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RAPID COMMUNICATION



Distribution of studtite and metastudtite generated on the surface of U_3O_8 : application of Raman imaging technique to uranium compound

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ABSTRACT

Studtite and metastudtite are uranyl peroxides formed on nuclear fuel in water through the reaction with H_2O_2 produced by the radiolysis of water. However, it is unclear how the two types of uranyl peroxides are generated and distributed on the surface of nuclear fuel. Here, we used Raman imaging technique to exemplify distribution data of the two uranyl peroxides formed on the surface of a U_3O_8 pellet through immersion in a H_2O_2 aqueous solution. As a result, we observed that studtite and metastudtite are heterogeneously distributed on the U_3O_8 surface. No clear correlation between the distributions of studtite and metastudtite was observed, suggesting that the two uranyl peroxides are independently generated on the surface of U_3O_8 . We anticipate that this Raman imaging technique could reveal how these uranyl peroxides are generated and distributed on the surface of the nuclear fuel debris in the Fukushima-Daiichi nuclear power plants.

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Raman imaging; uranyl peroxide; surface; distribution; immersion; hydrogen peroxide; triuranium octoxide

1. Introduction

Studtite, $[(UO_2)(O_2)(H_2O)_2](H_2O)_2$, and metastudtite, $(UO_2)(O_2)(H_2O)_2$, which is the dehydrated form of studtite, are solid phases of uranyl peroxides and have been found in spent nuclear fuel exposed to water [1] and UO_2 exposed to water under a radiation field [2]. The uranyl peroxides are formed through the reaction of UO_2 with H_2O_2 generated by the radiolysis of water [3,4], although the mechanism that determine which uranyl peroxide phase is generated remains unclear. Because the nuclear fuel debris in the Fukushima-Daiichi nuclear power plants are in contact with coolant water under a high radiation field, the uranyl peroxides are likely ones of the dominant alteration phases of the fuel debris that could determine the properties of the fuel debris.

Because of the significance of the uranyl peroxides as alteration phases on nuclear fuel [5], there have been many studies to characterize uranyl peroxides properties such as: thermal stability [6–8], stability under irradiation [9], electrochemical reactivity [10], solubility [11], and crystal structures [12,13]. However, previous studies have not paid much attention to how the two uranyl peroxides, studtite and metastudtite, are generated and distributed on the surface of nuclear fuels. Clarens et al. reported the formation of studtite from the reaction of UO_2 surface with H_2O_2 [4], whereas Sattonnay et al. found metastudtite as the dominant alteration phase on UO_2 irradiated by He ion beam in

water [2]. On the other hand, Hanson et al. observed the formation of studtite on spent nuclear fuel and at the same time metastudtite as suspended particles in the samples of their immersion experiments [1]. Therefore, to reveal the generation and distribution mechanism of the two uranyl peroxides on nuclear fuels, it is necessary to distinguish the two uranyl peroxides and observe their distributions on nuclear fuels.

Raman spectroscopy is a useful method used to identify the two uranyl peroxides [7,14]. However, Raman imaging technique, which can show the distributions of certain chemical species in a microscopic area [15,16], has not yet been applied to the study of the uranyl peroxides. In the present study, we used the Raman imaging technique and successfully demonstrated the distribution data of the two types of uranyl peroxides formed in microscopic areas on the surface of a U_3O_8 pellet. U_3O_8 was selected as the starting material because it has been unclear whether the uranyl peroxides were generated from U_3O_8 , although U_3O_8 is a key component generated from UO_2 in oxidized conditions [17]. From the distribution data, we discussed some aspects of the generation and distribution of the two uranyl peroxides on U_3O_8 . We anticipate that this Raman imaging technique will be applicable even to highly inhomogeneous nuclear materials, such as the nuclear fuel debris in the Fukushima-Daiichi nuclear power plants.

2. Experimental

2.1. Preparation of U_3O_8 sample

U_3O_8 sample stored at Tohoku university was heated at 800°C under air for 4 hours and confirmed as $\alpha\text{-U}_3\text{O}_8$ structure by XRD (Figure S1). The U_3O_8 powder was loaded into a tungsten carbide die and molded into a pellet form of 7 mm diameter. The powder weight was 0.23 g and the molding pressure was 30 MPa, and the thickness of the molded U_3O_8 pellet was ~ 1 mm. The molded U_3O_8 pellet was fixed on an acrylic support with epoxy resin. The U_3O_8 pellet was immersed in a H_2O_2 aqueous solution (1.5×10^{-4} mol dm^{-3}) for 30 days at room temperature. The H_2O_2 concentration is the equilibrium concentration generated by water radiolysis (c.a. 4 kGy) under aerated condition. Raman measurements were performed on the surface of the U_3O_8 pellet before and after the immersion. The sample pellet immersed in the H_2O_2 solution was dried for ~ 1 day in a vacuum desiccator at room temperature before Raman measurements were conducted.

2.2. Synthesis of studtite and metastudtite

In order to analyze Raman spectra measured on the surface of the U_3O_8 pellet with Raman spectra of studtite and metastudtite, we synthesized studtite and metastudtite and obtained their Raman spectra. Studtite was prepared from UO_2 powder by reaction with H_2O_2 [6]. A suspension of the UO_2 powder (c.a. 430 mg) in 1×10^{-3} mol dm^{-3} aqueous HCl solution (10 cm^3) was prepared in a plastic tube and then 30 wt% H_2O_2 solution (0.73 cm^3) was added to the suspension. The amount of the added H_2O_2 corresponds to the 2 times excess of the stoichiometric amount for the studtite formation. The suspension was then slowly shaken with a tube rotator at 20 rpm. After 1 to 3 days of reaction, the supernatant containing fine yellow powder was transferred to a glass flask. To precipitate, again 10 cm^3 of the HCl solution and 0.73 cm^3 of the H_2O_2 solution were added. This procedure was repeated 5 times to complete the reaction. Then, the fine yellow powder was obtained from the suspension and washed with 10 cm^3 of pure water 3 times by centrifuging and decantation. The washed powder was dried in a vacuum desiccator. All the synthesis procedures were performed at room temperature. Metastudtite was obtained by heating the studtite at 90°C for 10 minutes. The synthesis of studtite and metastudtite was confirmed by XRD (Figure S2 and Figure S3) and TG-DTA (Figure S4) analysis.

2.3. Raman imaging

A confocal Raman microscopy setup (NRS-4500, JASCO) was used to obtain Raman imaging data on the surface of the U_3O_8 pellet. A 532 nm laser of 0.5 mW was introduced on a sample stage through a 100x objective

lens. The spatial resolution is $XY < 1 \mu\text{m}$ and $Z < 1.5 \mu\text{m}$. By moving motor stages with $1 \mu\text{m}$ step in a $10 \mu\text{m} \times 10 \mu\text{m}$ square area for a two-dimensional scan, 121 Raman spectra were collected for the square area. The XY scan was conducted three times in different areas optionally selected, and $363 (= 121 \text{ spectra} \times 3 \text{ areas})$ Raman spectra were obtained. The distribution data of studtite and metastudtite generated on the surface of the U_3O_8 pellet were obtained using their strong bands in the $780\text{--}900 \text{ cm}^{-1}$ region. For the synthesized studtite and metastudtite, their Raman spectra were measured from a single point on the surface of their particles using a 20x objective lens.

3. Results and discussion

Figure 1(a, b) shows Raman spectra of the initial U_3O_8 pellet and the U_3O_8 pellet immersed in the H_2O_2 aqueous solution, respectively. Each spectrum is an averaged spectrum of 363 data measured at 363 positions on the surface of the U_3O_8 pellet before and after the immersion. The Raman spectrum of Figure 1(a) shows many noticeable bands due to U_3O_8 in the $50\text{--}800 \text{ cm}^{-1}$ region. After the immersion (Figure 1(b)), the bands due to U_3O_8 are still observed, but two intense bands appear at $\sim 820 \text{ cm}^{-1}$ and $\sim 865 \text{ cm}^{-1}$, showing the generation of chemical species on the surface of U_3O_8 by the immersion. Figure 1(c, d) shows Raman spectra of the synthesized studtite and metastudtite, and both uranyl peroxides show the two intense bands at $\sim 820 \text{ cm}^{-1}$ and $\sim 865 \text{ cm}^{-1}$, with small bands in the region lower than 400 cm^{-1} . The positions and the relative intensity of the $\sim 820 \text{ cm}^{-1}$ and $\sim 865 \text{ cm}^{-1}$ bands of studtite and metastudtite are very similar to those observed in the spectrum of Figure 2(b). Therefore, the two intense bands observed at $\sim 820 \text{ cm}^{-1}$ and $\sim 865 \text{ cm}^{-1}$ in the immersed U_3O_8 pellet (Figure 2(b)) are attributed to the uranyl peroxides.

Figure 2 shows an enlarged view of the four Raman spectra of Figure 1 in the region of $780\text{--}900 \text{ cm}^{-1}$. From the enlarged figure, it is evident that the bands at $\sim 820 \text{ cm}^{-1}$ and $\sim 865 \text{ cm}^{-1}$ observed for the immersed U_3O_8 (Figure 2(b)) are broader than those observed for studtite and metastudtite (Figure 2(c, d)). Furthermore, the band positions of studtite and metastudtite (Figure 2(c, d)) are slightly different between each other, and as indicated by the dashed lines, the broader bands in Figure 2(b) consist of the bands of studtite and metastudtite. Therefore, both uranyl peroxides, i.e. studtite and metastudtite, are generated on the surface of U_3O_8 through the immersion in the H_2O_2 aqueous solution.

Although Figure 2(b) clearly indicates that both studtite and metastudtite are formed on the surface of the U_3O_8 pellet after the immersion, any information about the distributions of the studtite and metastudtite generated on the U_3O_8 surface cannot be obtained, because Figure 2(b) is an averaged spectrum of 363 Raman spectra observed on the U_3O_8 surface. To illustrate the

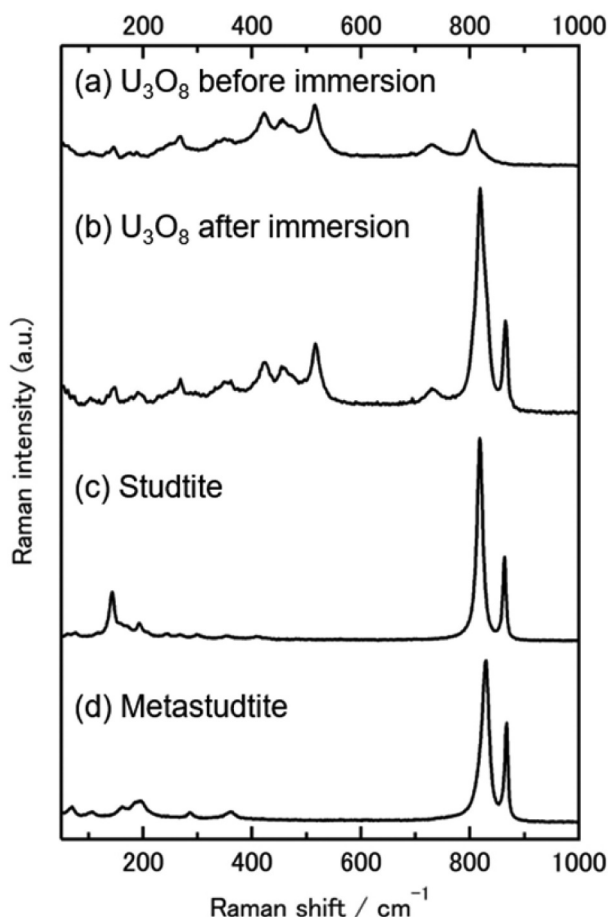


Figure 1. Raman spectra of (a) the initial U_3O_8 pellet and (b) the U_3O_8 pellet immersed in a H_2O_2 aqueous solution ($1.5 \times 10^{-4} \text{ mol dm}^{-3}$) for 30 days, (c) studtite, and (d) metastudtite. The relative intensity of each spectrum is roughly correct, so that the intensities of the four spectra are comparable with each other.

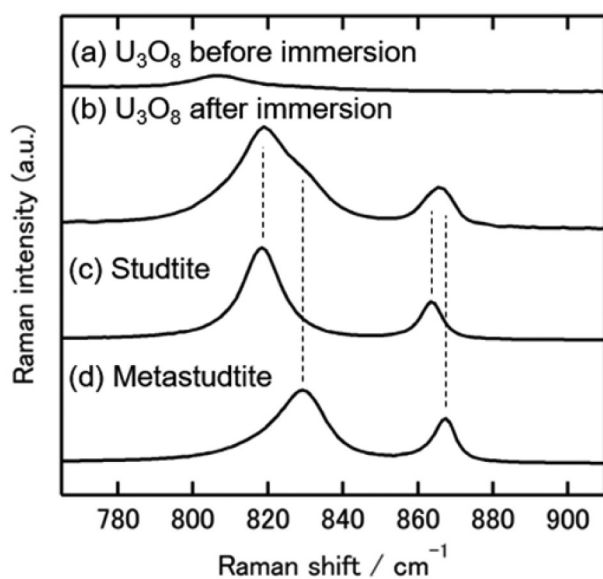


Figure 2. Raman spectra of (a) the initial U_3O_8 pellet and (b) the U_3O_8 pellet immersed in a H_2O_2 aqueous solution ($1.5 \times 10^{-4} \text{ mol dm}^{-3}$) for 30 days, (c) studtite, and (d) metastudtite in the $780\text{--}900 \text{ cm}^{-1}$ region. The relative intensity of each spectrum is roughly correct, so that the intensities of the four spectra are comparable with each other.

distributions of studtite and metastudtite generated on the U_3O_8 surface, we approximate each Raman spectrum of the immersed U_3O_8 as the linear combination of the two Raman spectra of studtite and metastudtite as follows:

$$\text{Immersed } \text{U}_3\text{O}_8 \text{ spectrum} = a \times \text{Studtite spectrum} + b \times \text{Metastudtite spectrum}, \quad (1)$$

where a and b are coefficients corresponding to the Raman intensity of studtite and metastudtite generated on the surface of U_3O_8 , respectively. The two coefficients were obtained by fitting with the spectra of the synthesized studtite and metastudtite in Figure 2(c, d) in the least-square method in the $780\text{--}900 \text{ cm}^{-1}$ region. Figure 3 shows two-dimensional plots of the two coefficients, a and b , for three $10 \mu\text{m} \times 10 \mu\text{m}$ square regions (Region 1, Region 2, and Region 3) on the surface of the immersed U_3O_8 pellet. The magnitude of the coefficients was expressed by the color scheme shown in the right side of the figure. The coefficients, a and b , were normalized by using the largest coefficient among all coefficients (N_{max}), and the normalized values, in this case, are a/N_{max} and b/N_{max} . Since the Raman intensity is proportional to the quantity of studtite and metastudtite on a measurement point, Figure 3 represents distributions of the quantity of studtite and metastudtite generated on the U_3O_8 surface. The optical images of the three regions are shown in the bottom of Figure 3 and show smooth surfaces of the pellet in the microregions. The measurements for the three regions were sequentially performed under the same experimental condition.

The relative relationship between the a and b values indicates the relative quantity of studtite and metastudtite generated on the U_3O_8 surface. Since the two spectra of Figure 2(c, d) retain the relative intensity of the synthesized studtite and metastudtite for the fitting, when $a = b$, the relative quantity of studtite and metastudtite generated on U_3O_8 surface ($q_{\text{studtite}, \text{U}_3\text{O}_8} / q_{\text{metastudtite}, \text{U}_3\text{O}_8}$) is the same as the relative quantity of the studtite and metastudtite per the same area size of the standard samples ($q_{\text{studtite}, \text{synthesized}} / q_{\text{metastudtite}, \text{synthesized}}$). Moreover, when $a > b$, in comparison with the ratio of studtite and metastudtite of the standard samples, the proportion of studtite is higher than that of metastudtite on U_3O_8 , and conversely when $a < b$, in comparison with the ratio of studtite and metastudtite of the standard samples, the proportion of metastudtite is higher than that of studtite on U_3O_8 .

Figure 4 shows examples of the spectral fittings at the three positions in Region 1: (a) $(X, Y) = (1, 10)$, (b) $(X, Y) = (9, 5)$, (c) $(X, Y) = (4, 7)$. In Figure 4, the black solid curves are Raman spectra measured at each position, the red solid curves are fitting spectra, and the blue and green dashed curves are the Raman spectral components of studtite and metastudtite. Each Raman spectrum is well reproduced, indicating that the distributions of studtite

and metastudtite generated on the U_3O_8 surface are accurately obtained by this analysis.

The distributions of studtite and metastudtite in Figure 3 show that the U_3O_8 surface is covered with the two uranyl peroxides, i.e. studtite and metastudtite, and they are heterogeneously distributed over the U_3O_8 surface. The heterogeneous distributions include a minimum unit area smaller than $1\ \mu\text{m} \times 1\ \mu\text{m}$ because there are some pixels that have very different intensities from neighboring pixels. The heterogeneous distribution patterns of the two uranyl peroxides cannot be observed from the optical images at the bottom of Figure 3, demonstrating high performance of Raman imaging technique for selective detection of studtite and metastudtite in such a microscopic area. Furthermore, it is apparent that the overall intensity of studtite is larger than that of metastudtite, indicating that studtite is preferentially distributed compared to metastudtite. The ratio of the averaged coefficients, $\langle a \rangle / \langle b \rangle = 0.34 / 0.23 = \sim 1.5$, indicates that the yield of studtite is ~ 1.5 times larger than that of metastudtite in the present experimental condition. The thickness of the layer of the uranyl peroxides formed on the U_3O_8 surface is estimated to be thinner than $\sim 3\ \mu\text{m}$

from depth profiles of the uranyl peroxides (Figure S5), and because of the thin layer of the uranyl peroxides, the U_3O_8 signals below the layer of the uranyl peroxides are clearly observed in Figure 1(b).

Finally, in order to investigate correlation between the distributions of studtite and metastudtite on the U_3O_8 surface, the two coefficients (a and b) obtained in each measurement position are plotted in Figure 5. No clear correlation between the two coefficients was observed. Additionally, the correlation coefficient, r_{ab} , was calculated with the following equation,

$$r_{ab} = \frac{\frac{1}{n} \sum_{i=1}^n (a_i - \langle a \rangle)(b_i - \langle b \rangle)}{\sqrt{\frac{1}{n} \sum_{i=1}^n (a_i - \langle a \rangle)^2} \times \sqrt{\frac{1}{n} \sum_{i=1}^n (b_i - \langle b \rangle)^2}} \quad (2)$$

where n is the data number ($= 363$), a and b are the coefficients defined in Equation (1), and brackets, $\langle \rangle$, stand for average. A near-zero value (-0.1) was obtained for the correlation coefficient, supporting the observation that there is no apparent correlation between the two coefficients. No clear correlation between the two coefficients indicates that the two uranyl peroxides, studtite

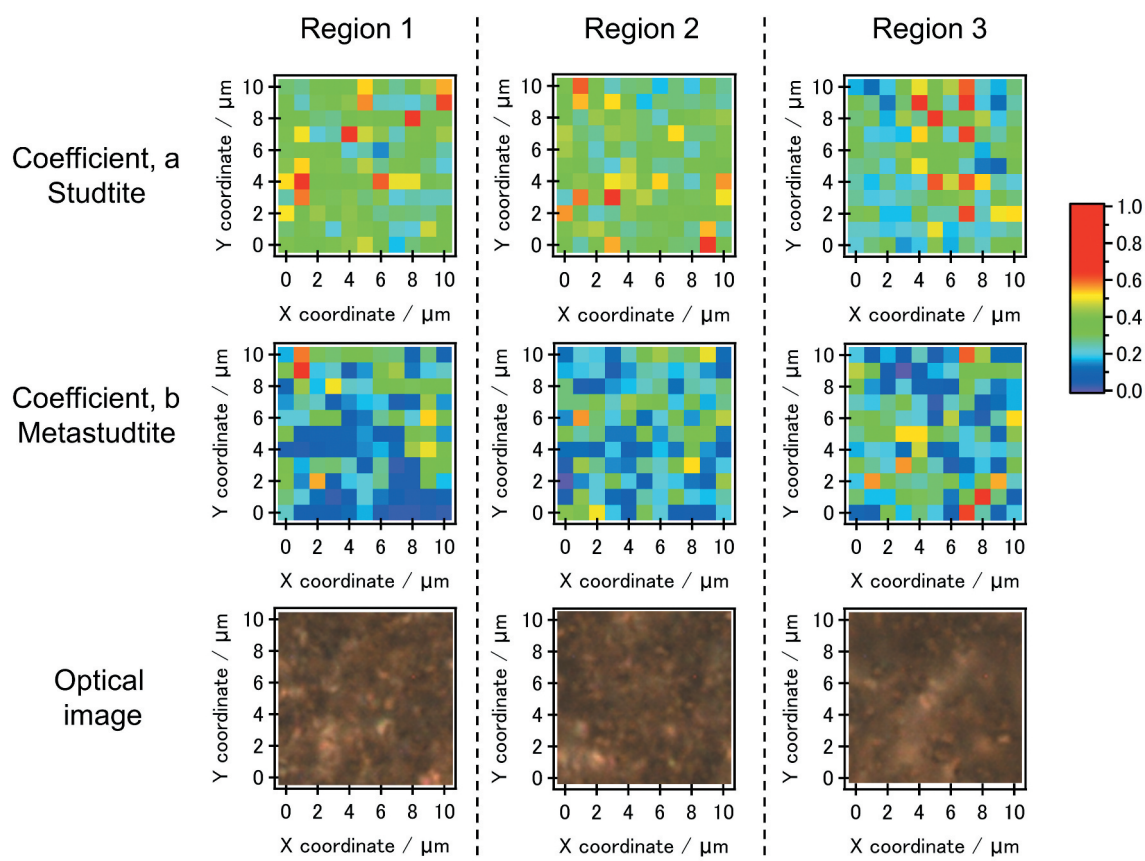


Figure 3. Two-dimensional plots of the coefficients, a and b , in Equation (1) corresponding to the relative quantity of studtite and metastudtite generated on the surface of U_3O_8 immersed in H_2O_2 solution. The plots are conducted for three $10\ \mu\text{m} \times 10\ \mu\text{m}$ square regions (Region1, Region 2, and Region 3) optionally selected on the U_3O_8 surface. The magnitude of the coefficients is expressed by the color scheme on the right side of the figure, and the values are normalized so that the coefficients range from 0 to 1. Optical images of the three regions are shown in the bottom.

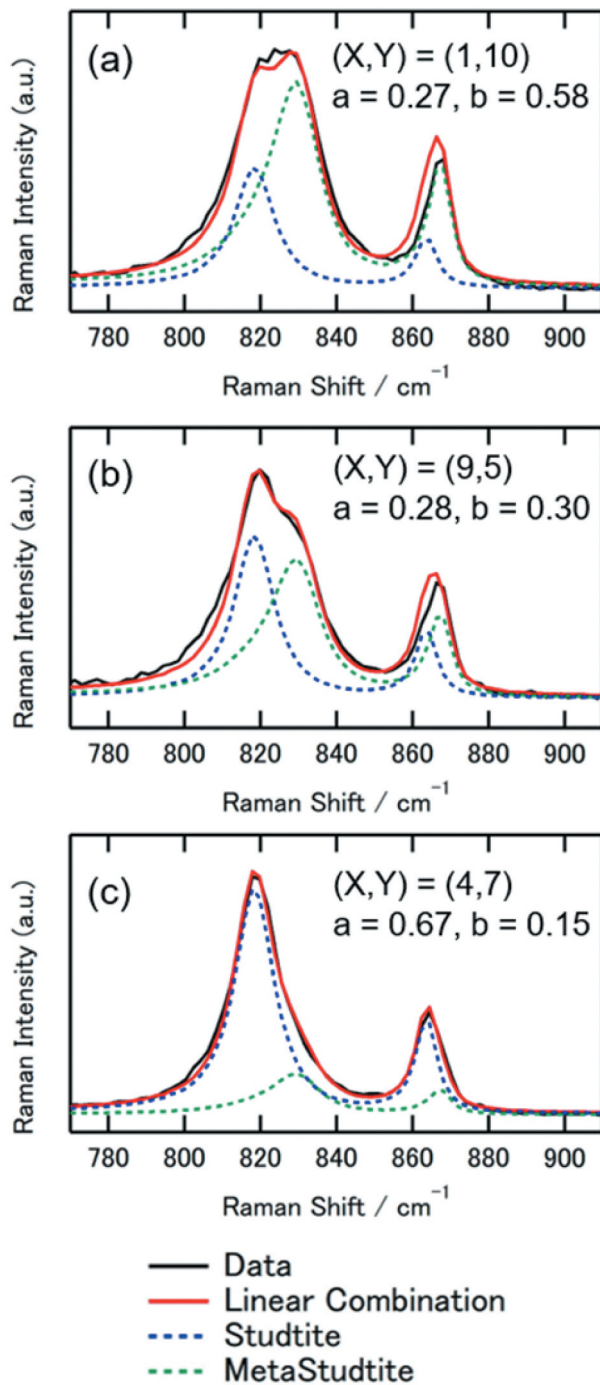


Figure 4. Examples of the spectral fittings at the three positions in Region 1 of Figure 3.

and metastudtite, are independently generated on the U_3O_8 surface. It should be noted that the metastudtite observed on the U_3O_8 surface is *not* generated through the thermal decomposition of studtite on the surface because if the observed metastudtite was generated from studtite, the quantity of metastudtite increases as that of studtite decreases, and this tendency is not observed in Figure 5. Furthermore, we checked whether metastudtite is generated on the U_3O_8 surface during the drying process of the immersed U_3O_8 , where the immersed U_3O_8 was dried in a vacuum desiccator for

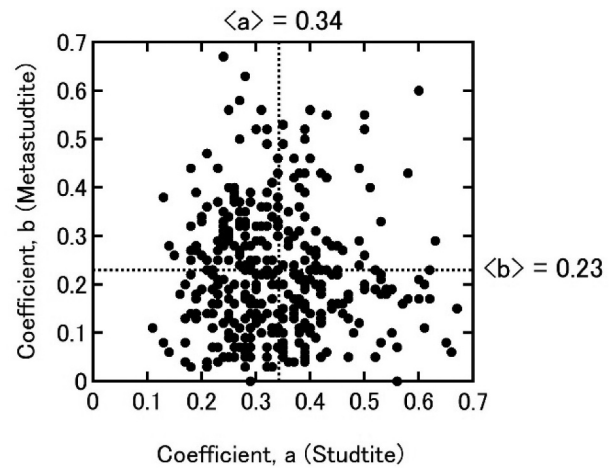


Figure 5. Scatter plot of the coefficients, a and b , defined in Equation (1).

3 months at room temperature. However, no increase in the amount of metastudtite was observed due to the drying process, supporting the conclusion that studtite and metastudtite are individually generated on the surface of U_3O_8 .

4. Conclusion

The distributions of studtite and metastudtite generated on the surface of U_3O_8 through the immersion of U_3O_8 in H_2O_2 aqueous solution were successfully observed using Raman imaging technique. It was revealed that the two types of uranyl peroxides cover the U_3O_8 surface and were heterogeneously distributed over the surface, while studtite was generated at ~ 1.5 times higher yield compared to metastudtite. Any correlations between the distributions of studtite and metastudtite were not observed, suggesting that the two uranyl peroxides are independently generated on the surface of U_3O_8 . The present study demonstrates that Raman imaging technique could potentially be used to obtain information about the formation and distribution mechanism of the alteration phases on the nuclear fuel debris in the Fukushima-Daiichi nuclear power plants.

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Disclosure statement

The authors declare no conflicts of interest associated with this manuscript.

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