Journal of Nuclear and Radiochemical Sciences, Vol. 9, No.1, pp. 13-18, 2008

Seasonal Variation of Iron Speciation in a Pearl-Raising Bay Sediment by Mössbauer Spectroscopy

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Received: December 27, 2007; In Final Form: January 25, 2008

Ago Bay in Mie Prefecture, central Japan, is world-famous for the site of Mikimoto pearl culture, but recently the production of pearls has considerably declined. Environmental deterioration of the bay is suspected of having caused the decline. The periodic investigation into iron speciation of the bay sediment by ^{57}Fe Mössbauer spectroscopy revealed its high pyrite (FeS_2) content from the surface to the 20-cm depth. The pyrite in the surface sediment decreased only in spring, three months after the dissolved oxygen in the bottom water was at maximum. Such oxygen-consuming material as pyrite accumulated through long-term biotic activity is a most-likely explanation for the prolonged environmental deterioration of the bay, which appears in the high chemical oxygen demand (COD) of the sediment.

1. Introduction

Ago Bay in Ise-Shima National Park, central Japan (Figure 1), is one of almost-enclosed bays that have been endangered by human's economic activities and therefore have collected much attention in environmental studies.[1-3] The bay is famous for the cultivation of pearl oysters, *Pinctada fucata*, because it is the place where Kokichi Mikimoto started the artificial culture of pearls in 1890, and the pearl culture has continued for more than 100 years. However, mass mortality of the oysters has often occurred in this bay.[4] Even though the bay's narrow channel to the open sea keeps high waves off the rafts for cultivation, it makes the seawater change sluggish and accelerates the water shifting toward under reducing condition.[5] Organic matter loading from the pearl culture to the water system further enhances reducing condition; feces of the pearl oysters and sewage from shell washing contain substantial amounts of organic matter, which promptly settles down onto the sediment. Thirty thousand people live in the water catchment area of Ago Bay and their domestic wastewater is another source of organic matter. Thus it is highly plausible that the released organic matter has broken the natural balance between its input and output. Harmful phytoplankton blooms called red tides have caused serious social problems and heavy damage to fisheries throughout the world.[6] Such algal blooms are often blamed on coastal pollution and eutrophication. Ago Bay has suffered frequent outbreaks of red tides.[7]

Tategami-ura is located in the inner part of Ago Bay (Figure 1). Chemical oxygen demand (COD) of the surface sediment collected at Tategami-ura (water depth of 10 m) in August has gradually increased since the annual measurement began in 1981 (Figure 2).[8] A linear regression gives an increase rate of 2.12 mg g^{-1} year^{-1}, and now the COD greatly exceeds 30 mg g^{-1}, the regulation limit for aquaculture. The COD of the surface

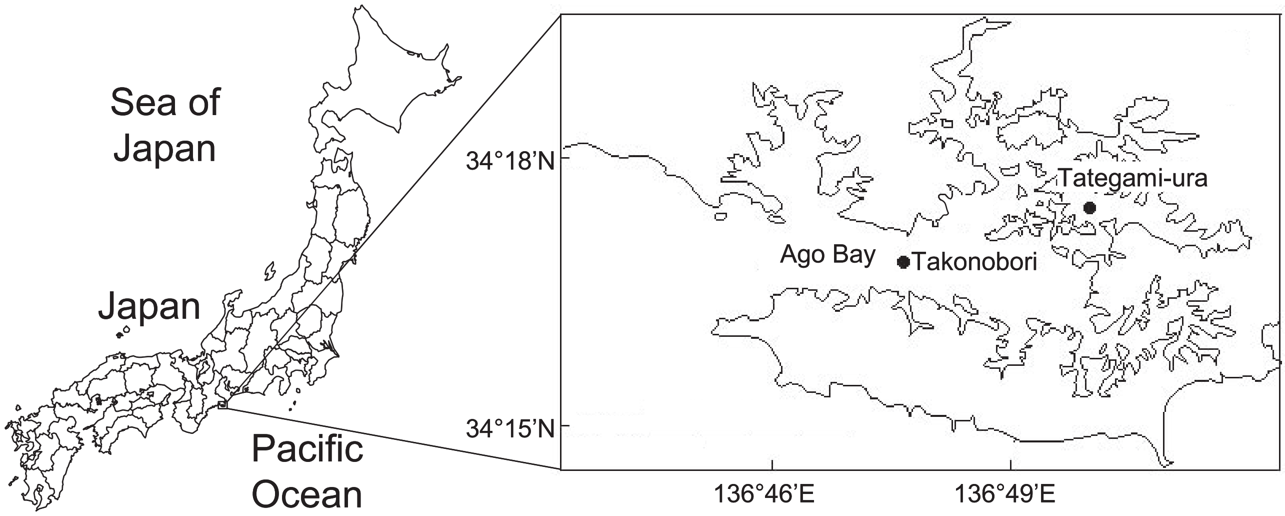

Figure 1. Sampling locations in Ago Bay, central Japan.

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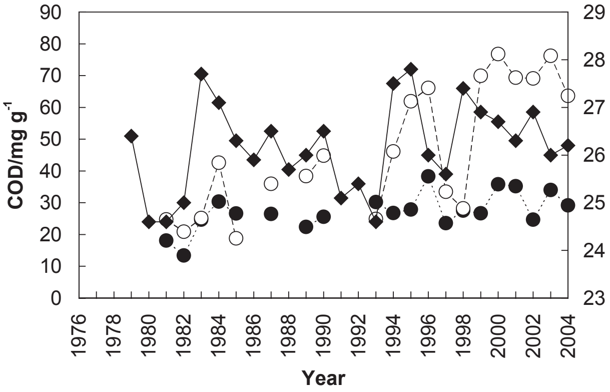

Figure 2. Time series of the average atmospheric temperature in August and the dry weight-based COD of the surface sediment collected at Tategami-ura and Takonobori. The COD was also measured in August and lacked in 1986, 1988, 1991, and 1992. The average temperature in August was measured in Minami-Ise, adjacent to Ago Bay. Open circles, COD at Tategami-ura; solid circles, COD at Takonobori; solid diamonds, average temperature in August.

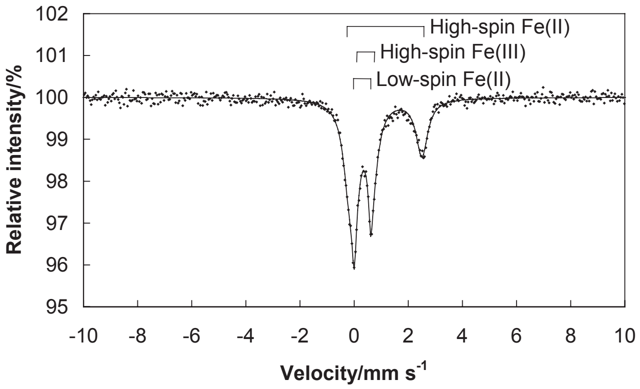

Figure 3. Mössbauer spectrum of the sediment collected from a depth of 0-0.5 cm at Tategami-ura on May 19, 2005. This was measured at 293 K. The guidelines at the top of spectrum show the positions of detected three doublets ascribable to paramagnetic high-spin Fe(II), paramagnetic high-spin Fe(III), and diamagnetic low-spin Fe(II) that corresponds to pyrite (FeS_2). The dots are observed data, and the solid line is the fit curve.

sediment collected at Takonobori (water depth of 25 m), located in the central part of Ago Bay, has not increased so sharply. The production of pearls reached a peak in 1960s and has decreased due to environmental deterioration, depression on pearl markets, etc. The present annual production dropped to less than 10,000 kg, about 20% of its maximum. In spite of the decreasing production of pearls, the COD of the surface sediment in the inner bay has been increasing. On the other hand, the average atmospheric temperature in August has slightly increased with a rate of 0.035 °C year^{-1} while the time-series COD also shows a similar increasing trend but one-year-delayed cycles (Figure 2). The increasing trend in temperature would be due to global warming. The correlation between COD and temperature thus found may be best explained by the fact that increasing temperature more promotes biological production of organic matter. But why was the response of COD delayed by one year? Is this delay the reason why the COD has been still increasing despite smaller organic matter loading than before?

To answer these questions, we have periodically investigated the vertical distribution of iron species in the sediments by ^{57}Fe Mössbauer spectroscopy. Mössbauer spectroscopy is one of the most useful, nondestructive means for determining chemical states of iron and has been applied to the characterization of a wide variety of environmental and geochemical samples.[9,10]

2. Experimental

2.1. Sampling. Vertical sediment cores of about 10 cm in length were collected at two stations every other month from May 2005 until May 2006. Tategami-ura is located in the inner part of Ago Bay and Takonobori in the central part. At Tategami-ura, the sample collection was continued until July 2007. The sediment cores were sometimes *ca.* 20 cm long. The collected samples were cut at 0.5–2 cm intervals and pore-water was extracted from the sediment by a pressure-filtration technique (5 atm, N_2).

2.2. Mössbauer Spectroscopy. Approximately 300 mg of each pressure-filtered sample was mounted in a sample holder (16 mm in diameter, 1 mm thick). Absorbers thus prepared contained 5 mg cm^{-2} of Fe, a quantity low enough so to allow relative peak areas to be used as a measure of the distribution of the corresponding Fe-bearing compounds. In order to avoid air oxidation, the pressure-filtered sediments were purged with nitrogen gas in oxygen-impenetrable plastic bags. The spectra were measured with an Austin Science S-600 Mössbauer spectrometer using a 1.11 GBq ^{57}Co/Rh source at 293 K and 78 K. The curve fitting of the resulting spectra was performed with a personal computer, assuming that the spectra were composed of peaks with Lorentzian line shapes. Half-widths and peak areas within each quadrupole doublet were constrained to be equal. Isomer shifts were expressed with respect to the centroid of the spectrum of metallic iron foil. Pyrite (FeS_2) peak positions were constrained (using values of $\delta = 0.307$ mm s^{-1}, $\Delta E_Q = 0.610$ mm s^{-1} at 293 K and $\delta = 0.405$ mm s^{-1}, $\Delta E_Q = 0.629$ mm s^{-1} at 78 K) as in Manning and Ash,[11] since the peak positions of paramagnetic high-spin Fe^{3+} and pyrite containing diamagnetic low-spin Fe^{2+} are in very close proximity. In addition to the measurements in the velocity range of –10.00 to 10.00 mm s^{-1}, the spectra were also measured in the velocity range of –3.33 to 3.33 mm s^{-1} for a better resolution. The total iron contents of the sediments were determined by atomic absorption spectrometry (AAS) after acid digestion.

3. Results and Discussion

Sediment cores were collected at Tategami-ura and Takonobori every two months from May 2005 until July 2007 and May 2006, respectively. First, the ^{57}Fe Mössbauer spectra of the sediments were measured in the velocity range of –10.00 to 10.00 mm s^{-1} at 293 K, and no significant magnetic sextet was detected (Figure 3). The spectra measured at 78 K did not show any sextet either, which indicates that the sediments did not contain fine particles showing a doublet at 293 K and a sextet at 78 K by a superparamagnetic effect.[12] Then, the samples were measured in the velocity range of –3.33 to 3.33 mm s^{-1} for a better spectral resolution. Their Mössbauer spectra consisted of three doublets: one for paramagnetic high-spin Fe(III), paramagnetic high-spin Fe(II), and diamagnetic low-spin Fe(II) that corresponds to pyrite (FeS_2). Table 1 lists the relative peak areas of iron components in the sediment cores. The paramagnetic high-spin Fe(III) would come from clay minerals and hydrated ferric oxides.[13] The paramagnetic high-spin Fe(II) is ascribable to clay minerals such as chlorite.[14,15] Although vertical sediment cores of about 20 cm in length were sometimes collected, the iron speciation in the sediment from a depth of 20 cm was not so different from that from a depth of 10 cm. The relative distribution of iron components approximately corresponds to the absolute distribution in this case because the total iron content of the sediment was almost constant throughout the core. The distribution of iron components did not change vertically so much. In spring, however, pyrite decreased in the near-surface sediment at Tategami-ura (Figure 4). The

TABLE 1: Relative peak areas of iron components in the sediment cores collected at Tategami-ura and Takonobori in Ago Bay

Site	Date	Depth/cm	Paramagnetic Fe(III)/%	Paramagnetic Fe(II)/%	Pyrite/%
Tategami-ura	May 19, 2005	0.0-0.5	49.6	39.0	11.4
		1.0-1.5	45.3	36.5	18.2
		3-4	36.1	34.4	29.4
		8-10	39.7	34.0	26.3
	Jul 7, 2005	0.0-0.5	33.4	41.2	25.4
		1.0-1.5	38.2	37.3	24.5
		3-4	41.5	30.1	28.4
		8-10	34.2	32.3	33.5
	Sep 21, 2005	0.0-0.5	39.4	31.4	29.2
		1.0-1.5	39.3	32.5	28.2
		3-4	36.0	27.6	36.4
		8-10	36.1	32.9	31.0
	Dec 14, 2005	0.0-0.5	35.9	36.6	27.5
		1.0-1.5	34.1	32.5	33.4
		3-4	39.2	29.1	31.7
		8-10	35.8	27.9	36.3
	Jan 17, 2006	0.0-0.5	36.9	36.1	27.0
		1.0-1.5	44.2	34.5	21.3
		3-4	42.5	29.5	28.0
		8-10	38.7	29.3	32.0
	Apr 20, 2006	0.0-0.5	43.8	38.2	18.0
		1.0-1.5	45.9	28.2	25.9
		3-4	38.2	31.4	30.4
		8-10	36.0	29.8	34.2
		20-22	32.1	38.0	29.9
	May 29, 2006	0.0-0.5	41.3	35.3	23.4
		1.0-1.5	48.2	32.2	19.6
		3-4	38.9	30.7	30.4
		8-10	30.6	33.5	35.9
	Jul 13, 2006	0.0-0.5	32.0	39.9	28.1
		1.0-1.5	41.7	33.5	24.8
		3-4	40.5	29.7	29.8
		8-10	31.3	29.3	39.4
		20-22	43.1	36.0	20.9
	Sep 7, 2006	0.0-0.5	34.5	38.2	27.3
		1.0-1.5	35.6	39.8	24.6
		3-4	30.8	31.1	38.1
		8-10	38.0	33.8	28.2
		20-22	39.1	37.6	23.3
	Nov 9, 2006	0.0-0.5	41.0	38.2	20.8
		1.0-1.5	41.7	38.5	19.8
		3-4	42.1	32.4	25.5
		8-10	42.4	31.1	26.5
		20-22	35.0	38.6	26.4
	Jan 17, 2007	0.0-0.5	44.3	30.6	25.1
		1.0-1.5	37.1	30.3	32.5
		3-4	38.2	28.2	33.6
		8-10	38.1	33.6	28.3
		20-22	32.3	36.0	31.7
	Mar 7, 2007	0.0-0.5	48.3	33.2	18.5
		1.0-1.5	36.6	34.6	28.8
		3-4	39.3	31.1	29.6
		8-10	36.5	32.2	31.3
		20-22	36.6	36.9	26.5

TABLE 1: Continued

Site	Date	Depth/cm	Paramagnetic Fe(III)/%	Paramagnetic Fe(II)/%	Pyrite/%
Tategami-ura	May 23, 2007	0.0-0.5	47.3	35.6	17.1
		1.0-1.5	41.4	35.1	23.5
		3-4	36.0	33.0	31.0
		8-10	33.4	33.7	32.9
		20-22	42.8	37.6	19.6
		30-32	49.4	36.8	13.8
	Jul 19, 2007	0.0-0.5	39.7	35.8	24.5
		1.0-1.5	39.1	37.9	23.0
		3-4	34.0	32.4	33.6
		8-10	34.6	30.3	35.1
		20-22	35.8	38.3	25.9
Takonobori	May 19, 2005	0.0-0.5	37.5	55.5	7.0
		1.0-1.5	37.3	52.6	10.1
		3-4	39.4	52.6	8.0
		6-8	36.6	52.2	11.2
	Jul 7, 2005	0.0-0.5	46.3	51.9	1.8
		1.0-1.5	38.3	53.9	7.8
		3-4	29.5	55.4	15.1
		8-10	33.3	51.0	15.7
	Sep 21, 2005	0.0-0.5	42.4	51.7	5.9
		1.0-1.5	43.0	51.4	5.6
		3-4	40.9	48.7	10.4
		8-10	39.3	51.5	9.2
	Dec 14, 2005	0.0-0.5	40.1	52.2	7.7
		1.0-1.5	35.3	51.5	13.2
		3-4	40.4	52.0	7.6
		6-7	32.3	51.7	16.0
	Jan 24, 2006	0.0-0.5	34.2	52.4	13.4
		1.0-1.5	45.3	42.0	12.7
		3-4	39.2	51.2	9.6
		8-10	36.3	51.0	12.7
	Apr 5, 2006	0.0-0.5	38.5	53.6	7.9
		1.0-1.5	40.7	50.4	8.9
		3-4	42.0	53.1	4.9
		8-10	30.9	51.0	18.1
	May 29, 2006	0.0-0.5	37.5	53.5	9.0
		1.0-1.5	33.4	50.7	15.9
		3-4	42.9	52.8	4.3
		8-10	39.7	50.9	9.4

paramagnetic high-spin Fe(III) varied complementarily to pyrite and, therefore, would be converted to pyrite. Pyrite at Takonobori was less abundant (Figure 5) than at Tategami-ura. In contrast, the paramagnetic high-spin Fe(II) was more abundant at Takonobori. Since the total iron contents of the Tategami-ura sediments were greater than those of the Takonobori sediments, both the pyrite and paramagnetic high-spin Fe(III) contents of the Tategami-ura sediments were also greater than those of the Takonobori sediments. The difference in the total iron contents would be due to the geological difference. The geology of this area mainly consists of eroded sedimentary rocks of the late Cretaceous accretionary complex, and the sand gravel layer after the late Pleistocene is observed at planation surfaces around the inner bay. Another possible explanation is the difference in sedimentation environment between the inner and central parts of the bay.

The Ago Bay Watch System has been monitoring the water quality such as dissolved oxygen (DO) since 2003. These parameters are automatically recorded every one-hour at five stations within the bay and are accessible through the Web.[16] The Tategami-ura and Takonobori monitoring stations are located at 34°17.642’N, 136°49.895’E and 34°17.098’N, 136°47.459’E, respectively. DO of the bottom water at Tategami-ura decreases in summer due to thermal stratification (Figure 6), resulting in oxygen-deficient water mass on the seafloor through bacterial digestion of organic matter in the sediment.[17,18] Red tides often occur when heating creates a stratified surface layer above colder, nutrient-rich waters.[6] The dissolved oxygen in the bottom water of Takonobori showed a similar seasonal variation, and therefore only that of Tategami-ura is shown in Figure 6 for brevity’s sake. Pyrite in the surface sediment at Tategami-ura increased with decreasing DO in summer but did not decrease in autumn when the DO in the bottom water increased again. Decrease in pyrite became

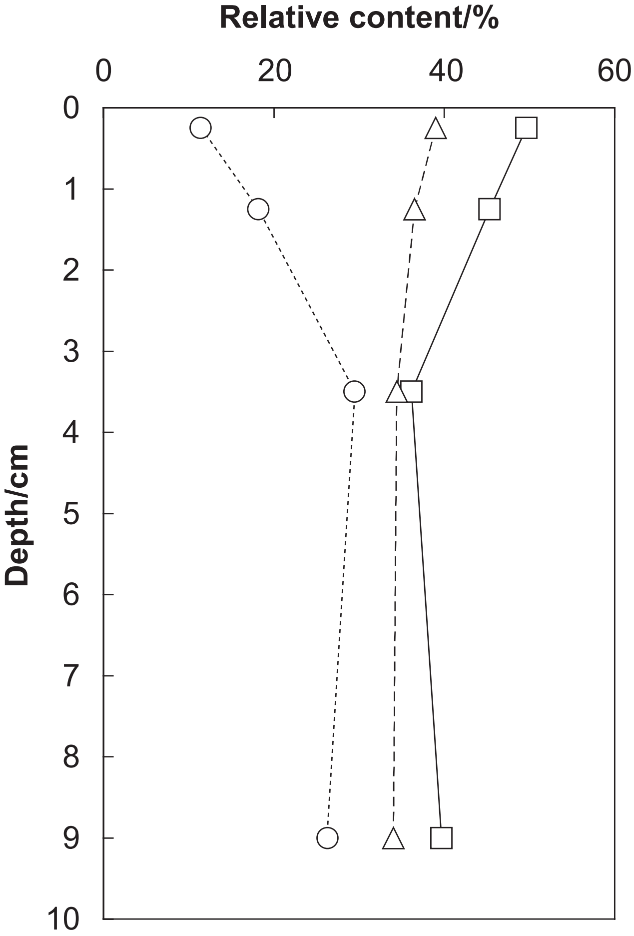

Figure 4. Vertical distribution of iron components in the sediment core collected at Tategami-ura on May 19, 2005. Circles, pyrite; triangles, paramagnetic high-spin Fe(II); squares, paramagnetic high-spin Fe(III).

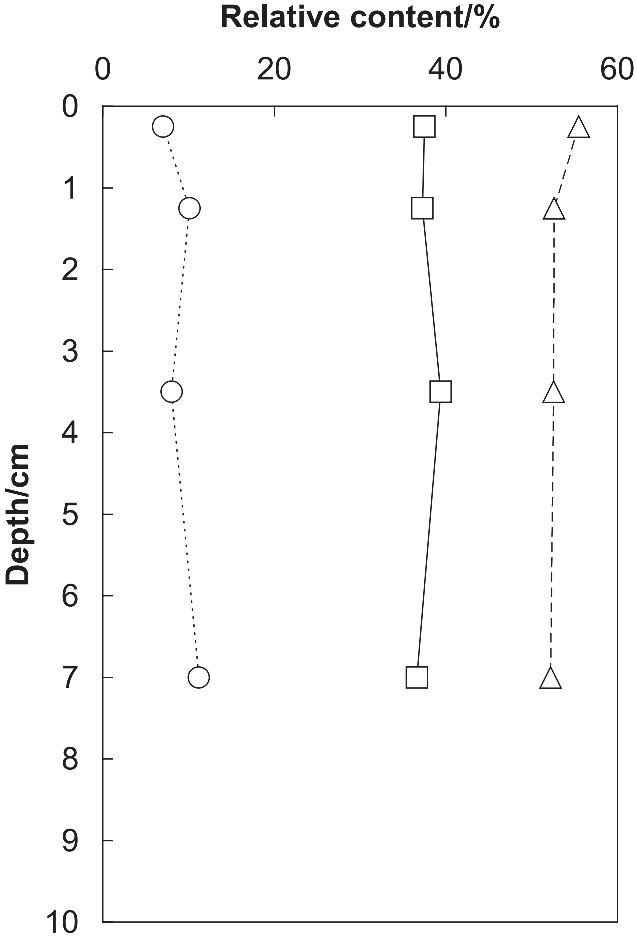

Figure 5. Vertical distribution of iron components in the sediment core collected at Takonobori on May 19, 2005. Circles, pyrite; triangles, paramagnetic high-spin Fe(II); squares, paramagnetic high-spin Fe(III).

obvious only in spring because it is rather chemically stable and slowly degrades.[19] The pyrite slightly decreased in November 2006 but got back to a high content in January 2007 in spite of the increasing DO. The total iron content of the sediment did not change seasonally so much. Therefore, the absolute abundance of pyrite showed similar seasonal variation to its relative abundance.

The pyrite at Takonobori in the central bay did not show much seasonal variation. The COD of the surface sediment at Takonobori was also lower than that at Tategami-ura (Figure 2), which suggests a relation to its lower pyrite content. The pearl culture has shifted from the inner bay to the central bay with increasing deterioration in the inner bay. Therefore, a difference in accumulation of organic matter is likely to bring the difference in the COD and pyrite content between Tategami-ura and Takonobori. The maximum production of pearls in 1960s has provided much organic matter to the sediment in the inner part of Ago Bay. The recent utilization of tough ropes for the cultivation rafts enabled a mass exodus of pearl oysters to the central bay with relatively high waves. However, the environment of the central bay would also be deteriorated in several years if much organic matter is accumulated in the sediment of the central bay.

During summer, thermal stratification interrupts the supply of dissolved oxygen to the bottom water and sulfate ion from seawater is reduced to hydrogen sulfide, which reacts with iron compounds to form iron sulfides in the sediment.[20] Iron sulfides thus produced consist of acid-volatile sulfides (AVS) and pyrite.[21,22] Pyrite is chemically more stable than AVS. Therefore, pyrite is inclined to more remain in the surface sediment than AVS, thus carried forward to the next year even though vertical circulation of seawater resumes in winter. These findings were obtained by both the periodic investigation into iron speciation of the sediment and the continuous monitoring of dissolved oxygen. The pyrite accumulated in this way is one of the major reasons for the fact that the COD

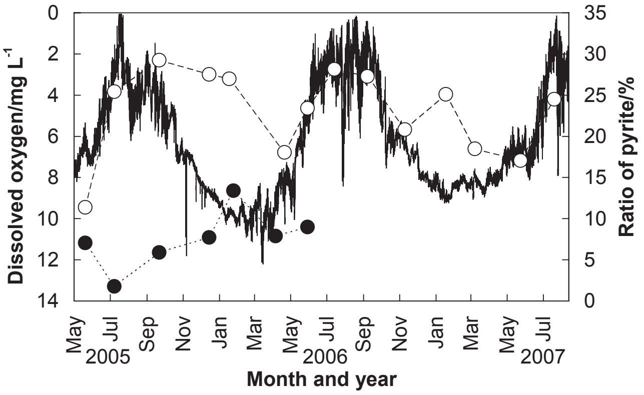

Figure 6. Time series of the dissolved oxygen in the bottom water of Tategami-ura and the ratios of pyrite in the surface sediment collected at Tategami-ura and Takonobori from May 2005 until July 2007. The sediment at Takonobori was collected until May 2006. The dissolved oxygen was automatically measured and recorded every one hour. The left ordinate is shown upside down for an easy comparison because less dissolved oxygen favors the production of pyrite. Open circles, ratio of pyrite at Tategami-ura; solid circles, ratio of pyrite at Takonobori; solid line, dissolved oxygen.

of the sediment has been increasing even though organic matter loading has been decreasing. Generally, environmental deterioration often persists after discharges from human activities are reduced (e.g., chlorofluorocarbons). The COD of the sediment in the inner part of Ago Bay is one of such examples. It may gradually decrease in the future but may take time. Ago Bay is one of enclosed coastal seas where much organic matter has been discharged onto the seafloor sludge for many years. In the future, similar phenomena may occur in other embayments that receive continuous loading of reducing materials such as organic matter. Therefore, the prolonged environmental deterioration of Ago Bay is not only a crisis in the pearl production but also a future threat to many people living around enclosed coastal seas. The iron compounds in the sediment fix hydrogen sulfide and reduced sulfur compounds in the form of iron sulfides. In other words, the iron compounds suppress a much release of hydrogen sulfide that threatens the health of living organisms and is responsible for malodor.[23] Further investigations and continued effort are necessary for the remediation of the deteriorated environment.

4. Conclusion

By means of Mössbauer spectroscopy, the vertical distribution of iron species in the sediments collected from two stations in Ago Bay was clarified, and its seasonal variation was investigated through periodic sampling. Three doublets ascribable to paramagnetic high-spin Fe(III), paramagnetic high-spin Fe(II), and diamagnetic low-spin Fe(II) that corresponds to pyrite were separated in their spectra. The pyrite in the surface sediment of the inner bay decreased only in spring, three months after the dissolved oxygen in the bottom water was at maximum. The delay would be caused by the stability of pyrite and may be related to the prolonged environmental deterioration of the bay. Mössbauer spectroscopy was thus successfully applied to the environmental monitoring of a bay with high organic matter loading in order to elucidate the seasonal variation of iron speciation in the sediments.

Acknowledgements. We are indebted to Professor B. Takano for constructive comments. This study was partly supported by the Mie Prefecture Collaboration of Regional Entities for the Advancement of Technological Excellence.

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