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## **OBSERVATION OF SURFACE DISTRIBUTION OF PRODUCTS BY X-RAY FLUORESCENCE SPECTROMETRY DURING D<sub>2</sub> GAS PERMEATION THROUGH PD COMPLEXES**

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*In-situ* measurement of transmutation of Cs into Pr was performed, and the surface distribution of Pr was investigated using XRF (X-Ray Fluorescence spectrometry) at SPring-8, a large synchrotron x-ray facility. The *in-situ* measurement indicated that Pr emerged and Cs decreased at some points after D<sub>2</sub> gas permeation, though any Pr cannot be observed before D<sub>2</sub> gas permeation at all the points on the Pd complex surface. Using small size X-ray beam in 100- and 500-micrometer squares, we obtained 2 dimensional XRF spectra for three permeated samples, from which we detected Pr. Pr was detected again by the two small x-ray beams as expected. The amount of Pr varied greatly at different locations of the Pd surface, however, a clear correlation between surface structures and distribution of Pr has not seen up to now. Experimental results suggest that nuclear transmutations do not occur uniformly but some uncertain factors, presumably condensed matter effects in the present Pd/D/CaO system, have a large effect on the rate or the process of the reactions.

### **1 Introduction**

Low energy nuclear transmutations in condensed matter have been observed in Pd complexes which are composed of Pd and CaO thin film and Pd substrate, induced by D<sub>2</sub> gas permeation through Pd multilayer complexes. We already reported transmutation reactions of Cs into Pr, Ba into Sm and Sr into Mo, respectively [1-5].

Fig. 1 shows schematic of our method. Our experimental method can be characterized by the permeation of D<sub>2</sub> gas through the Pd complex and the addition of an element that is specifically targeted to be transmuted. Permeation of deuterium is attained by exposing one side of the Pd complex to D<sub>2</sub> gas while maintaining the other side under vacuum conditions. On the D<sub>2</sub> gas side of the Pd complex, dissociative absorption causes the D<sub>2</sub> molecules to separate into D atoms, which diffuse through the Pd metal toward the vacuum side, where they emerge from the Pd metal, combine and are released as D<sub>2</sub> gas.

The second feature is the addition of an element targeted to be transmuted. Our sample is a Pd complex composed of bulk Pd on the bottom, alternating CaO and Pd layers, and a Pd thin film on top. After fabricating a Pd complex, Cs, Ba, Sr or the other element is deposited on the surface of the top thin Pd layer. We can observe transmutation of the added Cs or Ba. In other words, with this composition, we can provide a deuterium flux through the Pd complex on which a target element is placed as a target to be transmuted. We perform elemental analyses of the given elements after D<sub>2</sub> gas permeation by exhausting the D<sub>2</sub> chamber.

In this paper, *in-situ* measurement of transmutation of Cs into Pr and surface distribution are described. X-ray Fluorescence Spectrometry at SPring-8 (<http://www.spring8.or.jp/e/>) was used for this study. Transmutation reactions of Cs into Pr were confirmed by the *in-situ* measurement. Surface Pr distribution data were obtained and they showed that the amount of Pr changed greatly depending on the locations of the Pd surface.

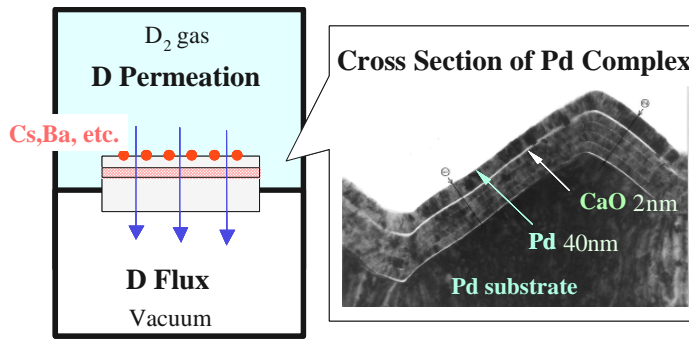


Figure 1. Schematic of our experimental approach.

## 2 Experimental

Fabrication of Pd complex is basically the same as before [1]-[5]. A Pd was washed with acetone and annealed in vacuum ( $<10^7$  torr) at  $900^\circ\text{C}$  for 10 h. It was then cooled to room temperature in furnace and washed with aqua regia to remove impurities on the surface of the Pd plate. The surface of the plate was covered by layers of CaO and Pd, which were obtained by five times alternately sputtering 20-Å-thick CaO and 200-Å-thick Pd layers. Then a 400-Å-thick Pd layer was sputtered on the surface of the CaO and Pd layers. These processes are performed by Ar ion beam sputtering method or magnetron sputtering method. After forming a Pd complex, Cs was deposited on the surface of the thin Pd layer. Cs was deposited by electrochemical method or ion implantation method.

Figure 2 shows the experimental setup for *in-situ* measurement. Synchrotron orbital radiation X-ray (5.97keV) is introduced into the permeation chamber through a Be window and attacks on the surface of Pd complex sample. X-ray intensity is about from  $10^{12}$  to  $10^{13}$  photons/s. Cs-L and Pr-L lines can be detected by a Silicon Drift Detector (SDD). The SDD is covered by a Cl filter for suppression of Pd-L x-ray. We made  $\text{D}_2$  gas permeated through a Pd complex with Cs for 10-14 days.  $\text{D}_2$  gas pressure is about 170kPa and the temperature was  $70^\circ\text{C}$ . XRF was performed during  $\text{D}_2$  permeation *in-situ* at the beginning and the end of experiments.

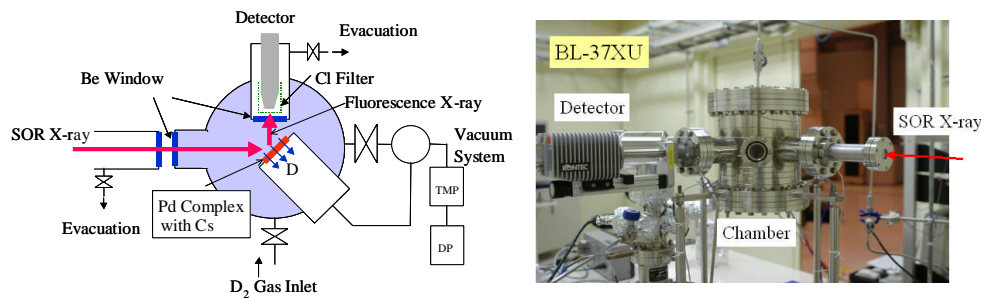


Figure 2. Experimental setup for *in-situ* measurement.

Surface distribution of Cs and Pr can be measured by the experimental setup shown in the Fig. 3. The synchrotron radiation x-ray is divided by slits and we get rectangular micro x-ray beam. In this study, we use 500-micron and 100-micron beams. The Pd complex sample is attached on a X-Y stage that can be moved by stepping motors. 2-dimensional XRF spectra can be obtained by this setup. Surface images can be taken by a microscope that is equipped for this 2-dimensional XRF spectrum analysis. We can obtain the information about correlation between distribution of elements and surface images.

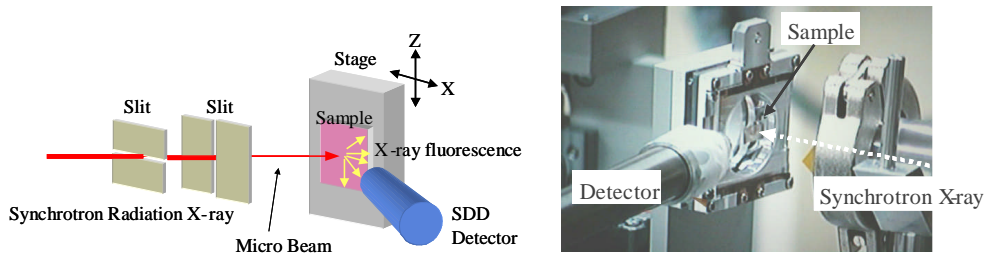


Figure 3. Experimental setup for the measurement of surface distribution of Cs and Pr.

### 3 Results and Discussion

First of all, we describe the results of *in-situ* measurement; sample name is SP-24. Initial (before D<sub>2</sub> gas permeation) and final (after D<sub>2</sub> gas permeation) XRF spectra are drawn in Fig. 4. Cs was deposited by the ion beam implantation method (voltage: 5kV, dose:  $2.5 \times 10^{14}/\text{cm}^2$ ). In this case, we use 1 mm square x-ray beam. As shown here, Cs peaks decrease and Pr peak emerge after D<sub>2</sub> gas permeation at the shown point. It can be seen that transmutation of Cs into Pr occurred at this point. However, no Cs was changed and no Pr was seen except this point in the case of SP-24.

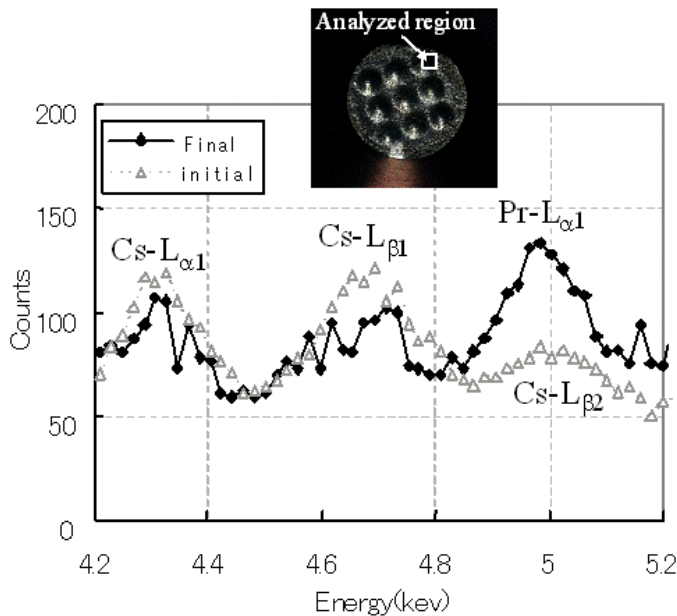


Figure 4. Confirmation of transmutation of Cs into Pr using ion beam implanted sample (SP-24) by *in-situ* measurement

Another example of *in-situ* measurement is shown in Fig. 5. Electrochemical deposition [1] was applied to this sample (SP-33). Pr was detected at the points 2, 3, 8 and 9, although no Pr was detected at the points 4, 5, 6, 10, 11 and 12. We could not see initial Cs at the points 1, 7, 13, 14, 15 because Cs distribution is not uniform if we applied electrochemical Cs deposition method. Initial and final XRF spectra at point 2 are shown in Fig. 2. Cs peaks decreased and a Pr peak emerged after D<sub>2</sub> gas permeation. The ratio of minor peak of Cs-L to major peak of Cs-L is always constant, so we can judge that the peak near 5keV is attributed to Pr-L x-ray. This result also demonstrates that transmutation reaction of Cs into Pr occurs in this experimental system.

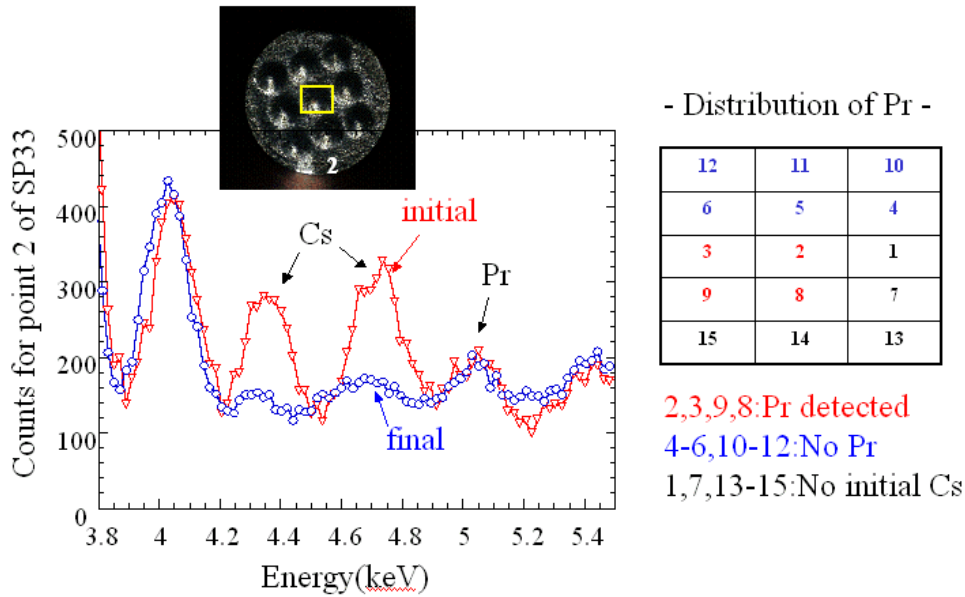


Figure 5. Confirmation of transmutation of Cs into Pr using electrochemically deposited sample (SP-33) by *in-situ* measurement

Let us move on to the next point. Figure 6 shows Pr detection by XRF method performed in 2003. FG1 was fabricated by the Ar ion beam sputtering method and permeated for 97 hours by D<sub>2</sub> gas at 70 C. FG2 was made by the magnetron sputtering method and permeated for 96 hours by D<sub>2</sub> gas at 70 C. Pr-L lines were clearly in both foreground samples, while no Pr peak could be seen in the background sample.

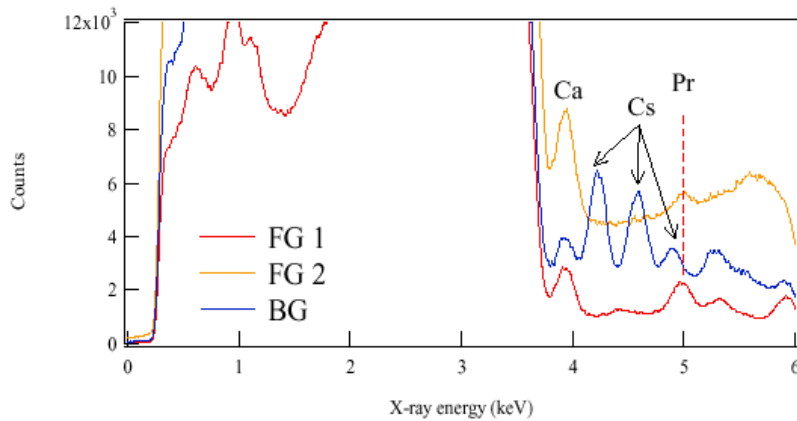


Figure 6. Detection of Pr by XRF in 2003 (FG1 and FG2; D<sub>2</sub> permeated samples, BG; No permeated sample)

Pr surface distribution measurements were done for FG1, FG2 and SP-24 by small size X-ray beams in 100- and 500-micrometer squares.

Mapping data of Pr for FG1 analyzed by 500-micron x-ray beam is shown in Fig. 7 (a) Pr could be detected from all the points (400 points) in the analyzed region in 10mmX10mm. Detection of Pr is consistent with the above XRF measurement in 2003. In addition to Pr, we detected the other peaks for 27 points. A peak around 4.5keV can be seen at point 284. Levels of Pr seem to be almost uniform for these points. We can estimate that these peaks correspond to about  $5 \times 10^{13}$  atoms/cm<sup>2</sup> by the comparison with XRF spectra using a reference sample in which Pr was already implanted. Figure 7 (c) shows corresponding surface image taken by a microscope. It seems that there are no specific or special features for the point 284 under this measurement condition.

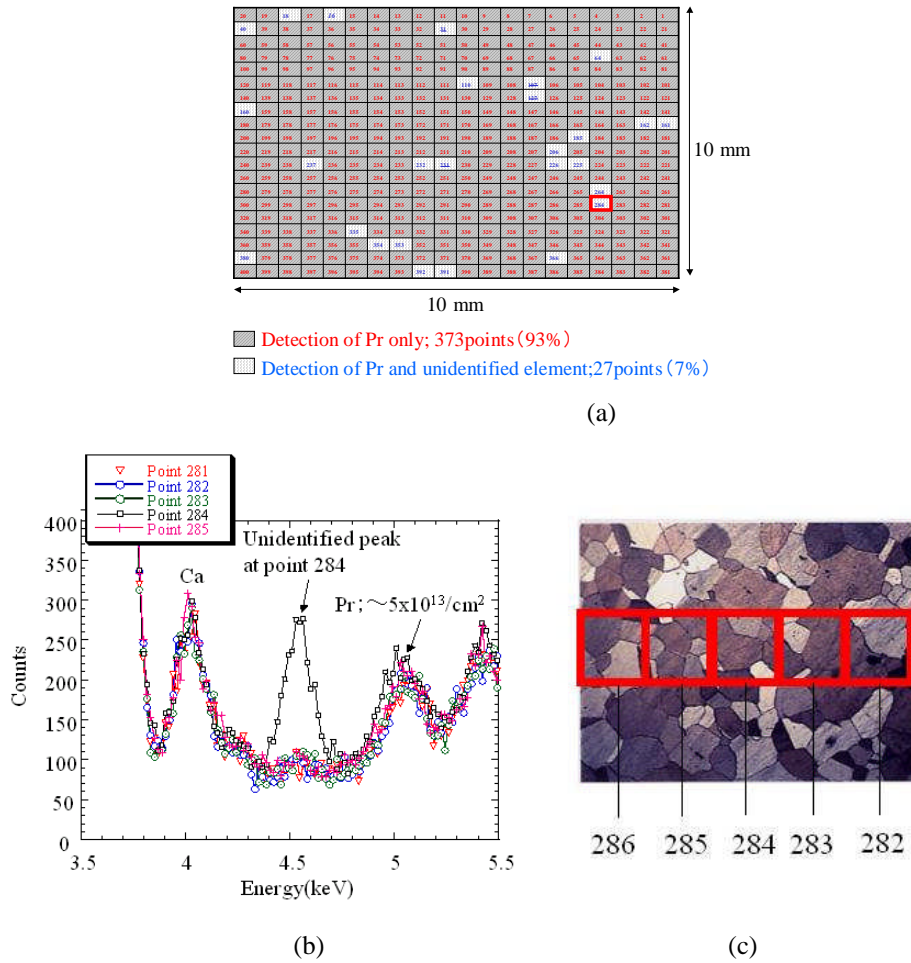


Figure 7. Surface Distribution of Pr for FG1 using 500 micron x-ray beam; (a) Mapping of Pr and unidentified element, (b) XRF spectra for the points 281-285, (c) Surface image of FG1 for the points 282-286.

Mapping data of Pr for FG2 analyzed by 500-micron x-ray beam is shown in Fig. 8 (a) Pr was observed at 61% points (74 points) in the analyzed region in 5.5mmX5.5mm. Detection of Pr is consistent with the 2003 XRF measurement shown Fig. 6. In this case, we could not see any “unidentified peaks” shown in Fig. 7 (FG1). No Pr was detected in 39% of the points. XRF spectra for points 75-79 by 500-micron beam are shown in Figure 9 (a). The strengths of Pr seem to be slightly changed depending on measured points, however, no clear difference seems to be seen as shown in Fig. 9 (b).

XRF spectra using 100-micron beam for the point 27 are illustrated in Fig. 9 (c) and the surface image for the corresponding region is shown in Fig. 9 (d). The “unidentified peak” emerged at the point 5-1 in the point 27, although we could not observe the “unidentified peak” if we used a 500-micron beam. This fact suggests that the “unidentified” element was so localized and so small that the signal from the element was buried when we used large beam (500-micron). It also seems there are specific or special features for the point 5-1; or if there are specific structures, they might be much smaller than this image.

Based on the XRF spectra, La, Ba and Ti are candidates for the unidentified peak. At the present stage, we cannot completely exclude the possibility that the peak is derived from a localized impurity. Further investigation by other measurement methods is necessary.

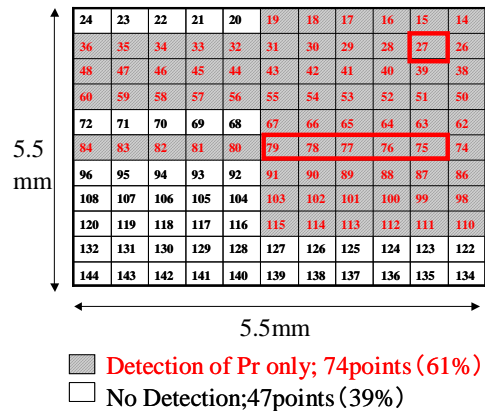
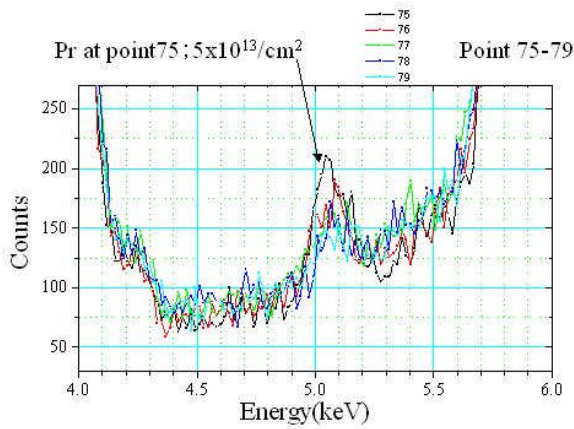
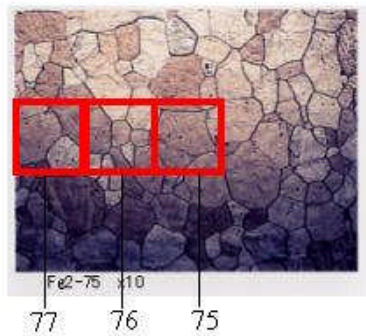


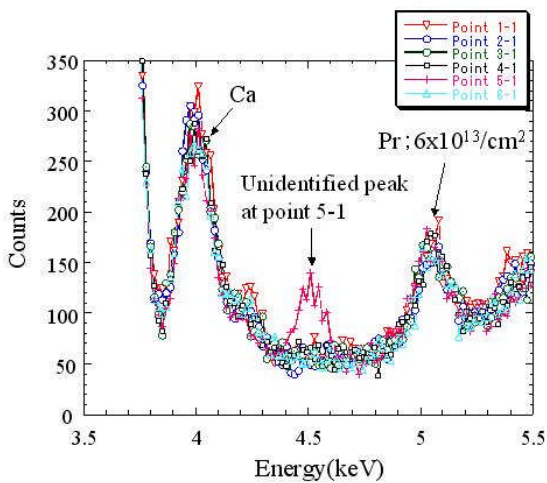
Figure 8. Surface Distribution of Pr for FG2 using 500-micron and 100-micron x-ray beams, mapping of Pr by 500-micron beam.



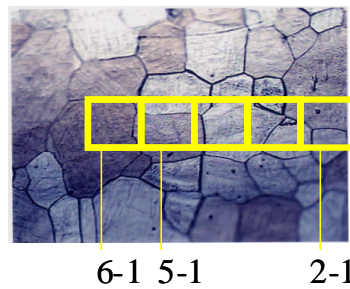
(a)



(b)



(c)



(d)

Figure 9. Surface Distribution of Pr for FG2 using 500-micron and 100-micron x-ray beams, continued: (a) XRF spectra for the points 75-79 by 500-micron beam, (b) Surface image of FG2 for points 75-77, (c) XRF spectra using 100-micron beam for the point 27, (d) Surface image of FG2 for the point 27.

Sample SP-24, originally measured *in-situ*, was analyzed by small size X-ray beams in 100- and 500-micrometer squares 5 months after the permeation experiment. Pr could be observed again in the same region as

the *in-situ* measurement. The surface distribution of Pr for SP-24 by 500-micron x-ray beam is shown in Fig. 9 (a). Pr was observed only at 6 points and the “unidentified” peak was observed at 2 points even though we used 500-micron x-ray beam. As for SP-24, reaction rate is lower than FG1 and FG2. At present, the authors cannot explain completely the difference of reaction rates between these 3 samples. It should be investigated further, since clarifying the factors that make influence on the transmutation rate is an important and valuable task to increase transmutation rate.

Figure 9 (b) and (c) show surface distribution of Pr and XRF spectra obtained by 100-micron x-ray beam for point 13-4 shown in Fig. 9 (a). The amount of Pr changed greatly depending on the locations of the Pd surface. Pr is localized at the specific points shown in Fig. 9(c). Surface image for the corresponding region is shown in Fig. 9 (d). No clear correlation between the localized Pr and surface image could be observed.

These experimental results suggests that transmutation reaction rate varies depend on the Pd surface region. And if we postulate that the unidentified peak is derived from a transmuted element, transmutation pass might be changed depending on location. Some uncertain factors, presumably relating to condensed matter effects in the present Pd/D/CaO system, must make a lot of effects on the rate or the process of the reactions. In order to make clear the uncertain factors, it would be necessary to use smaller X-ray beam, although it would take much more time for XRF measurement.

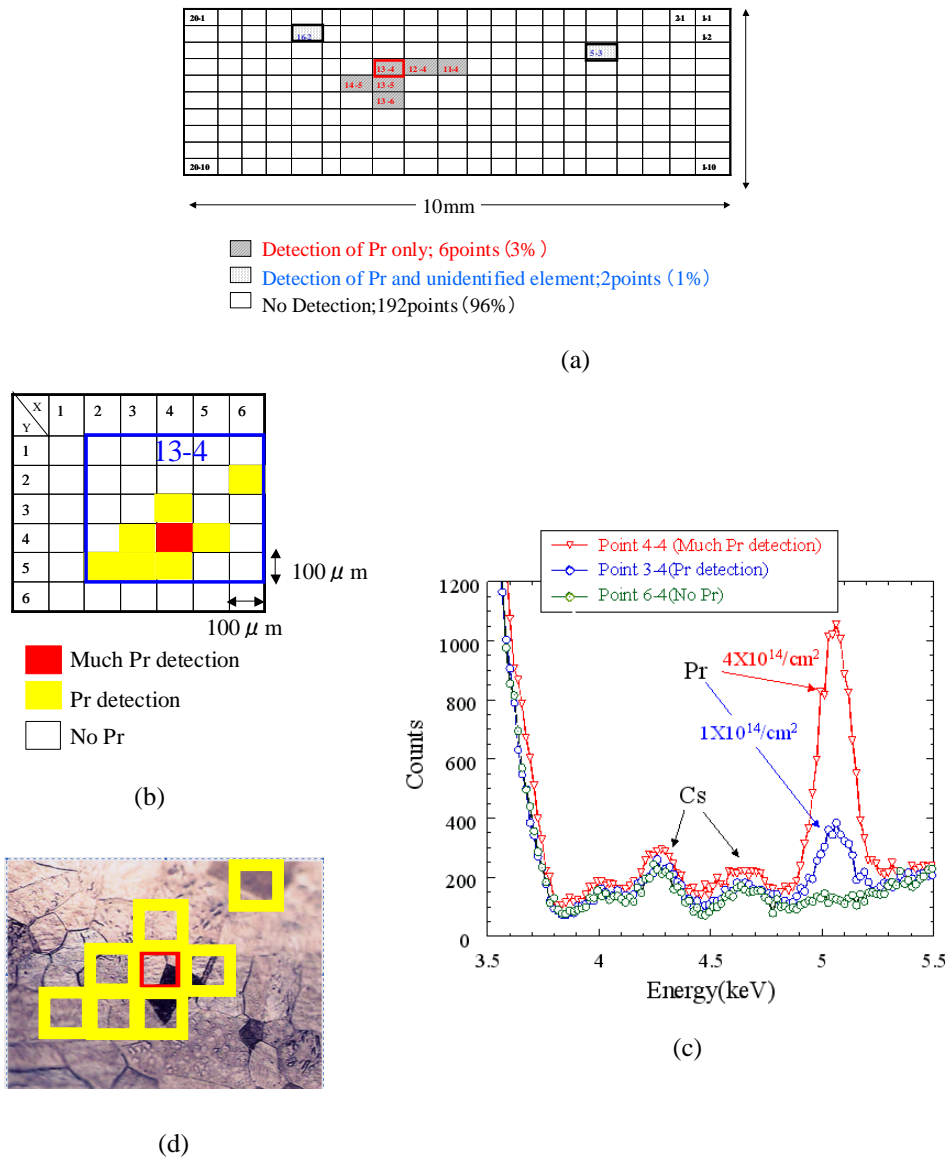


Figure 10. Surface Distribution of Pr for SP-24 using 500-micron and 100-micron x-ray beams; (a) Mapping of Pr by 500-micron beam, (b) Mapping of Pr by 100-micron beam at point 13-4. (c) XRF spectra depending on location obtained by 100-micron beam, (d) Surface image of SP-24 corresponding to XRF spectra

#### 4 Concluding Remarks

One of our experimental apparatus was carried to SPring-8 for the purpose of *in-situ* measurement and we obtained clear Pr signals after D<sub>2</sub> gas permeation by the X-ray fluorescence method. According to the micro x-ray beam measurement, we noticed that Pr was localized greatly. At present, the correlation between products and the surface structures is not clear. Further investigations are necessary, for example, using smaller X-ray beam or analyzing these samples by the other methods.

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