Appearance of H₂S-bearing bottom waters during the last glacial period in the Japan Sea

TOSHIYUKI MASUZAWA and YASUSHI KITANO

Water Research Institute, Nagoya University, Chikusa-ku, Nagoya 464, Japan

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Vertical profiles of total sulfur and organic carbon have been measured in two deep-sea piston cores from the Japan Basin of the Japan Sea. The concentration of total sulfur, most of which is present as pyrite, is less than 0.05% in the upper part, while it suddenly increases to 2.0% at certain depths and reaches 5.0 to 4.2% in both cores. The layers with the extremely high sulfur contents are considered to have deposited primarily as a result of the appearance of H₂S-bearing bottom waters. The ¹⁴C ages of the extremely high sulfur layers nearly coincide with the last glacial period.

INTRODUCTION

Deep and bottom waters of the Japan Sea (ca. 3,500m deep) are very uniform vertically in salinity, temperature, and dissolved oxygen concentration and indeed contain large amounts of oxygen (5.2 to 5.8ml l⁻¹; NITANI, 1972), despite the fact that these waters are connected with open seas only through four straits with maximum depths of 10 to 135m. From the views of climatic change and eustatic change in sealevel, the environmental change of the Japan Sea during the Late Quaternary has been of special interest (see UJIE, 1982). MIYAKE *et al.* (1968) proposed from uranium contents of two short cores that an anoxic bottom water appeared in the sea during the last glacial period. Iron sulfides (KOBAYASHI and NOMURA, 1972), framboidal pyrite (OKADA and SHIMA, 1973; ICHIKURA and UJIE, 1976; ARAI *et al.*, 1981), and high sulfur layers (MASUZAWA *et al.*, 1979) were found in several cores from the sea, and they have been considered to support the above mentioned idea of MIYAKE *et al.* Quite low Eh values in several cores (INOUE, 1971), however, suggested a possibility of diagenetic deposition of sulfides. The correlation of these sulfide-bearing layers among these

cores was not clear due to the lack of dating data of these core samples.

The occurrence of sulfides in sediments is proof of the presence of hydrogen sulfide in bottom and/or interstitial waters because the amount of land-derived sulfide minerals supplied to seas is negligibly small (KAPLAN *et al.*, 1963).

In areas with no hydrothermal activity, hydrogen sulfide for these sulfides is originated from microbial sulfate reduction. It, however, has two possible sources: hydrogen sulfide contained in overlying bottom waters and that generated through diagenetic sulfate reduction. To prove the appearance of euxinic bottom waters, the effect of diagenetic sulfate reduction on sulfide in sediments is needed to be evaluated. This evaluation is possible from a quantitative examination of the vertical profile of sulfate concentration in interstitial water (MASUZAWA and KITANO, 1983b).

In the present study, total sulfur and organic carbon have been determined in two deep-sea piston cores from the Japan Basin of the Japan Sea. Sudden and extremely high accumulations of sulfide-sulfur up to 5% are observed in the two cores although diagenetic deposition of sulfides is not observed or not important in the two cores.

MATERIALS AND METHODS

Two piston core samples were collected from the northeastern (KH-77-3-L4'; 43° 00.3'N, 138° 28.1'E; 3,540m deep; 528cm long) and the central (KH-77-3-M5; 41° 00.3'N, 137° 01.1'E; 3,300m deep; 974cm long but the layers below 612cm were disturbed by flowage at the coring) parts of the Japan Basin of the Japan Sea (Fig. 1) by the R/V Hakuho Maru, University of Tokyo (HORIBE, 1981). Since the sediment cores were highly laminated, they were sectioned every two to ten centimeters in thickness depending on the change in color of sediments. Then, interstitial waters were squeezed under air-tight and bottom water temperature conditions (MASUZAWA and KITANO, 1983a). The residual sediments were stored in a refrigerator, carried back to the laboratory, vacuum-dried at 60°C, and powdered in an agate mortar.

Fig. 1. Topography of the Japan Sea and locations of Cores KH-77-3-L4' and -M5 from the Japan Basin of the Japan Sea.

Total sulfur and organic carbon were determined by the methods reported previously (MASUZAWA and KITANO, 1983b). The observed total sulfur content was corrected by subtracting the amount of sulfur in the interstitial water still remaining in the dried sample. The fraction heavier than tetrabromoethane ($d=2.97\text{ g cm}^{-3}$) was separated for selected sediment samples and examined microscopically and by X-ray diffraction.

ARAI *et al.* (1981) identified the Tomakomai ash layer at 23 to 31cm and the Aira Tn ash layer (21 to 22kyr B.P.) at 468 to 469cm in Core M5, but found no known tephra in Core L4'. Radiocarbon ages of organic carbon were determined by K. KIGOSHI of Gakushuin University for five sections of Core L4' after removal of inorganic carbon with dilute hydrochloric acid.

RESULTS AND DISCUSSION

Vertical profiles of total sulfur and organic carbon contents of Cores L4' and M5 are illustrated in Figs. 2 and 3, respectively. Organic carbon content varies significantly with depth in both cores (Figs. 2b and 3b). Some peaks of organic carbon content appear at total sulfur

Fig. 2. Lithology (HORIBE, 1981) and vertical profiles of total sulfur (a) and organic carbon (b) contents of sediments in Core KH-77-3-L4' from the northeastern Japan Basin.

Fig. 3. Lithology and vertical profiles of total sulfur (a) and organic carbon (b) contents of sediments in Core KH-77-3-M5 from the central Japan Basin. Tm and AT denote the layers of Tomakomai ash and Aira Tn ash (21 to 22 kyr B.P.), respectively, identified by ARAI *et al.* (1981). Other notations are the same as those in Fig. 2.

peaks. In addition to these peaks, several peaks of organic carbon content are found even in layers with low total sulfur contents in both cores.

In Core L4' (Fig. 2a), the total sulfur content is less than 0.05% above 120cm except for the layer at 95 to 99cm, while it suddenly increases to 2.1% at 120cm. The layers between 120 and 176cm (An-Ia; called here), between 190 and 205cm (An-Ib), and between 474 and 505cm (An-II) accumulate sulfur greatly up to 2.5 to 5.0%. Another low peak is observed between 210 and 232cm (An-Ic). The total sulfur content is quite low (0.01 to 0.15%) between 240 and 467cm.

The vertical profile of total sulfur content in Core M5 (Fig. 3a) is similar to that in the upper half of Core L4' (Fig. 2a). The total sulfur content is less than 0.04% above 134cm and shows a low (0.6% in maximum) and broad peak between 141 and 283cm. Then it suddenly increases from 0.12 to 2.0% at 321cm. Two high sulfur layers are observed between 321 and 455cm (An-Ia) and between 470 and 507cm

(An-Ib) in the core, and their total sulfur contents reach 1.0 to 4.2%. Below 520cm, there appear several low peaks (An-Ic).

The sulfur in these layers constitutes mostly pyrite. This is inferred from that it is insoluble in 1M acetic acid but solubilized completely by hydrogen peroxide and elemental sulfur content is negligibly small. Actually, heavy minerals separated from these layers are composed mainly of framboidal pyrite spherules with diameters ranging from 4 to 35 μ m (Fig. 4). They were identified as pyrite also by X-ray diffraction (Fig. 5). It has been known that the framboidal microspherule is a common texture for authigenic sedimentary pyrite (LOVE and AMSTUTZ, 1966).

In Core L4', sulfate concentration in interstitial waters decreases little with increasing depth, suggesting that sulfate reduction is not appreciable (MASUZAWA and KITANO, 1983a). This indicates that the extremely high accumulations of sulfur in the core are not due to diagenetic deposition but due to primary deposition of sulfides at or near the bottom surface. In Core M5, sulfate concentration in interstitial waters decreases almost linearly with increasing depth, its gradient becomes a little steeper in the lower part, manganese dioxide reduction occurs in the upper part, and sulfate reduction is considered to take place in the lower part of the core (MASUZAWA and KITANO, 1983a).

Fig. 4. Microscopic photograph of the fraction heavier than tetrabromoethane separated from a layer at 165-169cm of Core KH-77-3-L4' from the northeastern Japan Basin. It is seen that framboidal pyrite spherules are the main component.

Layers with quite low sulfur contents are found in the lower part of the core; 0.09% at 461 to 466cm, 0.29% at 512 to 517cm, and 0.31% at 607 to 609cm. These facts indicate that diagenetic deposition of sulfides is not important in the core especially above 461cm and that the layers of quite high sulfur content were formed by primary deposition of sulfides at or near the bottom surface. The source for such a primary deposition of sulfides found in both cores is considered to be hydrogen sulfide contained in the overlying bottom water, because no recent extensive hydrothermal activity was reported in the Japan Sea area. In other words, these layers of quite high sulfur content indicate the appearance of H_2S -bearing bottom waters in the Japan Sea. The sulfur contents of the high sulfur layers are 1.2 to 5.0% in Core L4' and 1.0 to 4.2% in Core M5. These high values are also characteristic for bottom sediments of euxinic basins in the present deep-sea environments, such as the Black Sea (HIRST, 1974) and the Cariaco Trench (ATHEARN, 1965).

Figure 6 illustrates the ^{14}C ages of organic carbon *versus* depth in Core L4'. The ^{14}C age at the top of Core L4' is 3.95 ± 0.30 kyr B.P. ^{14}C age of organic carbon at the top of cores generally shows old values due to the presence of

Fig. 5. X-ray diffraction pattern of the fraction heavier than tetrabromoethane separated from a layer at 165-169cm of Core KH-77-3-L4' from the northeastern Japan Basin. The peaks except the 3.34 Å peak of quartz are from pyrite (ASTM 6-0710).

Fig. 6. Depth distribution of ^{14}C ages for organic carbon in Core KH-77-3-L4' from the northeastern Japan Basin determined by K. KIGOSHI of Gakushuin University (Gak-8324, 10953-10956) in kyr B.P.: 0-5cm, 3.95 ± 0.30 ; 74-79cm and 82-90cm, 9.34 ± 0.52 ; 143-150cm, 13.75 ± 0.55 ; 198-205cm, 20.24 ± 1.07 ; 260-269cm, 25.92 ± 2.38 .

land-derived old carbon, owing to the addition of anthropogenically mobilized fossil carbon, or owing to bioturbation (EMERY and BRAY, 1962; BENOIT *et al.*, 1979). The ages of Core L4' samples are estimated from the ^{14}C ages on the assumption that the ^{14}C age of primarily deposited organic carbon is the same as that at the top of the core. The ages of Core M5 samples are estimated from the Aira Tn ash layer (21-22 kyr B.P.) on the assumption that mass accumulation rate has been constant. Average sedimentation rates are estimated to be 12 and 22 cm kyr⁻¹ in Cores L4' and M5, respectively. Two different sedimentation rates were reported for cores from the Japan Basin: *ca.* 1.5 cm kyr⁻¹ by the ionium-thorium method (MIYAKE *et al.*, 1968) and 10-15 cm kyr⁻¹ estimated paleontologically (KORENEVA, 1961). The values in Cores L4' and M5 are close to the

latter value.

The ages of the upper ends of An-Ia for Core L4' (120cm) and Core M5 (321 cm) are estimated to be 8 and 13kyr B.P., respectively. This difference seems to be not due to the difference in the time of the disappearance of the last H₂S-bearing bottom water between the two locations but due to uncertainties of the assumptions for the two different age estimations because the vertical profiles of total sulfur content correlate well for the two cores (Figs. 2a and 3a).

The ages of the appearance of H₂S-bearing bottom waters (An-Ia to -Ib) are estimated to be 8 to 17kyr B.P. in Core L4' and 13 to 24kyr B.P. in Core M5. These ages are around the later part of the last glacial period (11 to 27kyr B.P.; MORLEY and HAYS, 1981). Recently, OBA *et al.* (1980) studied faunal and isotopic compositions of planktonic and benthonic foraminifera in two cores from the Oki Rise ca. 1,000m deep in the southern Japan Sea. They found a benthonic foraminifera barren zone around the lower two thirds of the layer between the Oki ash (9.3kyr B.P.; ARAI *et al.*, 1981) and the Aira Tn ash. The barren zone was attributed to the appearance of an anoxic bottom water. This barren zone seems to be related to the appearance of H₂S-bearing bottom waters found in the two cores from 3,300 and 3,540m depths in the Japan Basin.

The appearance of H₂S-bearing bottom waters during the last glacial period indicates that the vertical mixing of seawater, which prevails at present, was strongly reduced or stopped in the period. The high sulfur layer near the bottom of Core L4' (An-II) also indicates another period of the appearance of H₂S-bearing bottom water. The quite low sulfur content of the layer between An-I and An-II in Core L4' indicates that the bottom water was quite oxic and no sulfate reduction occurred even within the bottom sediment.

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