

# Sorption behavior of the Pt(II) complex anion on manganese dioxide ( $\delta$ -MnO<sub>2</sub>): a model reaction to elucidate the mechanism by which Pt is concentrated into a marine ferromanganese crust

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**Abstract** It is difficult to directly investigate the chemical state of Pt in marine ferromanganese crusts (a mixture of hydrous iron(III) oxide and manganese dioxide ( $\delta$ -MnO<sub>2</sub>)) because it is present at extremely low concentration levels. This paper attempts to elucidate the mechanism by which Pt is concentrated into marine ferromanganese crust from the Earth's continental crust through ocean water. In this investigation, the sorption behavior of the Pt(II) complex ions on the surface of the  $\delta$ -MnO<sub>2</sub> that is a host of Pt was examined as a model reaction. The  $\delta$ -MnO<sub>2</sub> sorbing Pt was characterized by X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine structure (XAFS) to determine the chemical state of the Pt. Hydrolytic Pt(II) complex ions were specifically sorbed above pH 6 by the formation of a Mn-O-Pt bond. XPS spectra and XANES spectra for  $\delta$ -MnO<sub>2</sub> sorbing Pt showed that the sorbed Pt(II) was oxidized to Pt(IV) on  $\delta$ -MnO<sub>2</sub>. The extended X-ray absorption fine structure (EXAFS) analysis showed that the coordination structure of Pt sorbed on  $\delta$ -MnO<sub>2</sub> is almost the same as that of the [Pt(OH)<sub>6</sub>]<sup>2-</sup> complex ion used

as a standard. Therefore, the mechanism for the concentration of Pt in marine ferromanganese crust may be an oxidative substitution (penetration of Pt(IV) into structure of  $\delta$ -MnO<sub>2</sub>) by a reduction-oxidation reaction between Pt(II) in [PtCl<sub>4</sub>-<sub>n</sub>(OH)<sub>n</sub>]<sup>2-</sup> and Mn(IV) in  $\delta$ -MnO<sub>2</sub> through a Mn-O-Pt bond.

**Keywords** Sorption of Pt ·  $\delta$ -MnO<sub>2</sub> · XPS · XAFS · Ferromanganese crust

## Introduction

When considering the transport of trace elements in the hydrosphere, it is important to investigate the geochemical uptake mechanisms on the surfaces of various solids. The ferromanganese crusts and nodules are among the representative solids in the ocean. It is well established that transition metals such as cobalt, copper, zinc, and nickel are concentrated in marine ferromanganese nodule. However, only a few reports have been published for platinum in marine ferromanganese crust and nodule, despite the fact that Pt is an element with a much higher concentration in the ferromanganese crust than in the Earth's continental crust through ocean (Takematsu 1998; Usui 2010). The mechanism by which Pt is concentrated into marine ferromanganese crust has attracted attention for its potential applications in energy innovation such as fuel cell in the future or even at present because of the demand of much Pt as an electrode and a catalyst.

According to studies by some researchers, Pt is enriched in ferromanganese crust and nodule from the Pacific Ocean: the Pt content varies from 6 to 940 ppb (Agiorgitis and Gundlach 1978; Halbach 1984; Hodge et al. 1985). Halbach et al. (1989) also reported the Pt content in ferromanganese crusts from the Central Pacific seamount areas ranges from 0.14 to 1.02 ppm.

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The average Pt content was  $0.51 \pm 0.24$  ppm, indicating that ferromanganese crust and nodule contain more than 100 times the concentration of Pt compared to the Pt concentration of  $\sim 5$  ppb in the Earth's upper continental crust (Halbach 1984). According to Terashima et al. (1989), there was a moderate positive correlation between Mn and Pt contents in samples from both the Ogasawara Plateau ( $r=0.55$ ) and the Antarctic Ocean ( $r=0.66$ ), while no clear correlation between Fe and Pt was observed. In the Ogasawara Plateau and the Central Pacific seamount, Fe and Pt were negatively correlated ( $r=-0.57$ ). These observations suggest that Pt in the manganese dioxide phase can be found in ferromanganese crusts that are a mixture of hydrous iron(III) oxide and manganese dioxide ( $\delta\text{-MnO}_2$ ). The Pt concentration in ocean water increases from 0.1 ppt in shallow water ( $\sim 200$  m) to 0.3 ppt in deep water ( $>2000$  m; Halbach et al. 1989). Relative to the Pt concentration in ocean water, the ferromanganese crusts contain on average more than  $2 \times 10^6$  times as much Pt. The dominant species of dissolved Pt in ocean water are considered to be Pt(II) complex ions from a thermodynamic consideration (Halbach et al. 1989). Although it is necessary to investigate the chemical state of Pt in ferromanganese crust to elucidate the uptake and concentration mechanisms, no investigation has been published because of the extremely low Pt content. We cannot directly observe the chemical state of Pt in ferromanganese crust by spectroscopic methods.

Because Pt is difficult to study directly, the sorption of Pt(II) complex anions onto  $\delta\text{-MnO}_2$  may provide a suitable model reaction for elucidating the uptake and concentration mechanisms of Pt from ocean water into ferromanganese crusts. Therefore, in this investigation, the sorption behavior of Pt(II) complex anions on the surface of  $\delta\text{-MnO}_2$  was examined. Moreover, Pt species sorbed on  $\delta\text{-MnO}_2$  were characterized by X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine structure (XAFS). This investigation describes chemical reactions at the geochemical interface between solid minerals and water, which is one of the most important reaction spaces for understanding the behavior of trace elements in the hydrosphere.

## Experimental

### Reagents and sample solutions

All reagents used were of analytical grade (Wako Pure Chemical Industry). All the solutions were prepared with pure water (Milli-Q SP system, Millipore).  $\text{K}_2\text{PtCl}_6$  or  $\text{K}_2\text{PtCl}_4$  was dissolved with water to prepare the stock solution (1000 and 5000 ppm as Pt). The Pt solutions for the sorption experiments were prepared by diluting the stock solutions. The Pt concentration of the solutions was determined by inductively coupled plasma emission spectrometry (ICP-ES). Manganese dioxide

(CMD 200, specific surface area  $203 \text{ m}^2 \text{ g}^{-1}$ ) as a sorbent of Pt(II) and Pt(IV) complex ions was supplied from Chuo Denki Kogyo Co., Ltd. The manganese dioxide was  $\delta\text{-MnO}_2$  that is X-ray amorphous.

### Procedures

The sorption experiments were conducted at room temperature by a batch method. All the sorption experiments were conducted in a dark room to avoid the effects of light. The pH of the Pt solution (5–500 ppm Pt) with NaCl ( $0.12 \text{ mol dm}^{-3}$ ) as a supporting electrolyte was adjusted to the desired pH by adding NaOH solution, and the appropriate amount of  $\delta\text{-MnO}_2$  powder was added. The pH was continuously monitored using a glass electrode equipped with a pH meter. The pH was maintained within  $\pm 0.1$ . The suspended solution was magnetically stirred (stirring rate, 300 rpm). At adequate intervals, aliquots of the suspension were taken out and filtered with a  $0.45\text{-}\mu\text{m}$  membrane filter (cellulose acetate) for collection of filtrate and with a  $0.40\text{-}\mu\text{m}$  membrane filter (glass fiber) for collection of the solid sample to prevent the reduction of the Pt(II) complex ion that was sorbed on the  $\delta\text{-MnO}_2$  by cellulose acetate. The Pt concentration in the filtrate was determined by ICP-ES. The solid samples that remained on the filter were dried in a vacuum desiccator at ambient temperature under dark conditions. The proportion of Pt adsorbed was estimated according to equation (1):

$$\text{Sorption proportion}(\%) = [(C_0 - C)/C_0] \times 100 \quad (1)$$

Here,  $C_0$  indicates the initial Pt concentration in solution and  $C$  indicates the concentration in solution at  $t$  (reaction time).

### XPS measurement

The chemical state of Pt in solid samples was analyzed by XPS (Shimadzu KRATOS-AXIS 165). Powder sample that adhered to the carbon tape was placed in an evacuated sample chamber (under  $10^{-10}$  torr, and at room temperature). The XPS spectra were acquired using a monochromatic Al  $K_{\alpha}$  X-ray source (1486.49 eV) operated at 30 W (15 kV, 2 mA). Survey spectra were collected over the range 0–1400 eV with pass energy of 80 eV. High resolution XPS spectra were acquired for C1s, O1s, Mn2p, and Pt4f using pass energy equal to 40 eV. In all cases, the photoelectron take-off angle was  $45^\circ$ . The XPS spectra were corrected internally using the peak position of Cls as a standard (284.6 eV) because the sample charging can shift the peak position in the XPS spectra. The spectra were obtained under conditions of 0.1 eV steps and the acquisition of 298 ms/point. The binding energies of Pt(II), Pt(IV), and Pt(0) states were obtained from  $\text{K}_2\text{PtCl}_4$ ,  $\text{K}_2\text{PtCl}_6$ , and Pt wire as standard materials of Pt(II), Pt(IV), and Pt(0),

respectively. The Shirley method was used to correct the background. After the corrections, the spectra were analyzed using a XPS PEAK 4.1 computer software.

### XAFS measurement

The chemical states of Pt in solid samples were also analyzed by X-ray absorption fine structure (XAFS). Pt L<sub>3</sub>-edge XAFS measurements were carried out at BL37XU of SPring-8 (Hyogo, Japan). The storage ring energy was 8 GeV with a typical current of 99.5 mA. Pt L<sub>3</sub>-edge (11.56 keV) XAFS spectra were measured using a Si(111) double crystal monochromator. XAFS data of the samples for Pt L<sub>3</sub>-edge were collected under ambient conditions in fluorescence mode. A 19-element Ge solid-state detector (19SSD) was used to measure the intensity of the incident X-rays. XAFS data of the standard materials (K<sub>2</sub>PtCl<sub>4</sub>, K<sub>2</sub>PtCl<sub>6</sub>, K<sub>2</sub>Pt(OH)<sub>6</sub>, and Pt foil as Pt(II), Pt(IV), Pt(IV), and Pt(0)) at the Pt L<sub>3</sub>-edge were collected under ambient conditions. The spectral analysis was carried out by the XAFS analytical softwares, Athena and Artemis (Ravel and Newville 2005). The extraction of the extended X-ray absorption fine structure (EXAFS) oscillation from the spectra, normalization by edge-jump, and Fourier transform were performed by Athena. The curve-fitting analysis was carried out in R space by Artemis. The k-range was 3.0–10.2 Å and r-range was 1.9–3.4 Å<sup>-1</sup>. In the curve-fitting analysis, the backscattering amplitude, phase shift, and the mean-free path of the photoelectron were calculated by FEFF8.4 (Ankudinov et al. 1998), and then the other parameters, that is, the number of neighboring atoms, the inter atomic distance between the absorbed atom to the neighboring atom, the Debye-Waller factor, and the absorption edge energy were treated as fitting parameters. The intrinsic loss factor was obtained by the curve-fitting analysis of the EXAFS data of the K<sub>2</sub>Pt(OH)<sub>6</sub> (Pt(IV)).

### TEM observation

TEM images of the solid samples were obtained by Philips CM 20 transmitted electron microscope.

### Zeta potential

In order to examine the surface charge of δ-MnO<sub>2</sub>, its zeta potential in NaCl solution (0.12 mol dm<sup>-3</sup>) was measured in the pH range 2–7 using a Malvern Zeta Master.

### Chloride ion selective electrode

In order to confirm the hydrolysis of [PtCl<sub>4</sub>]<sup>2-</sup> ion (substitution of Cl<sup>-</sup> ion with H<sub>2</sub>O or OH<sup>-</sup> ion), solid K<sub>2</sub>PtCl<sub>4</sub> was dissolved in water. The variation of Cl<sup>-</sup> ion concentration with time was measured using the Cl<sup>-</sup> ion selective electrode

(DKK-TOA CL-125B) equipped to an ion meter (DKK-TOA ION MATER IM-40S). In the titration experiment, the amount of OH<sup>-</sup> ion added to maintain the initial pH of 8 was compared to the amount of Cl<sup>-</sup> ion released in the solution. pH was measured at the same time using a pH meter (HORIBA pH MATER F-22).

## Results and discussion

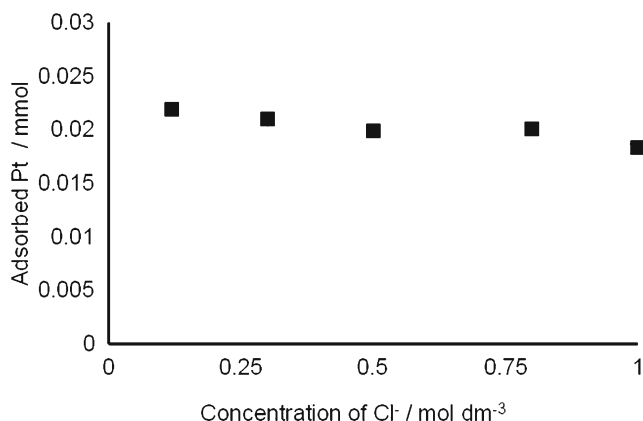
### Sorption behavior of Pt(II) and Pt(IV) complex ions

As the Cl<sup>-</sup> concentration of natural seawater is about 0.56 mol dm<sup>-3</sup>, the effect of Cl<sup>-</sup> concentration on the sorption of Pt(II) complex ions on δ-MnO<sub>2</sub> was first examined. Figure 1 shows the variation in the amount of Pt(II) complex ions sorbed on δ-MnO<sub>2</sub> with Cl<sup>-</sup> concentration. The amount of Pt(II) complex ions sorbed was almost constant in spite of wide Cl<sup>-</sup> concentration range (from 0.12 to 1.0 mol dm<sup>-3</sup>), revealing that the sorption of Pt(II) complex ion on δ-MnO<sub>2</sub> is not affected by Cl<sup>-</sup> concentration. Therefore, 0.12 mol dm<sup>-3</sup> of Cl<sup>-</sup> concentration was used in this investigation for convenience.

Figure 2 shows the variation in the proportion of sorption for Pt(II) and Pt(IV) complex ions on δ-MnO<sub>2</sub> with time for 6 h at pH 8. The initial concentration of Pt was 5 ppm, and 5 or 10 g of δ-MnO<sub>2</sub> was added. This initial Pt concentration was selected for the sensitivity of ICP-ES. Approximately 40–50 % of Pt(II) complex ion was sorbed on δ-MnO<sub>2</sub> after 6 h, but no Pt(IV) complex ion could be sorbed even after 6 h.

Figure 3 shows the sorption proportion of Pt(II) complex ions sorbed on δ-MnO<sub>2</sub> at various pH after 24 h. The proportion was highest at pH 6. However, the Pt(II) complex ion can be effectively sorbed on δ-MnO<sub>2</sub> even in the pH range of 8–10. The sorption of Pt(II) complex ions on δ-MnO<sub>2</sub> is not affected by Cl<sup>-</sup> concentration but is controlled by pH in Figs. 1 and 3. This finding indicates that the Pt(II) complex ion can be significantly sorbed on δ-MnO<sub>2</sub> from ocean water, which has a pH of approximately 8. However, no Pt(IV) complex ion could be sorbed in the pH range 2–10. We examined the hydrolysis of the [PtCl<sub>4</sub>]<sup>2-</sup> complex ion (the substitution of Cl<sup>-</sup> with OH<sup>-</sup> for the [PtCl<sub>4</sub>]<sup>2-</sup> complex ion) at pH 8 to identify the Pt(II) species that would preferentially sorb onto δ-MnO<sub>2</sub>. Because some researchers reported that Cl<sup>-</sup> ion in [PtCl<sub>4</sub>]<sup>2-</sup> complex ion can substitute with H<sub>2</sub>O molecule (Li et al. 1990; Jeanette and Byrne 2003; Azaroual et al. 2001), and [AuCl<sub>4</sub>]<sup>-</sup> hydrolyzes to [AuCl<sub>4-n</sub>(OH)<sub>n</sub>, n=1~4]<sup>-</sup> even at weak acid condition depending on the Cl<sup>-</sup> ion concentration (Ohashi et al. 2005a).

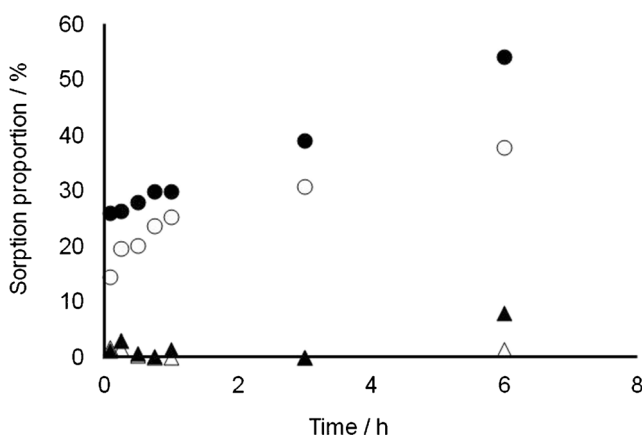
When solid of K<sub>2</sub>PtCl<sub>4</sub> is dissolved into water, whether Cl<sup>-</sup> ion in the [PtCl<sub>4</sub>]<sup>2-</sup> complex ion is substituted with H<sub>2</sub>O molecule or OH<sup>-</sup> ion has been quantitatively uncertain even at present. In a preliminary experiment in this study, it was



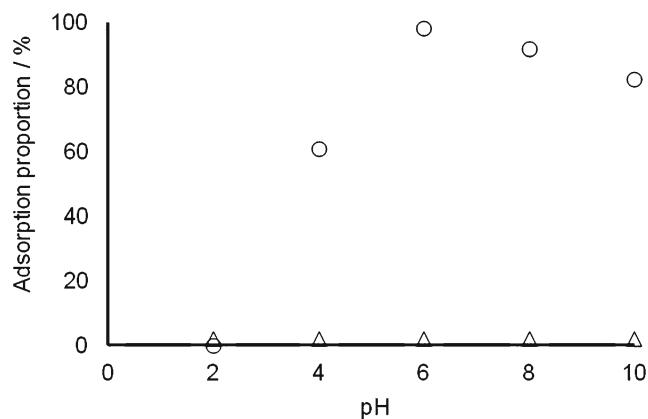
**Fig. 1** Variation of the amount of Pt sorbed on  $\delta$ -MnO<sub>2</sub> with Cl<sup>-</sup> concentration. Initial Pt concentration, 10 ppm. The amount of  $\delta$ -MnO<sub>2</sub> added, 0.5 g. pH, 8. Volume, 0.5 dm<sup>-3</sup>. Source of Cl, NaCl

confirmed that when K<sub>2</sub>PtCl<sub>4</sub> was dissolved into water, Cl<sup>-</sup> ion was released and pH of the solution decreased. Therefore, immediately after K<sub>2</sub>PtCl<sub>4</sub> was dissolved into water of pH 8, NaOH solution was added to maintain pH to 8. Figure 4 shows the variation of amount of Cl<sup>-</sup> ion released into water with time and the amount of OH<sup>-</sup> ion added to maintain pH to 8. The Cl<sup>-</sup> ion concentration increased with decreasing OH<sup>-</sup> concentration (pH) in the solution, suggesting that Cl<sup>-</sup> ion in [PtCl<sub>4</sub>]<sup>2-</sup> complex can be substituted with OH<sup>-</sup> ion in water.

Figure 4 suggests that the hydroxyl group is key to the sorption of Pt(II) complex ions on  $\delta$ -MnO<sub>2</sub>. Since the point of zero charge (PZC) of  $\delta$ -MnO<sub>2</sub> is approximately pH 4 and hydrolytic species ([PtCl<sub>4-n</sub>(OH)<sub>n</sub>]<sup>2-</sup>, n=1–4) form at pH 8, they can specifically sorb on  $\delta$ -MnO<sub>2</sub> to form a Mn-O-Pt bond by a condensation reaction between the surface OH group on  $\delta$ -MnO<sub>2</sub> and the OH group in the Pt(II) complex ion. Surprisingly, this condensation reaction is a strong reaction that overcomes the electrostatic repulsion between the negatively



**Fig. 2** Variation of sorption proportion for Pt(II) complex ions (white circle, black circle) and Pt(IV) complex ions (white triangle, black triangle) on  $\delta$ -MnO<sub>2</sub> with time. Initial Pt concentration, 5 ppm. The amount of  $\delta$ -MnO<sub>2</sub> added, 10 g (black circle, black triangle) and 5 g (white circle, white triangle). pH, 8. Volume, 0.5 dm<sup>3</sup>. NaCl concentration, 0.12 mol dm<sup>-3</sup>

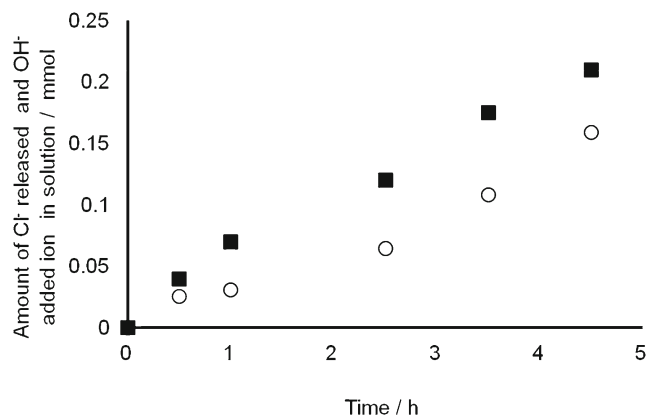


**Fig. 3** Sorption proportion of Pt(II) complex ions (white circle) and Pt(IV) complex ions (white triangle) on  $\delta$ -MnO<sub>2</sub> at various pHs. Initial Pt concentration, 5 ppm. The amount of  $\delta$ -MnO<sub>2</sub> added, 5 g. Volume, 0.5 dm<sup>3</sup>. Reaction time, 24 h

charged surface of  $\delta$ -MnO<sub>2</sub> above pH 4 and the Pt(II) complex anion.

### Oxidation state of Pt sorbed on $\delta$ -MnO<sub>2</sub>

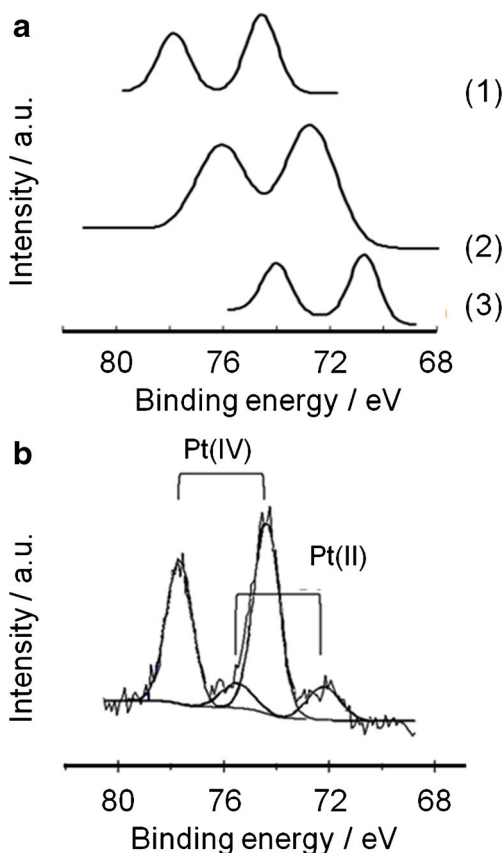
Halbach et al. (1989) and Terashima et al. (1989) proposed that Pt may be present as Pt(0) in ferromanganese crusts that are formed at depths with minimum dissolved oxygen concentrations. In contrast, some researchers have proposed oxidative sorption of Pt(II) to Pt(IV) on ferromanganese crusts (Hodge et al. 1985; Halbach et al. 1989; Goldberg et al. 1986; Banakar et al. 2007). Whether the Pt(II) complex ion is taken up as Pt(0) or Pt(IV) by ferromanganese crusts remains uncertain, even at present. Some authors have found that when the Au(III) complex ion is sorbed on  $\delta$ -MnO<sub>2</sub>, the Au(III) is reduced to Au(0) (Ohashi et al. 2005a; Ohashi et al. 2005b). Therefore, to examine whether Pt(0) particles were present on  $\delta$ -MnO<sub>2</sub>, the solid sample ( $\delta$ -MnO<sub>2</sub> sorbing Pt) was first



**Fig. 4** A relationship between the amount of Cl<sup>-</sup> (white circle) released from [PtCl<sub>4</sub>]<sup>2-</sup> complex ion sorbed and the amount of OH<sup>-</sup> (black square) added. The standard NaOH solution was titrated into solution to maintain the pH to 8. A 53-mg of K<sub>2</sub>PtCl<sub>4</sub> (solid) was dissolved into water (0.5 dm<sup>3</sup>) of pH 8

observed by TEM. In spite of the careful TEM observation, no Pt(0) particles were found in TEM images.

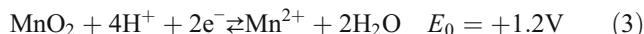
Next, to examine the valence state of Pt sorbed on  $\delta$ -MnO<sub>2</sub>, the XPS spectra for solid samples were measured. When preparing solid samples for XPS measurement in this sorption experiment, the initial Pt concentration was set at 500 ppm because of the low sensitivity of XPS. Figure 5a shows Pt4f XPS spectra for standard materials as Pt(0), Pt(II), and Pt(IV). From the XPS spectra, Pt(0), Pt(II), and Pt(IV) can be distinguished. Figure 5b shows the Pt4f spectra of a solid sample ( $\delta$ -MnO<sub>2</sub> sorbing Pt). It shows two doublet peaks. The peaks were assigned to Pt(II) and Pt(IV) by comparing the peak position to those of the standard materials. The major component of Pt sorbed on  $\delta$ -MnO<sub>2</sub> is Pt(IV), and Pt(II) is a minor component. However, Pt(IV) could not sorb on  $\delta$ -MnO<sub>2</sub>, as shown in Figs. 2 and 3. After sorption of Pt(II), Pt was sorbed on  $\delta$ -MnO<sub>2</sub>, despite the fact that Pt(II) was oxidized to Pt(IV).



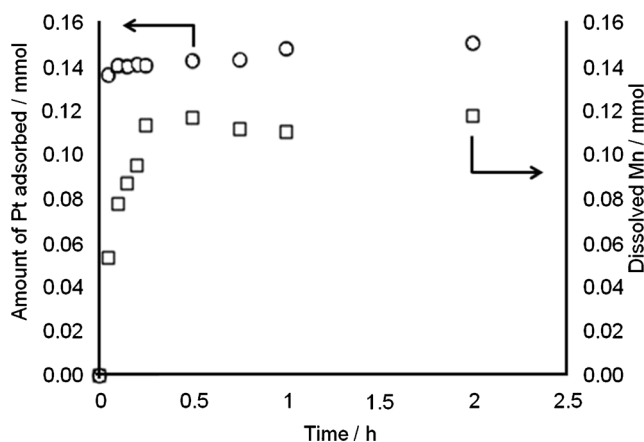
**Fig. 5** Pt4f XPS spectra of standard materials (a) and a solid sample (b). Standard materials: K<sub>2</sub>PtCl<sub>6</sub> (1), K<sub>2</sub>PtCl<sub>4</sub> (2), and Pt wire (3). Doublet peak positions of Pt4f spectra for standard materials were 74.6 and 77.9 eV (Pt(IV)), 72.7 and 76.0 eV (Pt(II)), and 70.7 and 74.0 eV (Pt(0)). Initial Pt concentration, 500 ppm. The amount of  $\delta$ -MnO<sub>2</sub> added, 10 g, pH, 8. Volume, 0.5 dm<sup>3</sup>. NaCl concentration, 0.12 mol dm<sup>-3</sup>. Reaction time, 24 h. The fitted peak positions for the solid sample were 72.2 and 75.5 eV (Pt(II)) and 74.4 and 77.7 eV (Pt(IV))

### Dissolution of Mn during sorption of the Pt(II) complex ion on $\delta$ -MnO<sub>2</sub>

The XPS data described here confirms that the Pt(II) complex ion is oxidized to Pt(IV) after sorption. The oxidation/reduction potential for the conversion from Pt(II) to Pt(IV) and from Mn(IV) to Mn(II) can be represented as follows although the oxidation reaction potential of hydrolytic species for Pt(II) and Pt(IV) is uncertain.



Based on Eqs. (2) and (3), although the Pt complex species adsorbed on  $\delta$ -MnO<sub>2</sub> may be different from the [PtCl<sub>4</sub>]<sup>2-</sup> complex ion, the oxidant of the adsorbed Pt(II) is expected to be Mn(IV) in  $\delta$ -MnO<sub>2</sub>. If this is correct, one Mn(II) should be released into solution after the oxidation of one Pt(II) to Pt(IV) by Mn(IV) because of transfer of two electrons from Pt(II) to Mn(IV). Therefore, the variation of Mn and Pt concentrations with time were simultaneously measured during the sorption experiment. The sorption experiment was performed at pH 4 to avoid the re-sorption/precipitation due to hydrolysis of the released Mn(II) on  $\delta$ -MnO<sub>2</sub>. At pH 8, no release of Mn was observed. As shown in Fig. 6, although the amount of Mn(II) released into solution was less than the amount of Pt adsorbed, a considerable amount of the Mn was dissolved during the sorption of the Pt(II) complex ion. A part of the Mn that is dissolved into solution may be re-adsorbed on  $\delta$ -MnO<sub>2</sub>. The data indicate that after sorption of Pt(II) on  $\delta$ -MnO<sub>2</sub>, the Pt(II) is oxidized by Mn(IV) in  $\delta$ -MnO<sub>2</sub> through a Mn-O-Pt(II) bond.

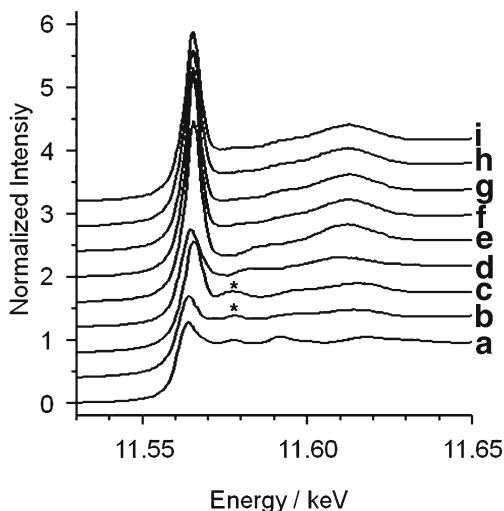


**Fig. 6** Variations in the amount of sorbed Pt (white circle) on  $\delta$ -MnO<sub>2</sub> and the amount of dissolved Mn (white square) with time. Initial Pt concentration, 100 ppm. Amount of  $\delta$ -MnO<sub>2</sub> added, 5 g, pH, 4. Volume, 0.5 dm<sup>3</sup>. NaCl concentration, 0.12 mol dm<sup>-3</sup>

## Structure of Pt sorbed on $\delta$ -MnO<sub>2</sub>

To examine the structure of Pt sorbed on  $\delta$ -MnO<sub>2</sub>, XAFS measurement was conducted. Figure 7 shows Pt L<sub>3</sub>-edge XANES spectra for standard materials of Pt (a–e) and the Pt sorbed on  $\delta$ -MnO<sub>2</sub> with various contents (f–i) (solid samples). The position of first peaks for Pt(0) and Pt(II) was different from that for Pt(IV) and solid samples. The shape of spectra of the solid samples is clearly different from that of Pt wire. The facts indicate that Pt sorbed on  $\delta$ -MnO<sub>2</sub> is not Pt(0) but Pt(IV). Moreover, although the spectra of K<sub>2</sub>PtCl<sub>4</sub> and K<sub>2</sub>PtCl<sub>6</sub>, which chloride ions coordinate to Pt ion, have a distinctive peak (Fig. 7) around 11.57–11.58 keV, the spectra of Pt(acac)<sub>2</sub> and K<sub>2</sub>Pt(OH)<sub>6</sub>, which oxide ions coordinate, do not show the peak. The solid samples did not show the peak around 11.57–11.58 keV, and the shape of their spectra closely resembles that of K<sub>2</sub>Pt(OH)<sub>6</sub>. Judging from the results of the XPS spectra in Fig. 5 and XANES spectra in Fig. 7, it can be reasonably concluded that Pt(II) sorbed on  $\delta$ -MnO<sub>2</sub> is oxidized to Pt(IV) accompanying ligand exchange from chloride ion to hydroxide ion. In addition, it should be emphasized here that structure conversion from square planar 4-coordinate structure for Pt(II) to 6-coordinate octahedral structure for Pt(IV) occurred.

In Fig. 5, no Pt(0) component was observed and the amount of Pt(IV) was considerably larger than that of Pt(II). It can be easily deduced that if the amount of Pt sorbed on  $\delta$ -MnO<sub>2</sub> is low, the existence of Pt(II) can be ignored. All of the atoms coordinated to Pt(IV) are oxygen because no Cl<sup>−</sup> ion was found in the wide XPS spectra, and the shape of the XANES



**Fig. 7** Pt L<sub>3</sub>-edge XANES spectra for standard materials of Pt(0), Pt(II) and Pt(IV) (a–e) and Pt species sorbed on  $\delta$ -MnO<sub>2</sub> (f–i). Standard materials: Pt wire (a), K<sub>2</sub>PtCl<sub>4</sub> (b), K<sub>2</sub>PtCl<sub>6</sub> (c), Pt(acac)<sub>2</sub> (d), and K<sub>2</sub>Pt(OH)<sub>6</sub> (e). Initial Pt concentration and weight % of Pt, 500 ppm 2.5 wt% (f), 200 ppm 1.0 wt% (g), 100 ppm 0.5 wt% (h), and 50 ppm 0.25 wt% (i). The amount of  $\delta$ -MnO<sub>2</sub> added, 10 g, pH, 8. Volume, 0.5 dm<sup>3</sup>. NaCl concentration, 0.12 mol dm<sup>−3</sup>. Reaction time, 24 h. Resolution of Pt L<sub>3</sub> XANES spectra, 0.0003 keV

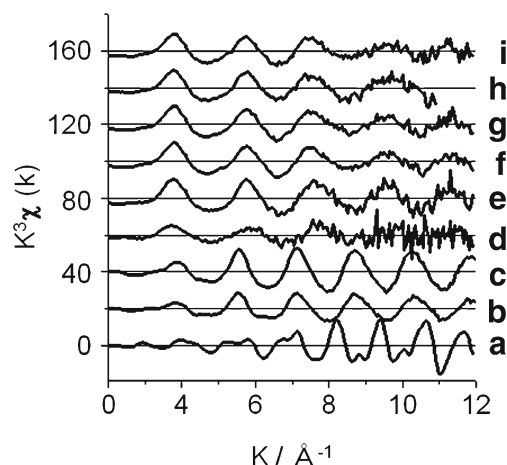
spectra was quite similar between the solid sample and [Pt(OH)<sub>6</sub>]<sup>2−</sup> as a Pt(IV) standard material.

Figure 8 shows the k<sup>3</sup>-weighted EXAFS oscillation for the corresponding standard materials (Fig. 7a–e) and the solid samples (Fig. 7 f–i). One of the most important points is that all the spectra for the solid samples closely resemble each other, and the spectra are almost the same as that of spectrum for K<sub>2</sub>Pt(OH)<sub>6</sub> as a standard material (Fig. 7e). These facts indicate that the chemical state of Pt in the solid samples (f–i) is almost the same in spite of different amounts of Pt sorbed on  $\delta$ -MnO<sub>2</sub> and the valence state is Pt(IV). In addition, the phase of the spectra for the solid samples at  $k=8.5$ – $8.7$  Å<sup>−1</sup> is opposite against that of K<sub>2</sub>PtCl<sub>4</sub> and K<sub>2</sub>PtCl<sub>6</sub> as standard materials (Fig. 7b, c). This opposite phase may be due to difference from coordinated atoms, that is, chlorine or oxygen. From this fact, it can be supposed that the atoms coordinated to Pt in the solid samples are oxygen and the coordination structure is PtO<sub>6</sub> system.

The radial structure functions which are Fourier transformations of the EXAFS oscillations are shown in Fig. 9. The structural parameters CN (coordination number), R (inter atomic distance, Pt–O), and the  $\sigma^2$  (Debye-Waller factor) were obtained by fitting the curve for the first shell EXAFS data in R space. The parameters obtained are shown in Table 1. These EXAFS functions fitted well, and the fitted EXAFS functions indicate that the interatomic distance for Pt–O in the solid sample was 1.99 Å and that the CN was 6. Therefore, interatomic distance for Pt–O in the solid sample coincides with that of K<sub>2</sub>Pt(OH)<sub>6</sub>.

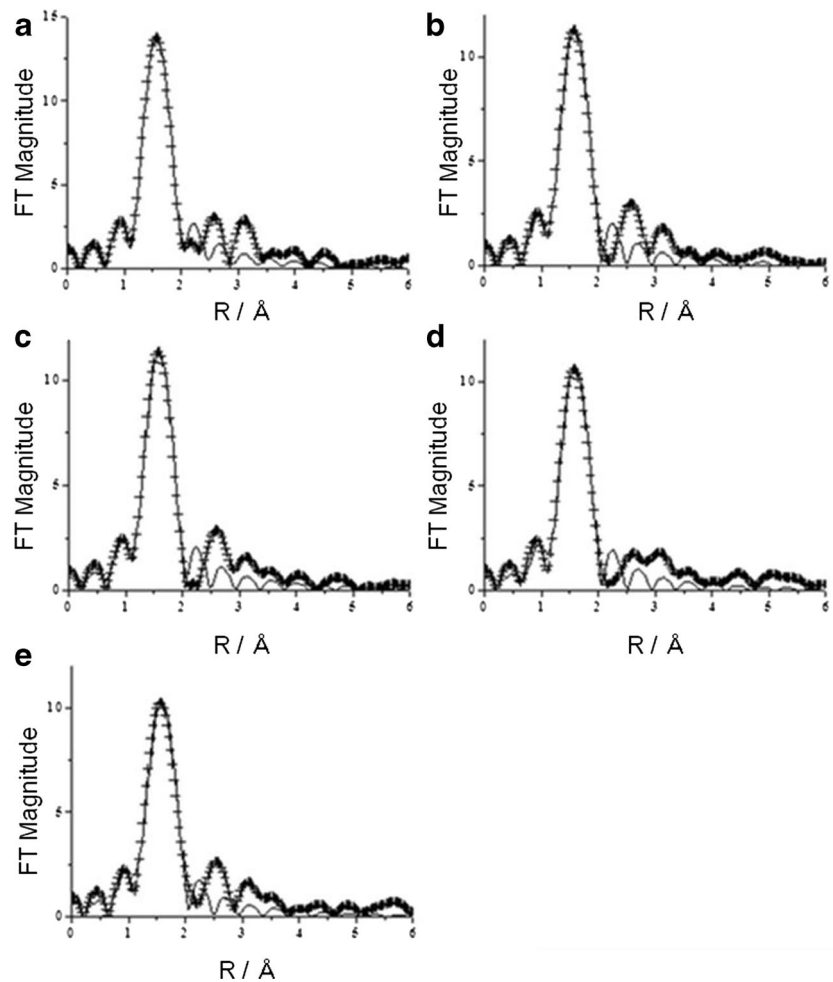
## Oxidative uptake model reaction of Pt by $\delta$ -MnO<sub>2</sub>

According to Takematsu (1998) and Usui (2010), Pt is concentrated into the crust and the Pt content



**Fig. 8** The k<sup>3</sup>-weighted EXAFS oscillations for standard materials (a–e) and solid samples (f–i) shown in Fig. 6

**Fig. 9** Radial structure functions for (a)  $K_2Pt(OH)_6$  as a standard material of Pt(IV) and solid samples: initial Pt concentration and weight % of Pt, 500 ppm 2.5 wt% (b), 250 ppm 1.0 wt% (c), 100 ppm 0.5 wt% (d), and 50 ppm 0.25 wt% (e). (plus sign Fourier transform data, minus sign fitting line)



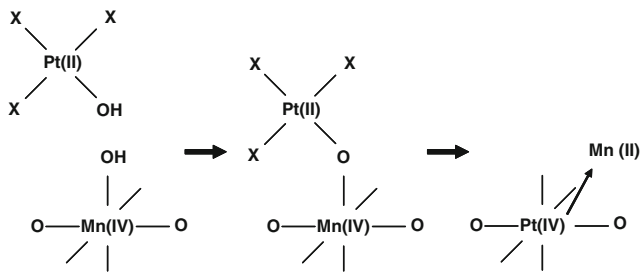
correlated with that of Mn, suggesting that Pt may be concentrated into  $\delta$ - $MnO_2$  phase in ferromanganese crust. Pt is present as Pt(II) complex ion in seawater such as chlorohydroxyl species ( $[PtCl_{4-n}(OH)_n]^{2-}$ ) based on the viewpoint of thermodynamics (Halbach et al. 1989). In this study, it is considered that the concentration mechanism of Pt into marine ferromanganese crust is due to the sorption reaction of Pt(II) complex ion on  $\delta$ - $MnO_2$ .

Based on the above data shown in this paper, Fig. 10 shows a schematic figure of the model reaction for the concentration of Pt into marine ferromanganese crusts whose manganese phase consists of  $\delta$ - $MnO_2$ . Pt(II) complex anion ( $[PtCl_4$

$n(OH)_n]^{2-}$ ) can be sorbed on  $\delta$ - $MnO_2$  and then the Pt(II) is oxidized to Pt(IV), to which six oxygen atoms coordinate. One of the reasonable interpretations for this sorption and oxidation/reduction mechanism of Pt(II) on  $\delta$ - $MnO_2$  is that there is an isomorphous substitution between Pt(IV) and Mn(IV) by oxidation of Pt(II) to Pt(IV) and reduction of Mn(IV) to Mn(II) through a Mn-O-Pt bond. The abundance of cobalt in ferromanganese nodules is considered to be due to isomorphous substitution between Mn(III) and Co(III) as a result of the oxidation of Co(II) to Co(III) and the reduction of Mn(IV) to Mn(III) (Burns 1976; Murray and Dillard 1979). The release of Mn(II) from  $\delta$ - $MnO_2$  during the

**Table 1** EXAFS fitting parameter of solid sample and standard materials

Sample	Shell	CN	R/Å	$\sigma^2/10^{-3} \text{ \AA}^2$	Rfactor (%)
$K_2Pt(OH)_6$	Pt-O	$6.0 \pm 0.5$	$2.00 \pm 0.01$	$0.9 \pm 0.7$	0.071
Pt/ $MnO_2$ (500 ppm)	Pt-O	$6.8 \pm 1.9$	$2.02 \pm 0.02$	$4.1 \pm 3.0$	0.496
Pt/ $MnO_2$ (200 ppm)	Pt-O	$6.5 \pm 1.2$	$2.02 \pm 0.01$	$3.7 \pm 1.9$	0.255
Pt/ $MnO_2$ (100 ppm)	Pt-O	$6.3 \pm 1.8$	$2.02 \pm 0.02$	$3.9 \pm 3.0$	0.639
Pt/ $MnO_2$ (50 ppm)	Pt-O	$6.9 \pm 2.6$	$2.02 \pm 0.02$	$5.4 \pm 4.2$	1.056



**Fig. 10** A proposed model of concentration mechanism for Pt onto  $\delta$ -MnO<sub>2</sub> through the isomorphous substitution between Pt(IV) and Mn(IV) ions. X=Cl<sup>-</sup>, OH<sup>-</sup>

sorption of Pt(II), as shown in Fig. 6, proves that the proposed oxidative uptake of Pt(II) is reasonable.

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