyright 2014, with permission from Elsevier.)

5.6 Methane and its carbon isotopes

Much attention has been paid to the distribution and behavior of methane (CH_4) in the ocean, because of its importance as a greenhouse gas and as a potential energy resource of methane gas hydrate. Gamo *et al.* (2012) measured vertical profiles of dissolved methane (CH_4) and its carbon isotope ratio ($^{13}\text{C}/^{12}\text{C}$ or $\delta^{13}\text{C}$) in the Japan Sea for the first time in 2007 during the KT-07-24 cruise as part of collaborative studies between Japan and Korea. The CH_4 concentration and its $\delta^{13}\text{C}_{\text{PDB}}$ were measured using continuous-flow isotope ratio mass spectrometry (CF-IRMS) at Hokkaido University (Tsunogai *et al.*, 2000). The $\delta^{13}\text{C}_{\text{PDB}}$ is defined as: $([R_x/R_{\text{std}}] - 1) \times 1000$ (‰), where R_x and R_{std} represent the $^{13}\text{O}/^{12}\text{O}$ ratios of a sample and the PDB international standard (belemnites from the Peedee Formation of South Carolina), respectively. Figure 16(a, b) shows the vertical profiles of CH_4 and those of $\delta^{13}\text{C}\text{-CH}_4$ in the three basins (Eastern Japan Basin, Yamato Basin, and Tsushima Basin), respectively.

The CH_4 concentrations in the surface seawaters ($D = 0$ m) were 2.6–3.8 nmol kg^{-1} , showing a supersaturation of $43 \pm 22\%$ compared with the solubility equilibrium value of 2.1–2.3 nmol kg^{-1} . The averaged $\delta^{13}\text{C}$ value of the surface CH_4 was -47.7 ± 0.6 ‰, almost the same as -47 ‰ of the present atmospheric CH_4 value. According to Wanninkhof (1992), the CH_4 flux from sea to air was estimated as $1.5(\pm 1.1) \times 10^{10}$ (g y^{-1}) for the entire Japan Sea, by using the above-mentioned supersaturation level and the mean wind speed during the cruise. This flux is approximately three or-

ders of magnitude lower than the global oceanic CH_4 flux, which seems reasonable if we remember that the area of the Japan Sea is $\sim 0.3\%$ of that of the global ocean.

In a subsurface photic zone, a sharp maximum of CH_4 concentration was observed between the depths of ~ 30 m and ~ 200 m (Fig. 16(a)). The CH_4 value observed was as high as 9.7 nmol kg^{-1} , $\sim 300\%$ supersaturation (this maximum value was obtained at an intermediate station (39°49'N, 137°41'E) between the Eastern Japan Basin and the Yamato Basin, and not shown in Fig. 16(a)). Judging from the $\delta^{13}\text{C}$ values (-45 ‰ to -55 ‰) of the subsurface CH_4 (Fig. 16(b)), both anaerobic methanogenesis in micro-environments and aerobic methane oxidation seem to have occurred at the same time. Below the subsurface maximum zone, the CH_4 concentration decreased with depth, probably due to methanotrophic bacteria, toward minimum values of ~ 1 nmol kg^{-1} ($\delta^{13}\text{C}$: -30 ‰ to -40 ‰) at 1,500–2,000 m depth.

Below a depth of 2,000 m, the CH_4 profiles differ slightly among the three basins; in the Eastern Japan Basin the CH_4 concentration remained almost constant down to the seafloor, whereas in the Yamato and Tsushima Basins it gradually increased with depth up to >2.0 nmol kg^{-1} (Fig. 16(a)). The CH_4 increase toward the bottom was accompanied by a decrease of $\delta^{13}\text{C}\text{-CH}_4$ to ~ -50 ‰ (Fig. 16(b)), suggesting supplies of microbial CH_4 (e.g., Whiticar, 1999) from bottom sediment in the Yamato and Tsushima Basins.

At a station (38°12'N, 137°46'E) inside the Toyama Deep Sea Channel north of Toyama Bay, a notable CH_4 plume with

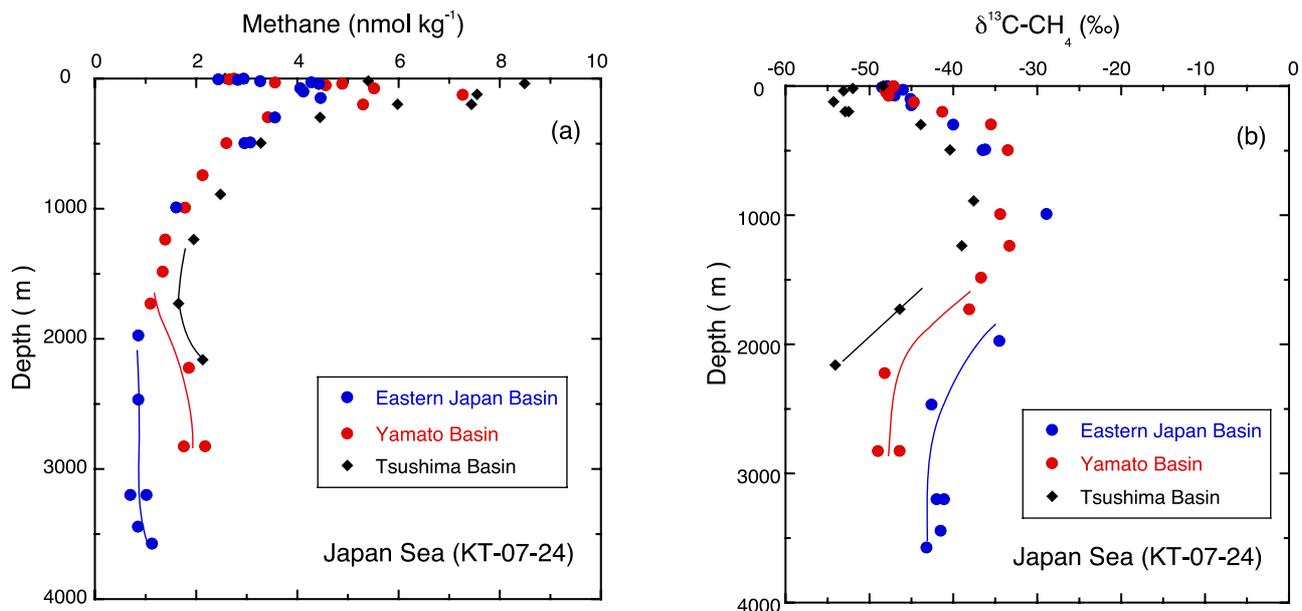


Fig. 16. Vertical profiles of methane (a) and its $\delta^{13}\text{C}$ in the three major basins in the Japan Sea. Data were obtained during the R/V *Tansei Maru* KT-07-24 cruise. (Modified from *Mar. Chem.*, 128/129, Gamo, T., U. Tsunogai, A. Hirota, N. Nakayama, D.-J. Kang, and K.-R. Kim, First measurements of methane and its carbon isotope ratio in the Japan Sea (East Sea), 92–99, Copyright 2012, with permission from Elsevier.)

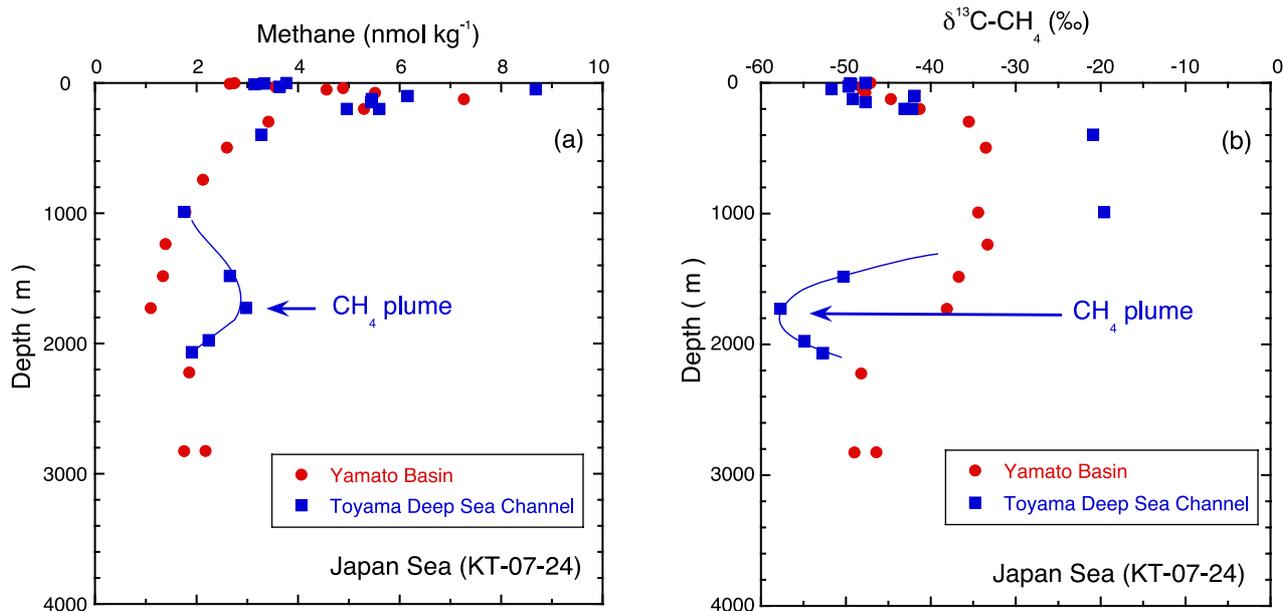


Fig. 17. A CH_4 plume observed at the Toyama Deep Sea channel station ($38^\circ 12' \text{N}$, $137^\circ 46' \text{E}$) as an anomalous peak of CH_4 concentration (a), and $\delta^{13}\text{C}$ of CH_4 (b), compared to the profiles at the Yamato Basin station ($38^\circ 00' \text{N}$, $135^\circ 36' \text{E}$). (Modified from *Mar. Chem.*, 128/129, Gamo, T., U. Tsunogai, A. Hirota, N. Nakayama, D.-J. Kang, and K.-R. Kim, First measurements of methane and its carbon isotope ratio in the Japan Sea (East Sea), 92–99, Copyright 2012, with permission from Elsevier.)

a microbial $\delta^{13}\text{C}$ of $\sim -60\text{‰}$ was found (Fig. 17), possibly associated with the subseafloor CH_4 hydrate observed thus far in the Japan Sea (Tomaru *et al.*, 2007; Snyder *et al.*, 2007; Hiruta *et al.*, 2009; Matsumoto *et al.*, 2009). In summary, the spatial variations of dissolved CH_4 in the Japan Sea are apparently associated not only with bottom water circulation but also with CH_4 supplies (some of them may be of gas hydrate origin) from bottom sediment.

5.7 Man-made persistent perfluoroalkyl substances (PFASs)

Many current projects are focused on nationwide surveys of man-made POPs (persistent organic pollutants) on land, but very few such studies have been conducted for oceanic environments. Among the many POPs, perfluoroalkyl substances (PFASs) such as PFOS (perfluorooctane sulfonate) and PFOA (perfluorooctanoic acid) may be useful as chemical tracers because of their solubility and persistence characteris-

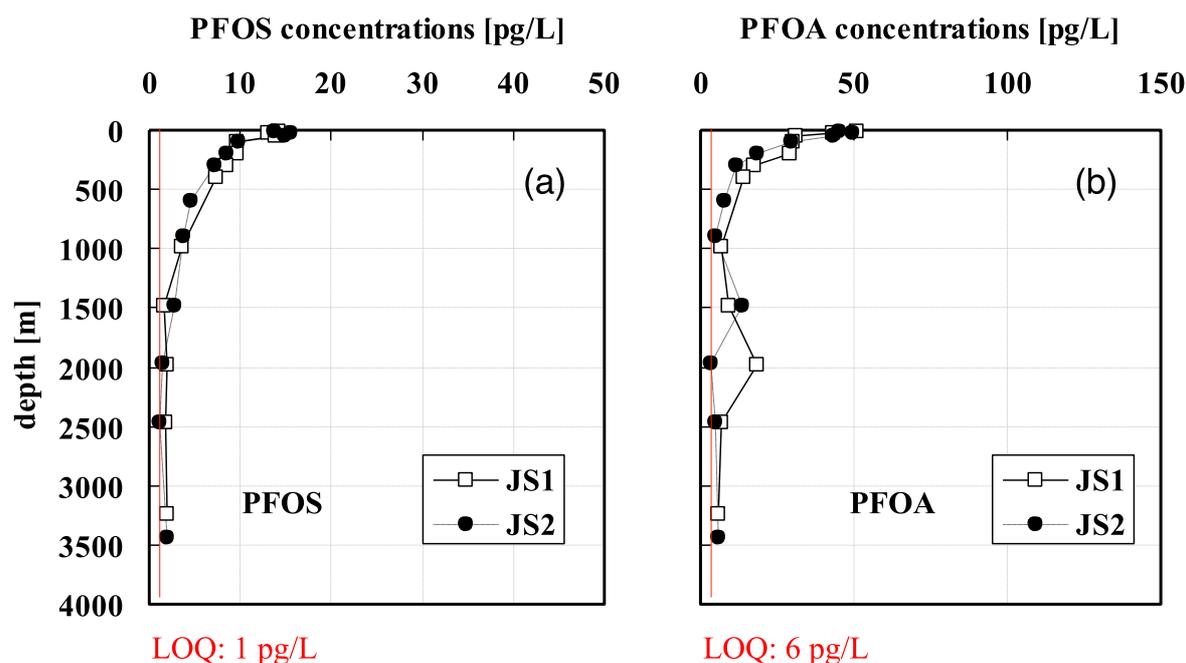


Fig. 18. Vertical profiles of PFOS (a) and PFOA (b) at two locations in the Japan Sea (JS1: 40°43'N, 136°34'E; JS2: 44°12'N, 138°54'E) measured during the R/V *Tansei Maru* KT-05-11 cruise. (Reprinted from *Chemosphere*, 70, Yamashita, N., S. Taniyasu, G. Petrick, S. Wei, T. Gamo, P. K. S. Lam, and K. Kannan, Perfluorinated acids as novel chemical tracers of global circulation of ocean waters, 1247–1255, Copyright 2008, with permission from Elsevier.)

tics. Since the Japan Sea is close to the Asian Continent, it is also at high risk of being polluted by PFASs. To enable reliable trace-level measurements of PFASs in water samples, the international standard method (ISO₂₅₁₀₁) was established in 2009 (ISO, 2009).

Yamashita *et al.* (2008) measured PFOS and PFOA profiles for the first time from the surface to the bottom of the Japan Sea during the KT-05-11 cruise in 2005. As shown in Fig. 18, the concentrations of PFOA were higher than those of PFOS, and a gradual decrease from the surface to the bottom was observed, similar to those of man-made materials in the Japan Sea such as tritium (Watanabe *et al.*, 1991; Gamo *et al.*, 2001; Postlethwaite *et al.*, 2005) and chlorofluorocarbons (Tsunogai *et al.*, 1993; Min and Warner, 2005). The deep convection or surface water sinking in the Japan Sea will transfer these PFASs to a deeper zone. The measurements using the KH-10-2 samples taken in 2010 revealed significant increases of PFOS and PFOA dissolved in intermediate to deep waters between 2005 and 2010 (Yamazaki *et al.*, 2013; Yamashita *et al.*, in preparation). Continuous monitoring of PFASs must be carried out in the future.

6. Temporal Change of the Japan Sea Bottom Water

The recent decreasing trend of bottom dissolved oxygen between 1977 and 2010 (Fig. 10), together with the tritium data from 1984 and 1998 (Fig. 11) strongly suggests the reduction or cessation of surface water sinking to the bottom layer, probably associated with climate change or global warming. According to the 4th Intergovernmental Panel for Climate Change (IPCC) report (Solomon *et al.*, 2007), the globally

averaged warming amounts to 0.13°C per decade over the last 50 years. Figure 19 shows the long-term variation of the monthly max. and min. air temperatures averaged for every winter season (Dec., Jan. and Feb.) at Vladivostok, Russia (data source: NOAA NCDC GHCN v2 raw). It is evident that Vladivostok has suffered a gradual increase (a few degrees Celsius) of air temperature during the winters over the past century. Figure 19 suggests a synchronized temperature increase of surface seawater around Vladivostok in winter, causing an obstruction of the bottom water formation by lowering the density of surface seawaters off Vladivostok, a possible place for the bottom water formation (e.g., Kawamura and Wu, 1998).

The wind speed in winter is also closely associated with the bottom water formation, because a stronger wind would result in more active water evaporation, increasing the heat flux from the surface seawater to the atmosphere. Varlamov *et al.* (1997) reported that the mean wind speed over the Japan Sea during the winter season had decreased by $\sim 1 \text{ m s}^{-1}$ between 1960 and 1990. Such a decreasing trend of wind speed in winter may have further lowered the efficiency of dense surface water formation in the northern Japan Sea.

Table 2 and Fig. 20 show the temporal changes of dissolved oxygen concentrations and the potential temperature in the bottom layer of the Eastern Japan Basin, the Yamato Basin, and the Tsushima Basin since 1977. There are two notable points in Fig. 20. First, almost one-sided decreasing and increasing trends have been observed for the bottom dissolved oxygen and potential temperature, respectively, in the three basins since 1977. The second point is a curious break at the beginning of the 2000s in the bottom O₂ records (Fig. 20(a)).

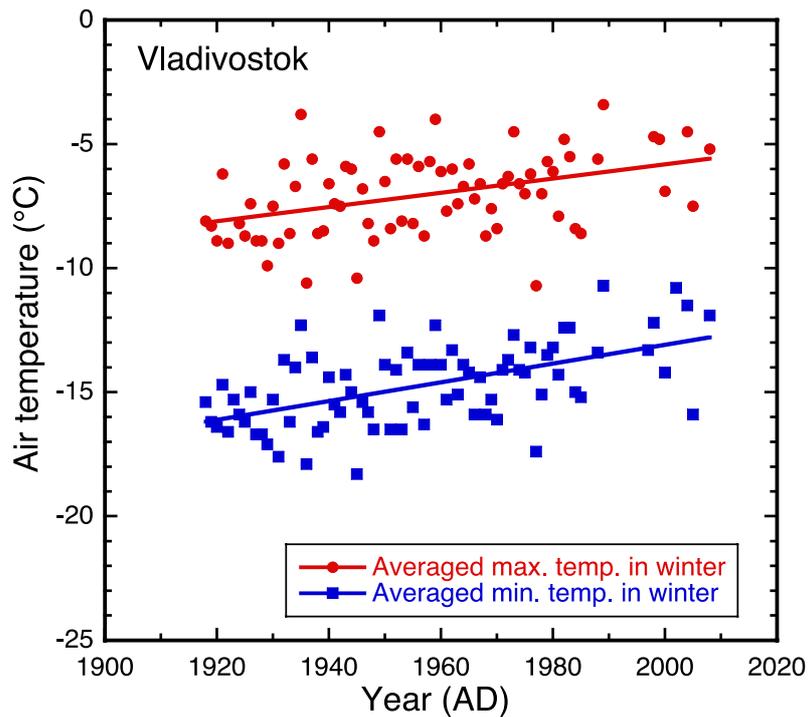


Fig. 19. Gradual increase of air temperature in winter at Vladivostok during the past century as expressed by the yearly variations of the averaged max. temperature and min. temperature observed in each winter months (Dec., Jan., and Feb.). Data are from NOAA NCDC GHCN v2 raw.

Table 2. Averaged values of dissolved oxygen and potential temperature of the bottom water of the Sea of Japan between 1977 and 2010, measured by the *Hakuho Maru* and *Tansei Maru* cruises.

Year	Cruise Name	Eastern Japan Basin		Yamato Basin		Tsushima Basin	
		Bottom Layer Dissolved O ₂ ($\mu\text{mol kg}^{-1}$)	Bottom Layer CTD Pot. Temp. ($^{\circ}\text{C}$)	Bottom Layer Dissolved O ₂ ($\mu\text{mol kg}^{-1}$)	Bottom Layer CTD Pot. Temp. ($^{\circ}\text{C}$)	Bottom Layer Dissolved O ₂ ($\mu\text{mol kg}^{-1}$)	Bottom Layer CTD Pot. Temp. ($^{\circ}\text{C}$)
1977	KH-77-3	229.9	—	222.2	—	222.0	—
1979	KH-79-3	226.6	0.041	220.4	0.052	223.3	0.039
1984	KH-84-3	222.7	0.036	217.2	0.048	223.6	0.037
1998	KH-98-3	213.2	0.062	208.0	0.079	—	—
2001	KT-01-15	211.2	—	—	—	—	—
2003	KT-03-9	214.3	0.073	208.4	—	—	—
2005	KT-05-11	212.1	0.078	207.9	0.093	—	—
2007	KT-07-24	210.4	0.074	203.4	0.091	201.0	0.091
2010	KH-10-2	206.6	0.084	201.1	0.101	—	—

Between 2001 and 2005, a slight increase or flattening of dissolved oxygen was present in the monotonous decreasing trend since 1977 in the bottom waters of the Eastern Japan Basin and the Yamato Basin. The second point will be discussed later in detail.

As already discussed in Subsections 5.1 and 5.2, the shift of the deep ventilation pattern from Mode A to Mode B (Fig. 12) has isolated the bottom water from the sinking fresh waters with low temperature and high dissolved oxygen, which are apparently reflected in the one-sided decrease of dissolved oxygen and increase of potential temperature in the bottom water (Fig. 20). During the 33 years from 1977 to 2010, dissolved oxygen decreased from 229.9 to 206.6 $\mu\text{mol kg}^{-1}$ (decrease rate: 0.71 $\mu\text{mol kg}^{-1} \text{y}^{-1}$) in the Eastern Japan Basin, and from 222.2 to 201.1 $\mu\text{mol kg}^{-1}$ (decrease rate: 0.64

$\mu\text{mol kg}^{-1} \text{y}^{-1}$) in the Yamato Basin. In the Tsushima Basin, dissolved oxygen decreased from 223.6 to 200.1 $\mu\text{mol kg}^{-1}$ (decrease rate: 1.02 $\mu\text{mol kg}^{-1} \text{y}^{-1}$) between 1984 and 2007. The increase of potential temperature has been commonly observed in all three basins by $\sim 0.05^{\circ}\text{C}$ since 1979, as shown in Fig. 20(b) and Table 2.

As shown in Fig. 20(a, b), the changing patterns of dissolved oxygen and potential temperature are almost parallel between the Eastern Japan Basin and the Yamato Basin; the offset of dissolved oxygen of $\sim 6 \mu\text{mol kg}^{-1}$ and that of the potential temperature of $\sim 0.015^{\circ}\text{C}$ have been steadily maintained since 1977. It is of interest, however, that the Tsushima Basin has shown a slightly different pattern of bottom O₂: little change between 1977 and 1987 followed by a steep decline, as shown by the dotted lines in Fig. 20(a), implying

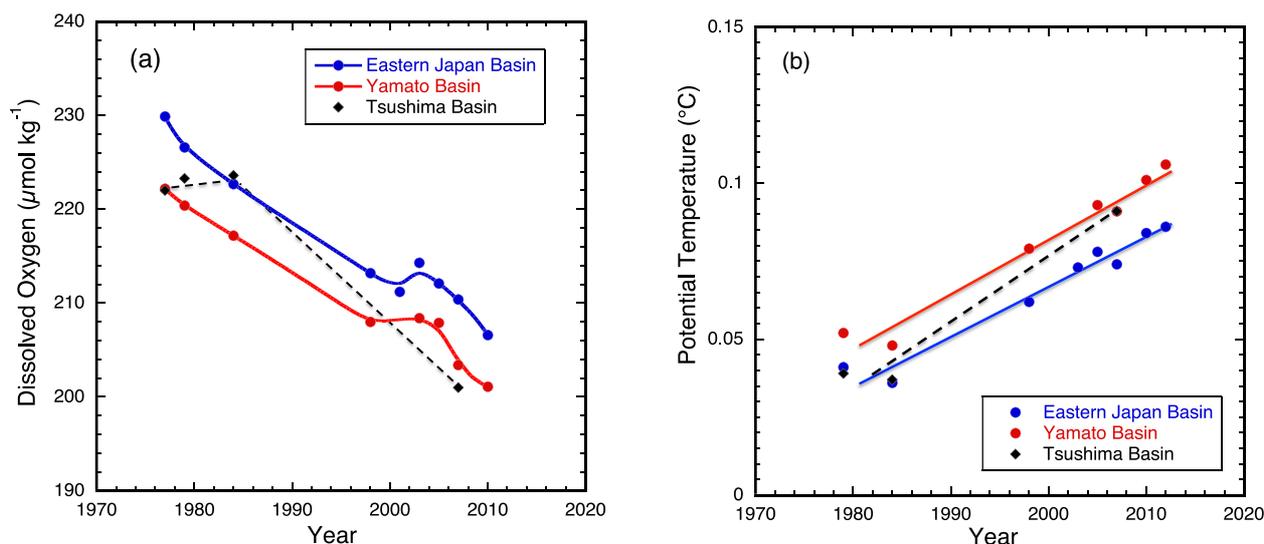


Fig. 20. Time-series variations of dissolved oxygen (a) and potential temperature (b) of the bottom water in the three basins of the Japan Sea between 1977 and 2010.

different deep convection or biogeochemical processes occurring in the Tsushima Basin compared with the other two basins. More data accumulation in the Tsushima Basin is desirable.

The clear break in the decreasing trend of dissolved oxygen in the bottom water at the beginning of the 2000s (Fig. 20(a)) could be related to the following event: a sudden formation of bottom water, probably during the severely cold winter of 2000–2001. This event was identified from water column anomalies of chemical tracers (dissolved oxygen, nutrients, and chlorofluorocarbons) just above the seafloor in the coastal zone off Vladivostok in the summer of 2001 (Kim *et al.*, 2002; Senju *et al.*, 2002; Talley *et al.*, 2003; Tsunogai *et al.*, 2003). By using moored current meters, Senju *et al.* (2002) observed strong bottom currents up to 8 cm s^{-1} from mid-February 2001, suggesting a spin-up of the thermohaline circulation in the Japan Sea. These physicochemical observations demonstrated that the abyssal circulation pattern (conveyor belt) of the Japan Sea could shift immediately as a response to major changes in climate and weather conditions.

No bottom water formation event has been detected since that of 2000–2001. It seems likely that the transient bottom water formation (or shift from Mode B to Mode A) such as the 2000–2001 event has been and will be occasionally realized during more periods of no bottom water formation, imprinting occasional breaks on the monotonous O_2 decreasing trend.

Watanabe *et al.* (2003) found a periodic oscillation in the Japan Sea bottom water, showing that the decreasing and increasing trends of dissolved oxygen and potential temperature, respectively, are characterized by bi-decadal oscillations, which are synchronized with the pattern observed in the North Pacific Index (NPI) (Minobe, 2000). Cui and Senju (2010), showing a positive relationship with ~ 20 -year periodicity between the NPI and the Arctic Oscillation (AO) index (Thompson and Wallace, 1998), suggested that the stronger cold-air outbreaks over the Japan Sea during a positive AO phase

should actuate the bottom water formation. The occasional bottom water formation events in the Japan Sea may be understood in relation to the large-scale interactions between the atmosphere and the ocean controlling heat flux and wind stress.

The international (Japan-Korea-Russia) cooperative program CREAMS (Circulation Research of the East Asian Marginal Seas), which started in 1993, have played important roles in advancing multi-disciplinary studies in the Japan Sea. The CREAMS confirmed significant changes in the ventilation system in the Japan Sea, a slowdown and complete stop of the bottom water formation for the past 50–60 years, which was quantitatively analyzed using a moving-boundary box model (e.g., Kang *et al.*, 2003, and many references therein). US scientists joined the CREAMS II program in 1998, expanding the research areas (e.g., Talley *et al.*, 2003; Min and Warner, 2005; Postlethwaite *et al.*, 2005).

7. Concluding Remarks

A miniature ocean, the Sea of Japan (or the Japan Sea), could be regarded as a huge natural aquarium that provides us with a useful field for large-scale oceanographic experiments. At the same time, the Japan Sea has significance as “the canary in the coal mine”, warning us of global environmental changes that are rapidly proceeding on our planet. It is therefore urgently important to conduct time-series oceanographic studies to elucidate the temporal changes and the detailed characteristics of the abyssal circulating system of the Japan Sea.

By using two research vessels, *Hakuho Maru* and *Tansei Maru*, we have been accumulating high-quality data on various chemical tracers (O_2 and its $\delta^{18}\text{O}$, CH_4 and its $\delta^{13}\text{C}$, $\delta^3\text{He}$, tritium, radiocarbon, ^{222}Rn , man-made perfluoroalkyl substances, etc.) toward a detailed characterization of the Japan Sea. In particular, the dissolved oxygen profiles in the Japan Sea between 1977 and 2010 have revealed that the bottom

water (depth > 2,000 m) has gradually lost dissolved oxygen by as much as 8%–10% per 30 years. Since this decrease has been accompanied by the increase of potential temperature, it is strongly suggested that global warming has interfered with the formation of bottom water to change the abyssal circulation pattern in the Japan Sea, leaving the bottom water in a stagnant condition with little supply of dissolved oxygen from the surface.

The break in the monotonous decreasing trend of bottom dissolved oxygen was observed at the beginning of the 2000s, in accord with the detection of an occasional bottom water formation in the winter of 2000–2001. There is a strong possibility that the abyssal circulation in the Japan Sea is controlled by large-scale interactions between the atmosphere and the ocean in the north Pacific and in the Arctic Ocean. Future observations will clarify this point.

Jenkins (2008) suggested that the reduction in abyssal ventilation of the Japan Sea will likely lead to a decrease in the nutrient supply to the surface water by upwelling, which may cause significant damage to the marine food web through the deterioration of new production. We must steadily continue the monitoring of the Japan Sea abyssal circulation and dynamics, not only from geochemical but also biological and ecological points of view, for a much better and interdisciplinary understanding of the Japan Sea for its environmental preservation.

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