

## <sup>57</sup>Fe Mössbauer Study of Specific Iron Species in the Antarctic Ocean Sediments

Katsumi Shozugawa,<sup>\*,a</sup> Akihito Kuno,<sup>a</sup> Hideki Miura,<sup>b</sup> and Motoyuki Matsuo<sup>a</sup>

<sup>a</sup>Graduate School of Arts and Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan

<sup>b</sup>Research Organization of Information and Systems, National Institute of Polar Research, Geosciences Group, Geology and Geomorphology, 1-9-10, Kaga, Itabashi-ku, Tokyo 173-8515, Japan<sup>†</sup>

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To elucidate the environment of sedimentation in the Scotia and Ross Seas in the Antarctic Ocean during the period from upper Pleistocene to the present, sediments from the seas were investigated by <sup>57</sup>Fe Mössbauer spectroscopy, instrumental neutron activation analysis, and X-ray absorption near-edge structure. In Mössbauer spectra of Scotia Sea sediment, a specific doublet peak (isomer shifts of 0.57–0.59 mm s<sup>-1</sup>, quadrupole splitting of 1.70–1.83 mm s<sup>-1</sup>) was observed, suggesting the generation of primary glauconite by detailed speciation. In contrast, sediment cores from the Ross Sea and another sea area around Antarctica had no specific peak in Mössbauer spectra. Concentrations of iron and other elements in both sediments hardly fluctuated, that is, sedimentation matter in the Scotia Sea sediments containing iron species was not affected by the origin of specific iron species but by factors such as early-stage diagenesis.

### 1. Introduction

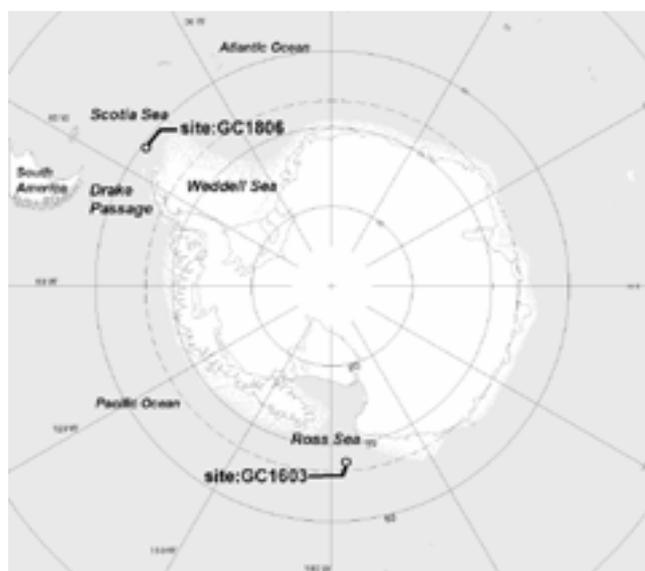
Sea sediments can be probed as records of the environment of sedimentation. Much attention has been given to clarifying the environment of sedimentation from an elemental composition point of view. Valuable information for paleoceanography has been obtained by several projects such as the Deep Sea Drilling Project and Ocean Drilling Program.<sup>1</sup> In general, the rate of sedimentation in the sea is lower than rates in rivers or estuaries,<sup>2</sup> except when there is a large scale variation such as massive climate change or an eruption of an undersea volcano in the sea area.<sup>3</sup> There is less pelagic sediment deposition from terrigenous materials in the deep sea than on the coast. Therefore, the long term variation in the environment of the sea can be determined with the analysis of sediment cores of short length.

Sea sediments comprise many kinds of heavy metals. Almost all iron supplied to the sea is included in the terrigenous fracture. These materials are carried and finally accumulate in the sea sequentially from the area along the shore through carriers such as the atmosphere and rivers. Since iron is an essential element for many sea organisms, which take in iron from seawater, organic matter as product of the food chain accumulate in the sediments.

In this paper, we focus on the chemical states of iron in Antarctic sediments. From the analysis of <sup>57</sup>Fe Mössbauer spectra, ferrous and ferric iron can be represented by silicate and clay minerals respectively. Uptake of iron from seawater by phytoplankton mainly causes a redox reaction in the cycle of photosynthesis and respiration. Consequently, the difference in chemical states such as ligand and valence states depends on the origin of the iron. In addition, chemical states of heavy metals such as iron and manganese in the sediments change upon reduction by organic matter. It is important to trace the processes of these reactions in discussing the environments of sediments.

### 2. Experimental

In this study, Antarctic Ocean sediments not subjected to anthropogenic influences were used. The cores for analysis were collected by JOGMEC (Japan Oil, Gas and Metals National Corporation) in the Ross and Scotia Seas from 1996 to 1997. Figure 1 shows the sampling sites of GC1806 and GC1603. The collection site GC1806 was at 60°11'08"S and 55°30'27"W in the Scotia Sea, off Elephant Island. The depth was 3,531 m, the core length was 474 cm and a gravity-corer was used for sampling. The GC1806 core had a lithographic boundary line at 203 cm. The upper part of the core (0–203 cm) was siliceous silty clay, presenting dark greenish gray from dark greenish yellow. The lower part of the core (203–474 cm) was silt presenting gray from dark greenish gray. Sediment samples were stored at 4 °C immediately after collection, cut every 2.7 cm, and kept in N<sub>2</sub> to prevent oxidization with air.



**Figure 1.** Sampling sites of GC1806 (60°11'08"S, 55°30'27"W, water depth 3531 m, core length 474 cm) and GC1603 (67°49'17"S, 178°17'00"E, water depth 3326 m, core length 430 cm).

\*Corresponding author. E-mail: cshozu@mail.ecc.u-tokyo.ac.jp  
Fax: +81-3-5454-6998

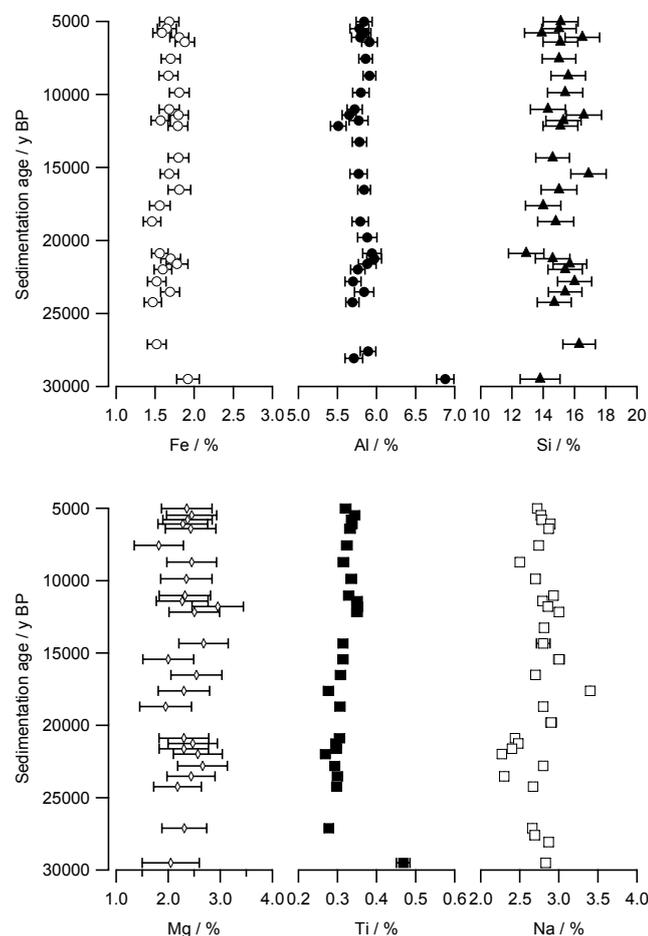
<sup>†</sup>Present address: 10-3 Midori-cho, Tachikawa-shi, Tokyo 190-8518, Japan.

Thereby samples were not altered until measurements of the chemical states were taken. For GC1806 and GC1603 cores, Beta Analytic Inc. analyzed radiocarbon dating of the sedimentation. A half-life of  $^{14}\text{C}$  of 5,568 years was applied and the isotopic separation was determined. According to the dating, the sediment age of the surface of the GC1806 core was estimated to be 5,000 y B.P. (Before Present) and the bottom was 32,000 y B.P. Sedimentation depth was transformed into sedimentation age using above values.

The GC1603 core was collected at  $67^{\circ}49'17''\text{S}$  and  $178^{\circ}17'00''\text{E}$  in the north Ross Sea for reference. GC1603 was silty clay and calcareous sandy silt presenting yellowish brown throughout the core. The sedimentation age of GC1603 was much older than that of GC1806, being 800 ky B.P. at the bottom.

$^{57}\text{Fe}$  Mössbauer spectroscopy and X-ray absorption near-edge structure (XANES) analysis were applied for the speciation of iron in the sediments. Instrumental neutron activation analysis (INAA) was applied for elemental determination. In the  $^{57}\text{Fe}$  Mössbauer measurement, 300–500 mg of sediment was mounted in a sample holder (16 mm in diameter, 1 mm thick) and packed in an oxygen-impenetrable plastic bag with  $\text{N}_2$ . Samples were kept in wetness. The Mössbauer spectra were measured with an Austin Science S-600 Mössbauer spectrometer using a  $\gamma$ -ray source of 1.11 GBq  $^{57}\text{Co}/\text{Rh}$  at room temperature (r.t.,  $\sim 293\text{ K}$ ) and liquid nitrogen temperature (77 K). Isomer shifts (IS) were expressed with respect to the centroid of the spectrum of metallic Fe foil, and the Mössbauer spectra were fitted by a least-squares method with restrictions of intensity and half width (HW) of peaks. All doublet peaks were treated as symmetric.

The conditions of INAA for iron determination were as follows. 50 mg quantities of dried ( $105\text{ }^{\circ}\text{C}$ , 2 hours) sediments



**Figure 2.** Concentrations of Fe ( $\circ$ ), Al ( $\bullet$ ), Si ( $\blacktriangle$ ), Mg ( $\diamond$ ), Ti ( $\blacksquare$ ) and Na ( $\square$ ) in GC1806.

were packed in double polyethylene film bags. Samples were irradiated with neutrons in the T-pipe, JRR-4 at Japan Atomic Energy Agency, Tokai, Ibaraki, Japan. Irradiation time was 5 minutes, and after 2 weeks cooling,  $\gamma$ -rays of 1099 keV were measured for 14,400 seconds.

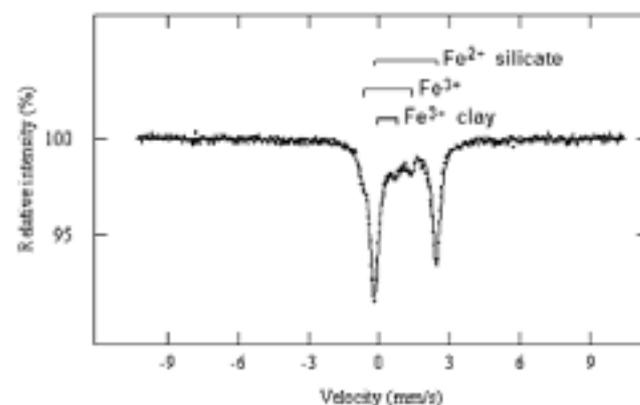
XANES was measured using a synchrotron radiation ring at the BL-9A and 12C facilities of the Photon Factory, KEK.<sup>4</sup> A Si (111) double-crystal monochromator was used. Each sample was cut to be 1 cm (*ca.* 150 mg), immediately sealed with prolene film, and kept at  $4\text{ }^{\circ}\text{C}$  until measurement. Being kept in a  $\text{N}_2$  atmosphere also prevented oxidization with air. XANES in iron K-edge spectra was measured in fluorescence mode using a Lytle-type detector at r.t. under atmospheric pressure. Reference materials were used as follows: hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), pyrite ( $\text{FeS}_2$ ), and goethite ( $\alpha\text{-FeOOH}$ ).

### 3. Results and Discussion

**3.1. Concentration.** In the measurement of INAA, certified reference materials, JLk-1 (Lake Sediment, Geological Survey of Japan, Advanced Industrial Science and Technology) and NIES No. 2 (Pond Sediment, National Institute for Environmental Studies), were irradiated and analyzed for the confirmation of accuracy. Concentrations obtained for the elements were in good agreement with the certified values.<sup>5,6</sup>

Concentrations of major elements in GC1806 are shown in Figure 2. The iron distribution showed no significant variation (*ca.* 1.8 %) from 28,000 y B.P. to 5,000 y B.P. within the relative concentration errors. In the case of sea sediments, it was quite common for the concentration of iron in the sediments to be approximately constant.<sup>7</sup> Furthermore, changes in the concentrations of major elements were not significant throughout the core of GC1806, suggesting the sources of sediments did not change during sedimentation. The source of the supply of iron to sediments was believed to be mainly terrigenous materials, because the sampling location is adjacent to the Antarctic Peninsula.

**3.2. Chemical states of iron.** A Mössbauer spectrum of GC1806 sediment with a 5,000 y B.P. sedimentation age at 77K is shown in Figure 3. Three doublet peaks were observed, and a sextet was not detected in the spectra. Among three species, a doublet peak with small quadrupole splitting (QS) was found to be  $\text{Fe}^{3+}$  from clay minerals, and a doublet peak with large QS was found to be  $\text{Fe}^{2+}$  from silicate minerals, empirically.<sup>8</sup> The third doublet was very specific, and the particular value of QS ( $1.7\text{--}1.8\text{ mm s}^{-1}$ ) prevented the determination of the minerals. We have measured many  $^{57}\text{Fe}$  Mössbauer spectra for river sediments,<sup>8</sup> lake sediments,<sup>9,10</sup> and tideland sediments.<sup>11</sup> Based on the current experience, the specific doublet was attributed to  $\text{Fe}^{3+}$ , considering the value of IS.



**Figure 3.** Mössbauer spectrum of GC1806 with 5000 y B.P. at 77K. Parameters of specific  $\text{Fe}^{3+}$  are IS of  $0.55 \pm 0.01$  and QS of  $1.79 \pm 0.02\text{ mm s}^{-1}$ .

Mössbauer parameters of GC1806 samples from each sedimentation age are shown in Table 1. Three doublet peaks including a specific doublet peak in the spectra were observed.

It is noticeable that the relative area of the specific doublet tended to decrease as sedimentation age increased from 5,500 y B.P. to 11,800 y B.P. This means iron species in sediment

**TABLE 1: Mössbauer parameters at 77K of GC1806 for different sedimentation ages**

Depth (cm)	Conventional sedimentation age (y B.P.)	Species	Relative area (%)	IS (mm s <sup>-1</sup> )	QS (mm s <sup>-1</sup> )	HW (mm s <sup>-1</sup> )
< 2	5,000	Fe <sup>2+</sup> silicate	55.6(4)	1.26(0)	2.89(0)	0.37(0)
		Fe <sup>3+</sup> clay	34.7(4)	0.43(1)	0.69(1)	0.67(3)
		Fe <sup>3+</sup> p. glauconite	9.7(3)	0.55(1)	1.79(2)	0.43(4)
4.1	5,500	Fe <sup>2+</sup> silicate	59.5(4)	1.26(0)	2.89(0)	0.37(0)
		Fe <sup>3+</sup> clay	20.7(4)	0.43(1)	0.69(1)	0.67(3)
		Fe <sup>3+</sup> p. glauconite	19.9(3)	0.55(1)	1.79(2)	0.43(4)
8.2	5,800	Fe <sup>2+</sup> silicate	52.0(4)	1.27(0)	2.89(0)	0.36(1)
		Fe <sup>3+</sup> clay	30.5(4)	0.43(1)	0.69(1)	0.68(3)
		Fe <sup>3+</sup> p. glauconite	17.5(3)	0.56(1)	1.83(2)	0.38(4)
16.4	6,400	Fe <sup>2+</sup> silicate	53.4(3)	1.24(0)	2.81(0)	0.34(0)
		Fe <sup>3+</sup> clay	36.8(3)	0.41(1)	0.51(1)	0.69(2)
		Fe <sup>3+</sup> p. glauconite	9.8(2)	0.55(1)	1.78(2)	0.29(4)
28.7	7,600	Fe <sup>2+</sup> silicate	57.9(4)	1.24(0)	2.82(0)	0.35(0)
		Fe <sup>3+</sup> clay	34.5(4)	0.40(1)	0.65(2)	0.69(3)
		Fe <sup>3+</sup> p. glauconite	7.7(3)	0.57(1)	1.74(3)	0.38(5)
41.1	8,700	Fe <sup>2+</sup> silicate	58.2(4)	1.26(0)	2.89(0)	0.36(0)
		Fe <sup>3+</sup> clay	34.2(4)	0.40(1)	0.66(2)	0.72(4)
		Fe <sup>3+</sup> p. glauconite	7.6(3)	0.56(1)	1.79(3)	0.42(6)
65.7	11,000	Fe <sup>2+</sup> silicate	54.2(3)	1.24(0)	2.82(0)	0.35(0)
		Fe <sup>3+</sup> clay	40.5(4)	0.40(1)	0.57(1)	0.70(3)
		Fe <sup>3+</sup> p. glauconite	5.4(3)	0.57(1)	1.68(3)	0.36(6)
69.8	11,400	Fe <sup>2+</sup> silicate	51.3(5)	1.26(0)	2.90(0)	0.36(0)
		Fe <sup>3+</sup> clay	37.8(5)	0.39(1)	0.54(1)	0.70(4)
		Fe <sup>3+</sup> p. glauconite	10.9(5)	0.56(3)	1.49(6)	0.61(7)
73.9	11,800	Fe <sup>2+</sup> silicate	57.0(5)	1.24(0)	2.82(1)	0.35(1)
		Fe <sup>3+</sup> clay	35.1(5)	0.40(1)	0.63(2)	0.66(4)
		Fe <sup>3+</sup> p. glauconite	8.0(4)	0.64(4)	1.52(7)	0.45(8)
102	14,000	Fe <sup>2+</sup> silicate	54.7(3)	1.24(0)	2.82(0)	0.33(0)
		Fe <sup>3+</sup> clay	45.3(3)	0.37(1)	0.64(1)	0.74(2)
		Fe <sup>3+</sup> p. glauconite	-	-	-	-
184	21,600	Fe <sup>2+</sup> silicate	58.8(6)	1.26(0)	2.90(1)	0.36(1)
		Fe <sup>3+</sup> clay	41.2(7)	0.43(1)	0.45(2)	0.58(4)
		Fe <sup>3+</sup> p. glauconite	-	-	-	-
201	22,800	Fe <sup>2+</sup> silicate	54.6(5)	1.26(0)	2.89(1)	0.37(1)
		Fe <sup>3+</sup> clay	42.2(6)	0.43(0)	0.47(2)	0.58(3)
		Fe <sup>3+</sup> p. glauconite	3.2(6)	0.49(2)	1.21(3)	0.44(6)

The errors in the least significant figure are given in parentheses.

change with sedimentation age in spite of the constant iron contents.

A comparison of the XANES spectra for reference materials and sediment samples showed that all sediment spectra passed the center of the spectra of both hematite ( $\text{Fe}^{3+}$ ) and olivine ( $\text{Fe}^{2+}$ ) in XANES regions, and hardly varied with sedimentation age. These trends supported the results of Mössbauer measurements, and suggested the averaged valence of iron in the GC1806 sediment did not change through the core.

### 3.3. Verification of specific peak.

*Temperature dependency.* Mössbauer spectra were measured both at 77 K and r.t. to certify the specific peak is not a ghost peak. The possibility of a ghost peak is attributed to the superparamagnetic effect. No significant difference between r.t. and 77 K was observed for all peaks of all sedimentation ages. Table 2 indicates parameters of surface sediment (5,000 y B.P.) at both 77K and r.t. as an example.

*Alteration by oxidation.* All samples were packed in oxygen-impenetrable plastic bags with  $\text{N}_2$ ; however, samples may have been oxidized by air during a prolonged preservation time. To check alteration by oxidation, Mössbauer spectra of sediments were measured again, one year after the first measurements, and the same parameters were obtained for sediment which had 5,000 y B.P. sedimentation age. This suggests that one year is too short a period for reactions in sediments, such as early-diagenesis, and the specific doublet is not attributable to oxidization with air. From the above discussion, it is evident there were iron species that had specific parameters in Mössbauer spectra of upper GC1806 sediments.

**3.4. Identification of the specific peak.** From the  $^{57}\text{Fe}$  Mössbauer data index,<sup>12</sup> a specific peak can correspond to several minerals. Of those minerals, it is reasonable that the specific peak corresponded to glauconite[(K, Na, Ca)( $\text{Fe}^{3+}$ , Al, Mg, Fe)<sub>2</sub>(Si, Al)<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>]. The peak has large IS as do clay minerals; however, its characteristic QS identified the peak as belonging to glauconite.<sup>13</sup>

Glauconite generates only at the seabed, and distributes mainly north and south of 40 degrees latitude. The generation of glauconite is not particularly clear. We tried mineral identification by X-ray diffraction; however, the low concentration does not allow the confirmation of character peaks of glauconite. Furthermore, a specific doublet peak of glauconite was not observed in GC1603, which has a different sedimentation age from GC1806 throughout the core. In addition, a specific doublet peak in Mössbauer spectra was not found in lake sediments on the Antarctic Continent.<sup>14</sup>

By contrast, although the sedimentation age was different from that of GC1806, similar chemical species were slightly detected in sediments collected from 15 locations in the Gulf of Admiralty at King George Island off the Antarctic Peninsula.<sup>15</sup> The chemical species were also detected in sedimentary rocks from the same location.<sup>16</sup>

For glauconite in GC1806, local diagenesis was expected in sediments off the Antarctic Peninsula. Crystalline glauconite hardly generate, taking the sedimentation age of GC1806 into consideration. Glauconite is a group of phyllosilicates, for which the generation time scale is generally of the Ma order.<sup>17,18</sup> Because there are differences in the quantity of glauconite generation with sedimentation depth or age, generation might be due to local sedimentation environments, such as those with oxidation-reduction potential.<sup>19</sup> In the case of clay rich sediment such as GC1806, glauconite was rare (< 1%) in the sediments.<sup>20</sup> The conditions for glauconite generation in the sea sediment were low sedimentation rate, low terrigenous material supply, low temperature, slightly reducing condition, and suitable substrates.<sup>21,22</sup> In spite of a short generation age, the conditions in GC1806 are in good agreement with the above conditions for glauconite generation. Therefore it is considered that mature glauconite did not generate but primary glauconite

**TABLE 2: Mössbauer parameters of surface GC1806 (5,000 y B.P.) at 77K and r.t.**

	Species	77K	r.t.
IS / mm s <sup>-1</sup>	Fe <sup>2+</sup> silicate	1.26	1.12
	Fe <sup>3+</sup> clay	0.43	0.32
	Fe <sup>3+</sup> p. glauconite	0.55	0.36
QS / mm s <sup>-1</sup>	Fe <sup>2+</sup> silicate	2.89	2.64
	Fe <sup>3+</sup> clay	0.69	0.84
	Fe <sup>3+</sup> p. glauconite	1.79	2.07

did in GC1806 sediment.

As a consequence, it is evident that  $\text{Fe}^{3+}$  with large QS in the Mössbauer spectra we obtained can be attributed to primary glauconite.

## 4. Conclusion

$^{57}\text{Fe}$  Mössbauer measurements for Antarctic Ocean sediments and a detailed discussion of the spectra showed primary glauconite in sediments of the surface. Primary glauconite existed at the sediment generated 5,000 – 18,000 y B.P., and tended to decrease as sedimentation age increased. A time scale of the 10<sup>6</sup> year order is necessary for the generation of glauconite, however, primary glauconite generated even for a sedimentation age of 5,000 y B.P. We were not able to detect the specific doublet peak corresponding to glauconite in Mössbauer spectra for the core of Ross Sea sediments. Taking into account the conditions of glauconite generation, it is believed the generation of primary glauconite in GC1806 was dependent on the specific environment of sedimentation.

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