Investigations on Adsorption of Inorganic Ions in Aqueous Solution to Some Metal Oxides, Hydroxides and a Carbonate by the X-Ray Spectroscopic Method

Hironori Ohashi,* Kotaro Yonezu,** Daisuke Kawamoto,* and Takushi Yokoyama***

*Department of Chemistry, Faculty of Science, Kyushu University, 744 Motooka, Nishi, Fukuoka 819-0395, Japan
**Department of Earth Resource Engineering, Faculty of Engineering, Kyushu University, 744 Motooka, Nishi, Fukuoka 819-0395, Japan

Why does the adsorption and concentration of inorganic chemical species proceed at aqueous-solid interfaces? In this review paper, we discuss the use of X-ray chemical state analysis to elucidate the intrinsic adsorption mechanism. Based on the chemical states of the species adsorbed to solids as determined by X-ray chemical state analysis, possible adsorption mechanisms are discussed. The driving forces of adsorption are represented by the Gibbs free energy change ($\Delta G_{chem} = \Delta G_{chem,1} + \Delta G_{chem,2}$) resulting from the formation of covalent bonds between metal ions (M) in metal oxides or hydroxides and adsorbed species (X) (M-O-X bond, $\Delta G_{chem,1}$) and the formation of new phases consisting of M and X ($\Delta G_{chem,2}$). The concept of $\Delta G_{chem,2}$ is proposed based on the experimental results from chemical state analyses. As examples, the following investigations are discussed in this review paper: the formation of mullite precursors by the adsorption of monosilicic acid to Al(OH)$_3$, the spontaneous reduction of Au(III) to Au(0) by adsorption of Au(III) to Al(OH)$_3$, MnO$_2$ and Ni(OH)$_2$ and the mechanism of concentration of Co$^{2+}$, Tl$^+$, Pb$^{2+}$, Pt$^{2+}$, Au$^+$, and Pd$^{2+}$ in marine ferromanganese crusts.

**Keywords** Adsorption mechanism, adsorption driving force, solid–aqueous interface, X-ray chemical state analysis

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1 Introduction

The adsorption of chemical species to solids from aqueous solutions is an important chemical process. For example, in the geochemistry of the hydrosphere, the cycling of inorganic trace elements is controlled by adsorption at the interfaces between minerals and natural water; in environmental chemistry, undesired inorganic species are removed from water by adsorption to solid adsorbents; and, in catalytic chemistry, the catalysts such as gold or platinum clusters supported on metal oxides (called environmental catalysts) are prepared by the adsorption of metal ions on solid supports.

Until 1980, the adsorption of inorganic species had been macroscopically investigated from the viewpoint of chemical thermodynamics, and the adsorption type and adsorption capacity had mainly been examined using adsorption isotherms. In addition, the adsorption kinetics had also been investigated for the estimation of the adsorption rate and activation energy. From a practical viewpoint, these data are useful for the chemical industry.

A classic definition of adsorption is that the concentration of a chemical species on the surface of an adsorbent is higher than that in the bulk solution. However, the chemical state of the adsorbed inorganic species has scarcely been considered because of difficulty in analyzing the chemical states. Thus, in many cases, the adsorption mechanism has only been speculated. To elucidate the detailed adsorption mechanism, it is essential to investigate the chemical state of inorganic species adsorbed on solid adsorbents. Since around 1980, spectroscopic methods such as X-ray photoelectron spectroscopy (XPS), nuclear magnetic resonance (NMR), and Mössbauer spectroscopy have been applied to the microscopic investigation of adsorption, as described in this paper. In addition, synchrotron radiation facilities, such as KEK and SPring-8 in Japan, have become more easily available since the turn of the millennium, and X-ray absorption spectroscopy (XAS) has been applied actively to the chemical state analysis of inorganic species adsorbed on solid adsorbents because of its broad applicability for many elements. XAS can give information about both the valence state and local structure (average interatomic distances and coordination numbers) of target elements. In addition, it can be applied to both amorphous solids, liquid phases, and crystalline solids. However, complete information cannot always be obtained from XAS alone, and other methods are required to complement the XAS results. In this paper, the investigation of the adsorption mechanism of inorganic species on solids by a combination of XAS and other spectroscopic methods is discussed.

Although they are not described for want of space, there are other new methods to investigate adsorption of inorganic ions in aqueous solution on solid surfaces, such as atomic force microscopy in liquid, infrared spectroscopy, X-ray crystal truncation rod scattering, etc. Using these techniques, interesting studies have been performed.

2 Driving Force for the Adsorption Reaction

The adsorption of ions on the surface of metal oxides and hydroxides from aqueous solutions can be described thermodynamically by Eq. (1a). The term \( \Delta G_{\text{chem,2}} \) as proposed by the authors, is defined by Eq. (1b) and discussed later.

\[
\Delta G_{\text{ads}} = \Delta G_{\text{chem,2}} + \Delta G_{\text{elec}} + \Delta G_{\text{tem}}
\]

(1a)

\[
\Delta G_{\text{chem}} = \Delta G_{\text{chem,1}} + \Delta G_{\text{chem,2}}
\]

(1b)

Here, \( \Delta G_{\text{ads}} \) is the net change in the Gibbs free energy for the adsorption of ions on the surface of metal oxides and hydroxides, \( \Delta G_{\text{chem,2}} \) is the Gibbs free energy change caused by electrostatic effects, \( \Delta G_{\text{elec}} \) is that due to dehydration effects when hydrated ions are adsorbed on the surface of metal oxides and hydroxides, and \( \Delta G_{\text{chem,2}} \) is that due to the formation of chemical bonds between the ion and surface of metal oxides and hydroxides (\( \Delta G_{\text{chem,1}} \)) or by the formation of new phases consisting of adsorbed ions and metal ions in the oxides and hydroxides (\( \Delta G_{\text{chem,2}} \)). In this review paper, the driving force for each adsorption reaction is considered based on the changes in the chemical states of the elements in the adsorbents and adsorbed chemical species. The concept of \( \Delta G_{\text{chem,2}} \) has been proposed by our research group based on several experimental facts. We deduce that, when the amount of chemical species adsorbed exceeds a critical amount, the formation of a new phase may be initiated. Thus the quantification of \( \Delta G_{\text{chem,1}} \) and \( \Delta G_{\text{chem,2}} \) is an important future research direction.

3 Chemical State of Al (Al K-edge XAS and \(^{27}\text{Al} \) MAS NMR)

3-1 Adsorption of monosilicic acid to Al(OH)$_3$: Thermodynamic interpretation

The specific adsorption of anions at mineral/aqueous solution interfaces has been explained from the correlation between the pK values of the conjugate acids of the anions and the pH values at which specific adsorption shows a marked change. On the basis of this explanation, specific adsorption depends on the ease of dissociation of the conjugate acids at the mineral surface. In this model, the pH at which the adsorption of monosilicic acid to gibbsite (Al(OH)$_3$) is greatest is consistent with the theoretical pH. However, the observed amount of adsorbed monosilicic acid is greater than the theoretical amount at other pH values, as shown in Fig. 1. This discrepancy could arise because monosilicic acid is a polybasic acid (pK$_1$ – pK$_n$). This adsorption model is called the constant capacitance model.

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Hironori Ohashi received his Ph.D. degree in 2007 from Kyushu University. He joined the research group at Tokyo Metropolitan University (2007 – 2010), Kyushu University (2010 – 2015) and Fukushima University (2015 –). His research interests are in state analysis for chemical species on the surface of metal oxides and hydroxides from aqueous solutions. He started a new research on material synthesis for final storage of radioactive cesium and its characterization using XRD and XAFS.

Kotaro Yonezu received his Ph.D. degree in 2009 from Kyushu University. He has worked at the Department of Earth Resources Engineering, Faculty of Engineering, Kyushu University as Assistant Professor (2010 – 2014) and Associate Professor (2014 –). His research interests are geochemistry of ore formation (Au, Cu, REE, etc.) and geothermal system including silica scaling based on both geo-analytical technique (ICP-MS, EPMA, XRF, XRD, XPS, XAFS, etc.) and field observation.
In this model, $\Delta G_{\text{chem}}$ is not considered.

### 3-2 Change in chemical state of Al during the crystallization of mullite from its precursors

Before around 2000, mullite (3Al$_2$O$_3$·2SiO$_2$) was considered a promising high-temperature structural and electronic ceramic material. Although mullite is a natural mineral, it can be produced industrially by heating a precursor composed of Al$_2$O$_3$ and SiO$_2$. The mullite precursor is often prepared by the coprecipitation of monosilicic acid (Si(OH)$_4$) with aluminum hydroxide (Al(OH)$_3$). When the precursor is prepared by the coprecipitation of Si(OH)$_4$ with Al(OH)$_3$, it is often difficult to control the composition and the polymerization degree of silicic acid accurately. Compared to the coprecipitation method, the adsorption method is considered to provide more accurate control over the Si/Al ratio. Yokoyama et al. found that monosilicic acid adsorbs rapidly on amorphous Al(OH)$_3$ until the Si/Al molar ratio reaches 1/3, which is the composition of mullite (3Al$_2$O$_3$·2SiO$_2$). Until an Si/Al ratio of 1/3, the adsorbed monosilicic acid polymerizes to form silica. In addition, the Al(OH)$_3$ reacts with the adsorbed monosilicic acid and is almost perfectly converted to aluminosilicate (a monophasic precursor). To produce mullite with good crystallinity at low temperatures, it is important to elucidate the relationship between the chemical properties of the mullite precursor and the crystallization of mullite.

$^{27}$Al magic angle spinning (MAS) NMR spectra of samples prepared by the adsorption of Si(OH)$_4$ to Al(OH)$_3$ have been obtained. The $^{27}$Al MAS NMR method can give information about the coordination number of Al, although no structural information such as the interatomic distance is included. When a sample with a Si/Al molar ratio of 1/3 is heated to 1000°C, the structure around Al changes as the temperature increases, and the crystallization of mullite occurs at approximately 980°C. To examine the changes in the structure, Al K-edge XAS data were obtained for samples heated to set temperatures (heating rate: 10°C/min) and were compared to the $^{27}$Al MAS NMR spectra. The XAS data were obtained using a laboratory X-ray absorption fine structure (XAFS) spectrometer, Technos EXAC 800. The detailed optical conditions for the measurements are shown in Table S1.

Figures 2 and 3 show the $^{27}$Al MAS NMR data for aluminum hydroxide with adsorbed silicic acid (RT: unheated) and samples heated to set temperatures. Chemical shifts relative to $[\text{Al(H}_2\text{O)}_6\text{]}^{3+}$: 0 – 30 ppm six-coordinate Al, 30 – 40 five-coordinate Al, and 40 - 80 four-coordinate Al.

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Daisuke Kawamoto received his Ph.D. degree in 2015 from Kyushu University. He has worked at the Department of Chemistry, Faculty of Science, Kyushu University as Research Fellow (2015 – 2017), the Department of Chemical and Biological Sciences, Faculty of Science, Japan Women’s University as Assistant Professor (2017 – 2020) and the Department of Chemistry, Faculty of Science, Okayama University of Science as Lecturer (2020 –). His research interest is solid-liquid interfacial reaction between metal ions and minerals (metal oxides and carbonates).

Takushi Yokoyama received his Ph.D. degree in 1980 from Kyushu University. He has worked at the Department of Chemistry, Faculty of Science, Kyushu University as Assistant Professor (1980 – 1989), at the General Education College of Kyushu University as Associate Professor (1989 – 1994), at the Department of Chemistry, Faculty of Science, Kyushu University as Associate Professor (1995 - 2002) and as Professor (2002 – 2017). His research interest is geochemistry of silicic acid and the importance of adsorption reactions of inorganic ions in geochemistry.
based on chemical shift relative to that of $[\text{Al(H}_2\text{O)}_6]^{3+}$. The NMR chemical shift ranges for six-, five-, and four-coordinate Al are 0 – 30, 30 – 40, and 40 – 80 ppm, respectively. Figures 4 and 5 show the changes in the proportion of four-, five-, and six-coordinate Al with temperature estimated from the NMR peak intensities and the Fourier transforms of the extended X-ray absorption fine structure (EXAFS) oscillations extracted from the Al K-edge XAS data in Fig. 3, respectively. Table 1 lists the Al–O interatomic distances ($r$, Å) and averaged coordination numbers ($N$) obtained from the EXAFS analysis.

With increase in the heating temperature, both the Al–O distance and the coordination number decreased, suggesting that the proportion of six-coordinate Al decreased. In contrast, the proportion of four-coordinate Al increased, as shown in Fig. 4. The $^{27}$Al MAS NMR spectra of the unheated sample and sample heated to 130°C reveal that there are two kinds of four- and six-coordinate Al species. In contrast, the samples heated to 530 and 930°C still contain five-coordinate Al, as well as four- and six-coordinate Al. The Al–O interatomic distance ($r$, Å) and coordination number ($N$) of aluminum in gibbsite (standard material), unheated samples, and samples heated to set temperatures $^{15}$

| Sample     | $r$  | $N$  |
|------------|------|------|
| Gibbsite   | 1.92 | 6    |
| RT         | 1.88 | 5.2  |
| 130°C      | 1.80 | 5.2  |
| 530°C      | 1.78 | 4.9  |
| 930°C      | 1.78 | 4.8  |
| 980°C      | 1.88 | 4.8  |

Table 1. $^{a}$Fixed.

Fig. 3  Al K-edge XAS spectra for Al in aluminum hydroxide with adsorbed silicic acid (RT: unheated) and samples heated to set temperatures. $^{15}$

Fig. 4  Variation in the proportion for four-, five-, and six-coordinate Al in heated samples. RT: unheated, ○: four-coordinate Al, △: five-coordinate Al, and ●: six-coordinate Al. $^{16}$

Fig. 5  Fourier transforms of EXAFS oscillations extracted from Al K-edge XAS spectra of gibbsite (standard material), an unheated sample (RT), and samples heated to set temperatures. $^{15}$

Fig. 6  Normalized Al K-edge XANES spectra for gibbsite (standard material), an unheated sample (RT), and samples heated to set temperatures. $^{15}$

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based on chemical shift relative to that of $[\text{Al(H}_2\text{O)}_6]^{3+}$. The NMR chemical shift ranges for six-, five-, and four-coordinate Al are 0 – 30, 30 – 40, and 40 – 80 ppm, respectively. Figures 4 and 5 show the changes in the proportion of four-, five-, and six-coordinate Al with temperature estimated from the NMR peak intensities and the Fourier transforms of the extended X-ray absorption fine structure (EXAFS) oscillations extracted from the Al K-edge XAS data in Fig. 3, respectively. Table 1 lists the Al–O interatomic distances ($r$, Å) and averaged coordination numbers ($N$) obtained from the EXAFS analysis. With increase in the heating temperature, both the Al–O distance and the coordination number decreased, suggesting that the proportion of six-coordinate Al decreased. $^{15}$In contrast, the proportion of four-coordinate Al increased, as shown in Fig. 4. The $^{27}$Al MAS NMR spectra of the unheated sample and sample heated to 130°C reveal that there are two kinds of four- and six-coordinate Al species. In contrast, the samples heated to 530 and 930°C still contain five-coordinate Al, as well as four- and six-coordinate Al. $^{16}$ Figure 6 shows the X-ray absorption near edge structure (XANES) spectra of the samples. In gibbsite, all the Al ions are six-coordinate, and the peak at 1573 eV can be assigned to six-coordinate Al. The absorption edge spectra for the unheated sample and the sample heated to 130°C can be
divided into two Gaussian-shaped peaks at approximately 1570 and 1573 eV. As a result, the peak at 1570 eV can be assigned to four-coordinate Al. However, a peak corresponding to five coordinate Al was not observed in the XANES spectra. In conclusion, the changes in the Al-O distance and average coordination number with heating temperature were detected by XAS, but the appearance of five-coordinate Al was detected only by $^{27}$Al MAS NMR.

Al K-edge XAS studies have been performed to examine the chemical state of Al in aluminosilicate minerals including noncrystalline mullite precursors. Interestingly, a peak arising from five-coordinate Al was observed in the XANES spectra, and the position of the peak was located between those of four- and six-coordinate Al.

In addition, XAS analysis has been applied to examine the chemical state in a natural diatom. The results showed that the four-coordinate Al is present in the natural silica network, whereas six-coordinate Al could result from changes to the biogenic silica.

3-3 What is the driving force for the adsorption of silicic acid to Al(OH)$_3$?

For the adsorption of monosilicic acid to Al(OH)$_3$, the maximum adsorption occurs at approximately pH 10. Because the isoelectric point of Al(OH)$_3$ is about pH 9, its surface charge is negative at pH 10. Consequently, neutral Si(OH)$_3$ adsorbs to the surface of Al(OH)$_3$, which is negatively charged. The electrostatic interaction between a neutral molecule and an Al-O site may result in changes in $\Delta G_{ads}$ and $\Delta G_{chem}$. The specific adsorption is driven by the formation of Al-O-Si bonds, and the formation of the Al-O-Si bond may cause changes in $\Delta G_{chem}$. If $\Delta G_{chem}$ is the main contribution to the formation of Al-O-Si bonds (see Eq. (1a), the conversion of six-coordinate Al to four-coordinate Al (the formation of the mullite precursor) cannot proceed. Here, we propose that $\Delta G_{chem}$ should be divided into two factors: $\Delta G_{chem,1}$ (the formation of covalent bonds) and $\Delta G_{chem,2}$ (the formation of a new phase such as mullite precursor). A change in $\Delta G_{chem,2}$ may occur when the amount of adsorbed species (adsorption density) exceeds a critical value. In adsorption experiments of monosilicic acid to $\gamma$-Al$_2$O$_3$, $\Delta G_{chem}$ was estimated to be ~12RT, and this corresponds to the formation of Al-O-Si bonds and the formation of aluminosilicates (Al$_2$Si$_3$(OH)$_8$ at < pH 9 and Al$_2$Si$_3$((OH)$_7$;O$_{0.5}$ at > pH 9). In addition, when monosilicic acid was adsorbed to the surface of Mg(OH)$_2$, the formation of a magnesium silicate was observed.

4 Chemical State of Au (Au L$_3$-edge XAS, Au 4f/XPS and $^{197}$Au Mössbauer Spectroscopy)

4-1 Importance of the adsorption of gold complex anions

Gold is generally transported in natural solutions as complexes with one or more ligands, such as Cl$^-$ and HS$^-$, depending on the environmental conditions. The adsorption of gold on mineral surfaces may be an important mechanism affecting the gold concentration in many natural solutions. Therefore, the adsorption behavior of Au(I) and Au(III) complexes on ubiquitous minerals such as iron(II) hydrous oxides, aluminum oxides and hydroxides, manganese dioxides, and silicates and carbonates has been extensively investigated.

4-2 Adsorption of Au(III) complex ions on metal oxides and hydroxides: Thermodynamic study

The gold(III) chloride ([AuCl$_4$]$^-$) complex is the most stable gold complex in acidic conditions (pH < 5.8) in oxidizing environments. At higher pH values, the exchange of Cl$^-$ to OH$^-$ can lead to the formation of mixed chloro-hydroxyl complexes. Figure 7 shows a species distribution diagram of gold(III) chloride complexes in solution. However, the identities of the adsorbing species and the chemical states of the adsorbed species after adsorption are unknown. In a study of the adsorption of Au(III) complex ions on hematite ($\alpha$-Fe$_2$O$_3$) by potentiometry, the adsorbed species were $\text{FeOHAuCl}$ between pH 3 and pH 6, $\text{FeOHAuClO}_4$ from pH 6 to pH 8, and $\text{FeOHAu(OH)}$ above pH 8. When Au(III) chloride complexes were adsorbed on goethite (FeOOH), they adsorbed specifically to the A-type hydroxyl groups on the surface of FeOOH, which act as an ideal template for bidentate coordination. For the adsorption of Au(III) chloride complexes on bimneseite (MnO$_2$), which has strong oxidation power and adsorption ability, whether and how Au(III) chloride complexes could be transformed to Au(I) complexes or Au(0) (elemental gold) is controversial. Further, macroscopic modeling studies cannot verify the adsorption mode at the molecular scale, and this can only be done using appropriate molecular scale spectroscopic or scattering methods such as XAS or surface-sensitive $^{197}$Au Mössbauer spectroscopy.

4-3 Adsorption of Au(III) complex ions on metal oxides, hydroxides, and carbonates: Spectroscopic studies at the atomic scale

Gold coexists intimately with hydrous iron(III) and aluminum oxides that are ubiquitous in the subsurface environment. In lateritic environments, gold is often observed with goethite and bauxite. In low sulfidation gold veins, gold is often found near adularia or smectite, which might have been primarily precipitated as amorphous aluminum hydroxide, in chalcedonic or fine-grained quartz. The concentration of gold complex ions to iron(III) and aluminum oxides and hydroxides from aqueous solution is considered to be a main factor affecting the formation of gold deposits. On the other hand, gold in gold ore is generally present as Au(0). How are Au(III) or Au(I) complex ions adsorbed on Fe(III) and Al oxides and hydroxides reduced? This is an interesting research theme.

In investigations into the coprecipitation of Au(III) complexes with aluminum hydroxide and iron(III) hydroxide using electron microscopy, some of the Au(III) complex ions that coprecipitated were found to have been reduced to Au(0) in the absence of a
specific reducing agent. Although Berrodier et al. noticed that some Au(III) complex ions had adsorbed on iron(III)- and Al-(oxy)hydroxides and been reduced to Au(0), they ignored this result and excluded the samples from their study. Ohashi et al. were first able to determine the proportion of Au(0) formed when Au(III) complex ions are adsorbed on δ-MnO₂. Figures 8 and 9 show the 4f Au XPS spectra and ¹⁹⁷Au Mössbauer spectra for Au species adsorbed on δ-MnO₂. Based on the spectroscopic results, only 20% of the adsorbed Au(III) was reduced to Au(0). Ando et al. studied the adsorption of Au(III) chloride complex ions on nickel hydroxide (Ni(OH)₂) and nickel carbonate (NiCO₃). Figures 10 and 11 show the Au L₃-edge XANES spectra for standard materials (a–c) and samples (d and e) and the Fourier transform of the EXAFS oscillations extracted from the Au L₃-edge spectra for standard materials (a–c) and a sample, respectively. From their results, it can be concluded that the Au(III) complex ions adsorbed on Ni(OH)₂ were reduced to Au(0), but the Au(III) complex ions adsorbed on NiCO₃ as [Au(OH)₃Cl]⁻ were not reduced at all. A high proportion of adsorbed Au(III) complex ions was reduced to Au(0) compared to those adsorbed on Al(OH)₃, Fe(OH)₃, and MnO₂.

The subsequent reaction is proposed as Eq. (2). The equilibrium constant, K, was estimated to be 10⁻⁶¹ at 25°C. Therefore, the AuCl₄⁻ complex ion cannot be reduced in aqueous solution.

\[
\text{Au(s) + 3H}^+ + 4\text{Cl}^- + 3/4\text{O}_2(\text{g}) \rightleftharpoons [\text{AuCl}_4]^- + 2/3\text{H}_2\text{O} \quad (2)
\]

With increase in pH, AuCl₄⁻ is hydrolyzed and converted to AuCl₄₋(OH)ₓ, which can be adsorbed specifically on the surface of metal oxides and hydroxides (Fig. 7). In a study of the
adsorption of Au(III) chloride complex ions on CeO₂, the Au(III) was adsorbed as mono and bidentate surface complexes, as shown below. The reduction of the Au(III) complex ions adsorbed on CeO₂ was not detected.  

\[
\text{Au(OH)}_2^{2-} + 2\text{CeO}_2 \rightleftharpoons \text{Au}^{3+} + 2\text{Ce}^{4+} + 2\text{H}_2\text{O}
\]

Ce-OH + H\text{O}Au(OH)₃ → Ce-O-Au(OH)₂ + H₂O (monodentate)  
Ce-OH  
|  
|  
O  
|  
OH⁻,⁺electrostatic adsorption  
|  
|  
\text{Au(OH)}_2^{2-} \rightleftharpoons \text{Au}^{3+} + 2\text{H}_2\text{O} (bidentate)

The structure of the bidentate Au(III) complex was found to be considerably distorted (unpublished data) by Au L₃ XAS (EXAFS analysis) and ⁹⁵Au Mössbauer spectroscopy.⁴⁰ If the [AuCl₄⁻(OH)]⁻ ion is bonded to two hydroxyl groups on the surface of metal oxides (bidentate coordination), its oxidation-reduction potential could be changed by the distortion of the coordination structure (such as the O-Au-O bond angle and Au-O bond distance). If the metal-O-Au bond is monodentate, this distortion would be very slight. As a result, the reverse reaction of Eq. (2) would not occur, as shown in Eq. (3); that is, H₂O molecules act as a reducing agent and reduce the adsorbed AuCl₄⁻(OH)₂⁺ ions to Au(0) on metal oxides and hydroxides.

\[
\text{Au}^{3+} \text{(distorted on Ni(OH)₂)} + 3/2\text{H}_2\text{O} \rightarrow \text{Au}(0) + 3\text{/2O}_2 + 3\text{H}^+
\]  

As an example, a proposed model for the adsorption behavior of Au(III) complex ions on NiCO₃ and Ni(OH)₂ is shown in Fig. 12.

### 4-5 What is the driving force for the adsorption of Au(III) complex ions on metal oxides and hydroxides?

The adsorption of Au(III) complex ions to Ni(OH)₂ and NiCO₃ was measured between pH 9 and 10. In this pH range, the zeta potential of Ni(OH)₂ and NiCO₃ is positive, as shown in Fig. 12, and the Au(III) complex ion is present as Au(OH)₃⁺. The electrostatic interaction between NiO₃⁻ sites and Au(OH)₃⁻ may result in the changes in ΔG_{red} and ΔG_{sub}. After the initial electrostatic interaction, a Ni-O-Au(III) covalent bond is formed, resulting in a change in ΔG_{chem}. Because most of the Au(III) complex ions are bidentately coordinated, they are reduced to Au(0) because of the change in ΔG_{chem} (reduction of Au(III) to Au(0) by H₂O). On the other hand, the Au(III) complex ion is adsorbed on the surface of NiCO₃ by electrostatic interactions only, which is related to ΔG_{sub}.

### 5 Chemical States of Some Elements in Marine Ferromanganese Deposits (XPS and XAS)

The slopes and tops of undersea mountains in the deep ocean are often covered with iron and manganese oxides, the so-called “ferromanganese crust”. The marine ferromanganese crust, which is one of many types of chemical sediments in the ocean, is a sink of many elements including some rare metals. They are concentrated in the ferromanganese crust relative to seawater. The crust has been formed by the direct deposition of iron and manganese oxides from seawater. The growth rate of the crust is slow, estimated to be several millimeters every million years. Therefore, the concentration of rare metals in the deposits is considered to be caused by their adsorption on the crust from the seawater because of the long contact time.

The ferromanganese crust is regarded as a mixture of hydrous iron(III) oxides, such as goethite, and manganese dioxides, such as δ-MnO₂. Under ocean conditions, the surface charges of the iron and manganese oxides are positive and negative, respectively. The isoelectric points of iron and manganese oxides are pH 8 – 9 and pH 4, respectively. Therefore, anions can be adsorbed by the iron oxides, and cations can be adsorbed by the manganese oxides, as reported by Kochinsky and Halbach.⁴¹ Their model was proposed based on the results of the sequential leaching of marine ferromanganese precipitates. However, the sequential leaching method often yields doubtful results because of the differences in dissolution rates of the various (Mn and Fe) crystal phases, as well as the various bonding modes of the target elements.⁴² For example, which is the preferred phase for each element? This is an important problem in geochemistry. We introduce here adsorption experiments of some important rare metals concentrated in marine ferromanganese crusts and discuss the driving forces for the adsorption and concentration reactions based chemical state analysis. The order of concentrations of rare metals in the deposits is slow, estimated to be several millimeters every million years. Therefore, the concentrations of rare metals in the deposits is considered to be caused by their adsorption on the crust from the seawater because of the long contact time.

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### 5-1 Chemical states of cations

In 2015, a textbook about the earth science of marine
ferromanganese deposits was published. In this book, Takahashi describes in detail the application of XAS to characterize trace elements, including rare metals, in marine ferromanganese deposits. Here, the chemical states of Co, Ti, Ce, and Pb in marine ferromanganese crust are discussed because of the geochemical interest in these species. The adsorption behavior of Co, Ce, Ti and Pb are described in Supporting Information 5.1 in detail.

5-2 Chemical states of anions

As discussed above, according to the model of Kochinsky and Halbach, cations are adsorbed by manganese dioxide in marine ferromanganese crust. On the other hand, Pt, Au, and Pd, which are present as anions in seawater, as discussed later, are also enriched in the ferromanganese crust.

5-2-1 Platinum (Pt 4f/XPS, Pt L3-edge XAS)

The marine ferromanganese crust is a potential Pt resource. According to a recent study, the Pt content in marine ferromanganese crusts ranges from 44 to 3207 ppb and the average value is 575 ppb. The dissolved Pt ferromanganese crusts ranges from 44 to 3207 ppb and the average value is 575 ppb. According to a recent study, the Pt content in marine ferromanganese crusts ranges from 44 to 3207 ppb and the average value is 575 ppb.

Thus, the oxidative adsorption mechanism of \([\text{Pt(OH)}_n\text{Cl}_{4-n}]^{2–}\) can be represented by Eq. (4).

\[
\text{MnO}_2(s) + [\text{Pt(OH)}_n\text{Cl}_{4-n}]^{2–} + (4 + n)\text{H}^+ \rightarrow \text{Mn}^{n+} + \text{Pt}^{4+}(s) + (4 + n)\text{Cl}^- + (2 + n)\text{H}_2\text{O} \tag{4}
\]

Here, \(\text{Pt}^{4+}(s)\) means the Pt\(^{4+}\) incorporated in MnO\(_2\) structure. The dissolved Pt\(^{4+}\) in seawater has a four-coordinate square planar structure, but Pt\(^{4+}\) has a six-coordinate octahedral structure. Through the transformation of the coordination structure of Pt(II), Pt\(^{4+}\) may substitute Mn\(^{4+}\) in MnO\(_2(s)\), as shown in Fig. 13. The dissolution of Pt\(^{4+}\) in seawater has a four-coordinate square planar structure, but Pt\(^{4+}\) has a six-coordinate octahedral structure. Through the transformation of the coordination structure of Pt(II), Pt\(^{4+}\) may substitute Mn\(^{4+}\) in MnO\(_2(s)\), as shown in Fig. 13.

In 2020, Koschinsky et al. reported the Pt L\(_2\) and L\(_3\)-edge XANES spectra for Pt adsorbed on FeOOH and \(\delta\)-MnO\(_2\). The Pt L\(_2\) and L\(_3\)-edge XANES spectra showed that the Pt concentration increases with depth, from 100 pg/L in the uppermost layer to 1000 pg/L in the bottom layer. The Pt L\(_2\) and L\(_3\)-edge XANES spectra showed that the Pt concentration increases with depth, from 100 pg/L in the uppermost layer to 1000 pg/L in the bottom layer.

5-2-2 Gold (Au L\(_3\)-edge XAS)

The Au content in marine ferromanganese crusts ranges from 2.5 to 397 ppb, and Au is enriched in the marine ferromanganese crust by a factor of 10\(^3\) to 10\(^5\) compared to its average concentration in seawater, which is 29 ± 9 pg/L. Au may be present as Au(I) complex ions such as \([\text{AuCl}_2]^–\) or AuOH(H\(_2\)O) in seawater. However, no chemical state analysis of Au in natural marine ferromanganese crusts has been reported to date. Yonezu et al. studied the adsorption behavior of \([\text{Au(S}_2\text{O}_3)_2\text{Cl}_4]^2–\) complex ions, which are stable as Au(I) complex under oxic condition. On alumina using Au L\(_3\)-edge XANES measurements and found that the adsorbed Au(I) complexes were converted to Au(0). The results suggest that the adsorbed Au(I) complexes disproportionate to Au(0) and Au(III), as shown in Eq. (5), and the Au(III) may be reduced spontaneously to Au(0), as discussed above.

\[
3[\text{Au(S}_2\text{O}_3)_2\text{Cl}_4]^2– + (4 – n)\text{Cl}^- + n\text{OH}^- \rightarrow 2\text{Au}(0) + [\text{AuCl}_{4-n}\text{OH}_n]^– + 6\text{S}_2\text{O}_3^2– \tag{5}
\]

Au(I) complex ions are strongly adsorbed to oxides of Fe(III) and Mn(IV). The adsorbed Au(I) complex ions probably disproportionate to Au(0) and Au(III) and, finally, the Au(III) complex ions are reduced to Au(0), as described above.

There is another reduction mechanism for the \([\text{AuCl}_{4-n}\text{OH}_n]^–\) ion in Eq. (5) in addition to spontaneous reduction. The Au(III) complexes can be coprecipitated with manganese hydroxide (Mn(OH)\(_2\)) followed by their stoichiometric reduction to Au(0). As described above, when Co\(^{2+}\) and Ti\(^{4+}\) are adsorbed on \(\delta\)-MnO\(_2\), their oxidation occurs to release Mn\(^{4+}\), which is hydrolyzed to form Mn(OH)\(_2\). Then, Mn\(^{4+}\) in Mn(OH)\(_2\) is oxidized to Mn\(^{4+}\), which forms a new layer of MnO\(_2\), and this occurs in parallel with the reduction of the Au(III) complex ions.

Pt and Au exist in seawater as complex ions of Pt(II) having a square planar structure and Au(I) having a linear structure; however, the Pt(II) complex ion is oxidized to Pt(IV) after adsorption on \(\delta\)-MnO\(_2\), whereas the Au(I) complex ion is spontaneously reduced to Au(0), as described above. Thus, it could be speculated that if the host mineral of Au is manganese oxide in marine ferromanganese crust, Au may be present as Au(0).

5-2-3 Palladium (Pd K-edge XAS)

Pd is a platinum group element. The Pd concentration in seawater ranges from 20 to 60 pg/L, and the Pd/Pt atomic ratio is about 4.5. The Pd concentration in marine ferromanganese crusts ranges from 1 to 37 ppb, and the average value is 7.3 ppb (\(N = 124\)), which is lower than that of Pt. In contrast to that in seawater, the Pt/Pd atomic ratio of ferromanganese crust is about 87.5. The difference in the Pt/Pd ratios between seawater and Pt adsorbed above pH 6 by the formation of Mn–OH groups in \(\delta\)-MnO\(_2\) and Pt–OH groups in the \([\text{Pt(OH)}_n\text{Cl}_{4-n}]^{2–}\) complex ion.

EXAFS analysis showed that the coordination structure of Pt adsorbed on \(\delta\)-MnO\(_2\) is almost the same as that of the \([\text{Pt(OH)}_6]^2–\) complex ion. EXAFS analysis showed that the coordination structure of Pt adsorbed on \(\delta\)-MnO\(_2\) is almost the same as that of the \([\text{Pt(OH)}_6]^2–\) complex ion. EXAFS analysis showed that the coordination structure of Pt adsorbed on \(\delta\)-MnO\(_2\) is almost the same as that of the \([\text{Pt(OH)}_6]^2–\) complex ion. EXAFS analysis showed that the coordination structure of Pt adsorbed on \(\delta\)-MnO\(_2\) is almost the same as that of the \([\text{Pt(OH)}_6]^2–\) complex ion.
and marine ferromanganese crust is called the “Pt-Pd anomaly”. Tanaka et al. examined the adsorption behavior of Pd complex ions on δ-MnO₂ and the chemical state of the adsorbed Pd using Pd K-edge XAS measurements. Pd was found to be present as [PdCl₃OH]²⁻ complex ions in seawater, and [PCl₃OH]²⁻ complex ions were specifically adsorbed at pH values above 5 by the formation of a Mn-O-Pd bond through condensation between Mn-OH group on δ-MnO₂ and Pd-OH group in the [PdCl₃(OH)]²⁻ complex ion. Through the adsorption reaction, a Cl ligand was exchanged with an O ligand (OH group). The curve fitting of the EXAFS spectra revealed the formation of two different inner-sphere complexes: bidentate-mononuclear and bidentate-binuclear complexes. However, the valence state of Pd(II) was not changed.

5-3 What is the driving force for the enrichment of cations and anions in marine ferromanganese crusts?

Cations are first adsorbed on manganese dioxides by electrostatic interactions because of the negative surface charge on δ-MnO₂ under ocean condition, and this affects ΔG_red and ΔG_chem. Secondly, inner-sphere complexes are formed through the formation of Mn-O-cation bonds causing changes in ΔG_chem. In the cases of Co³⁺ and Ti⁴⁺, oxidation occurs from Co²⁺ to Co³⁺ and from Ti⁴⁺ to Ti⁵⁺ through the Mn-O-Co³⁺ and Mn-O-Ti⁴⁺ bonds by coupling to the reduction of Mn⁴⁺ to Mn³⁺. After these redox reactions, Co³⁺ and Ti⁵⁺ may be incorporated in the manganese oxide structure. These redox reactions and incorporation are considered to correspond to changes in ΔG_chem. In the case of Pb, although redox reactions do not occur, the formation of DES and TCS may correspond to changes in ΔG_chem, as shown in Fig. S1.

In contrast to cations, anions may adsorb on δ-MnO₂ by overcoming the electrostatic repulsion between the negative charge of the anion and negative surface charge on δ-MnO₂. In this system, ΔG_red may be positive and ΔG_chem,1 and ΔG_chem,2 may be large and negative. In the case of Pd, the oxidation of Pt⁴⁺ to Pt⁵⁺ and the substitution of Mn⁴⁺ by Pt⁴⁺ in manganese oxide occur. In the case of Au, Au⁺ disproportionate to Au³⁺ and Au⁰, and the Au⁰ is reduced spontaneously to Au⁰. For Pd, ligand exchange from Cl to OH occurs. These reactions correspond to changes in ΔG_chem,2.

6 Conclusions

The adsorption of ions from aqueous solution involves specific chemical reactions at the interface of the solid and solution and is an interesting chemical phenomenon. One of our research aims is to elucidate these adsorption mechanisms and the corresponding driving forces. To achieve this, it is essential to determine the chemical states of the adsorbed species. XAS is one of the most useful methods for chemical speciation. By determining the chemical states and structures, both the adsorption mechanism and driving forces of the adsorption reaction can be resolved.

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8 Supporting Information

XAS measurement condition (Table S1) and chemical state analysis for cations in marine manganese crust in S1. This material is available free of charge on the Web at http://www.jasac.or.jp/analsci/.

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