Thermoluminescence and afterglow color images from ancient pottery pieces

Tetsuo Hashimoto*, Emiko Nishiyama*, Toshikazu Mitsuji***

***Department of Chemistry, Faculty of Science, Niigata University, Ikarashi-ninocho, Niigata, 950-2181, Japan**
*****Nara Educational University, Takabatakecho, Nara, Japan**

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Abstract : *Some radiation-induced luminescence color images, including afterglow (AG) or radiophosphorescence, and thermoluminescence (TL), were conveniently photographed by means of a commercially available negative color film after the irradiation of X-ray on pottery slices. The resultant photographs, particularly AG color images (AGCIs), showed a variety of emission patterns dependent on kinds of minerals or thermal history of pottery. The AGCIs from archaeological pottery slices are subjected to the color image analysis to obtain more quantitative information. The relationships of two color intensity-ratios, such as green/red and blue/red, were found to reflect clearly the origin of pottery. While, the dependence of luminescent color properties on the heating temperatures suggests to clarify thermal history of kilns and potteries using stepwise heating of their ingredient-clay.*

Introduction

Some radiation-luminescence phenomena, including afterglow (AG) and thermoluminescence (TL), are observed when dielectric minerals are irradiated with ionising radiation. These luminescence color images from slice samples have been successfully photographed by means of a commercially available negative color film after X-ray irradiation (Hashimoto et al., 1991, 1995a). Though the color photographic method provides less quantitative with aspects of spectrometry, this technique is very useful to understand and especially suitable for two-dimensional luminescence analysis in addition to a simple color tone identification (Hashimoto et al., 1997, 1998).

Particularly, afterglow color images (AGCIs) show a variety of emission patterns depending on kinds of mineral or thermal history (Hashimoto et al., 1995b, 1996). Additionally, AGCIs from some pieces of earthenware and ancient pottery indicated colorful patterns reflected the minerals as well as the temperature of kiln. Therefore, it is expected that archaeological information, such as an origin of pottery and a thermal condition, can be revealed using the AGCIs.

In the present paper, AGCIs from slices of Japanese archaeological relics, named as Sueki, and its ingredients were photographed. These images were subjected to the color image analysis to obtain more quantitative information.

The discussion was made on that provenance identification of ancient ceramics and thermal history of kilns could be evaluated using AGCIs from the slices.

Experimental

Sample preparation

Pottery pieces excavated around kiln relics are suitable for the investigations concerned with the possibility of provenance search of pottery, because it is presumably ascertained that the potteries might be burnt using the local clay. In addition, the dependence of the heating effects on luminescence color could be clarified if the clay ingredients were assigned.

On the basis of above, 48 Sueki pottery pieces and some pottery ingredients were selected to prepare the slice samples for the color images. The details of samples collected are given in Fig. 1. Sueki is known to the oldest pottery burnt using a kiln in Japan. It was used as ritual utensil during the 5~ 6th century. Later (the 7~10th century), they became a daily use one by judging from their abundance and the external form.

After cutting the pottery pieces into round plates (approximately ϕ = 9.4mm and 1mm in thickness), the surfaces were polished with an alumina emulsion solution to eliminate surface irregularities.

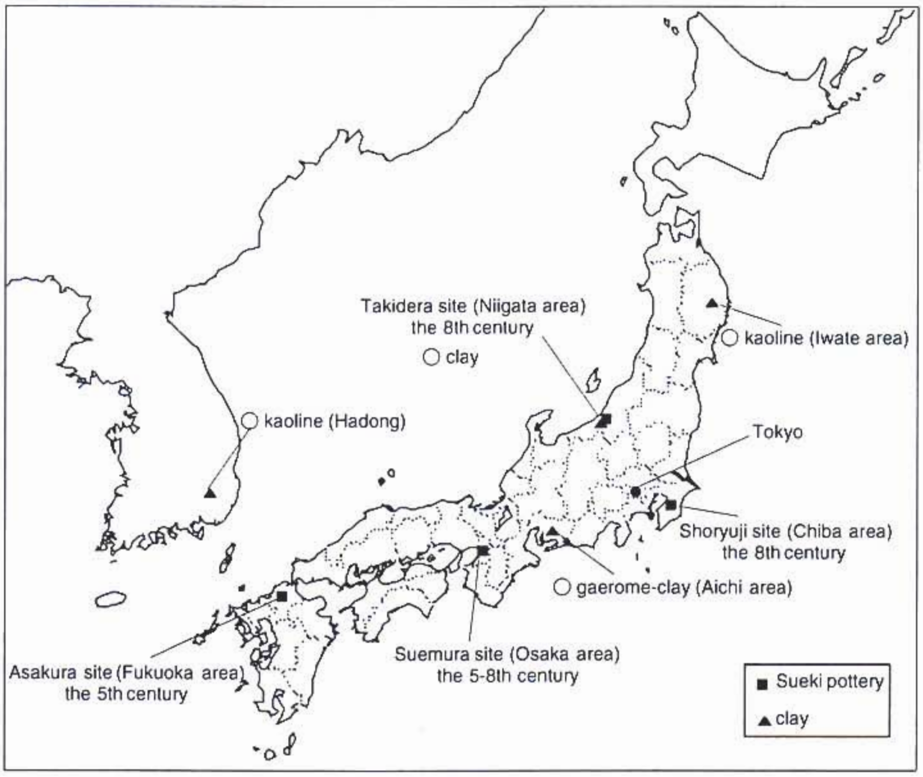

Figure 1.
The details of samples used in the present study.

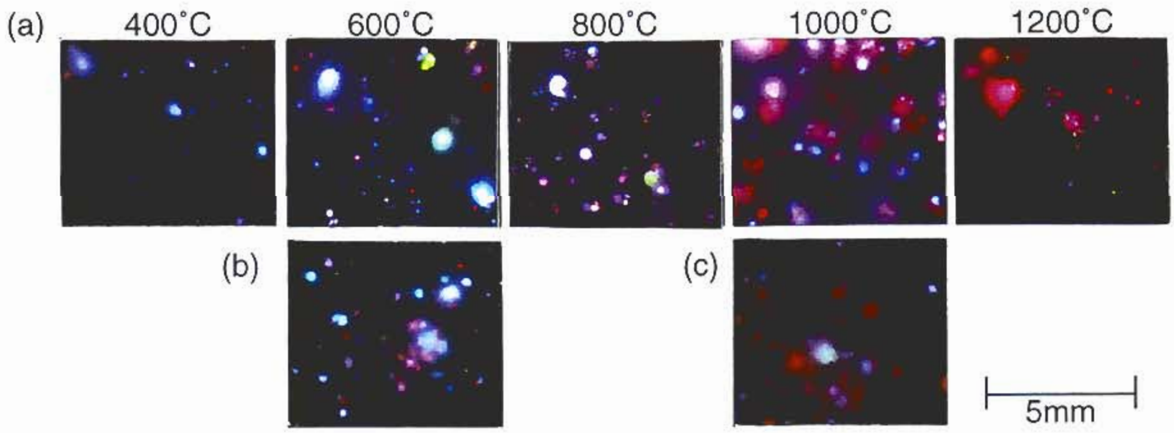

Figure 2.
Changes of AGCIs with thermal history.(a) annealed clay collected around the Takidera kiln, (b) 30~40 cm depth from the surface of the kiln, (c) the real surface of the kiln. Every plate was irradiated to X-ray of 3.5kGy. The thermal annealing treatment was carried out for 24 hours in each temperature.

All clay samples except for the Takidera kiln relics were annealed in an autoclave under an oxidation condition in air atmosphere between 400~1200 °C for 24hours. Heating and cooling rates were controlled as 10 °C/min and −1 °C/min, respectively. When they were hard to make as a slice, their color images were taken by fixing grain samples on melting thin teflon sheets (beyond 300 °C) after sieving into 150~250μm grains in diameter.

X-ray irradiation and observation of luminescence patterns.

All AGCIs were conveniently observed after the X-ray irradiation. The dose-rate at the irradiation position was estimated to be 700Gy/min. Inserting 30sec interval after the X-ray irradiation for 5min, AGCIs are photographed by contacting directly with the sensitive side of color negative film for 3min in a dark bag (Hashimoto et al., 1991).

Subsequently, the TL color images (TLCIs) from Sueki pottery pieces were photographed over the temperature range of 120 to 380 °C after the X-ray irradiation for 10min by operating the camera shutter controlled with a microcomputer in a dark room; a constant heating rate of 1 °C/s was applied by a heater controller

All color negative films used for the photography were FUJICOLOR SUPER G ACE 800. The exposed film was developed at a commercially available facility

Color image analysis

In a normal color reader, almost all of visible colors are separated into the three primary colors, red, green and blue. All AGCIs as negative images on a photo film were subjected to the color image analysis using digital values of these colors to obtain quantitative information. On the other hand, TLCIs were too weak to be analysed. The color data in every 720dpi (dots per inch) from AGCIs were acquired into personal computer memory using a color image scanner (Nicon, cool scan II). The scanned images were divided into the primary three color values. The emission amount of the whole image was evaluated for each color value by summing up all pixels of the levels corresponding to the lightness. The level ranged from 0 to 255. The amounts have the following forms:

$$A_{red} = \sum_i (\text{red level}_i \times \text{pixels}_i),$$

$$A_{green} = \sum_j (\text{green level}_j \times \text{pixels}_j),$$

$$A_{blue} = \sum_k (\text{blue level}_k \times \text{pixels}_k)$$

where A is the totally evaluated values of color, red, green, or blue in a certain area. The threshold of the level was 100, since the AGCIs contains background.

Results and discussion

Changes of AG color with annealing temperatures and estimation of thermal history

AGCIs from the clay collected around Takidera kiln clearly show changes of emission color with annealing temperatures, as shown in Fig. 2 (a). It is obvious that an emission color of AG changes from blue to red with heating temperatures. Fig. 2 (b) and (c) indicate the AGCIs from some parts of kiln-materials gathered from the 30~40cm depth from the surface of Takidera kiln and from the real surface of the kiln, respectively. Compared the images shown in Fig. 2, the surface of the kiln was sufficiently burnt in high temperature, while the 30~40 cm depth from the surface was affected to relatively low temperature

Figure 3 shows a result of the color image analysis. The ratios of A_{red}/A_{blue} were significantly changed from 400 to 1000 °C. However, when the clay was annealed over 1100 °C, or completely sintered, the ratios were almost constant values. Inserting the ratios from the real kiln on the experimental curve would be the thermal history of the kiln. In this case, it was ascertained the clays as kiln-materials were burnt almost 1100 °C and 600 °C at the surface of the kiln and the 30~40cm depth, respectively.

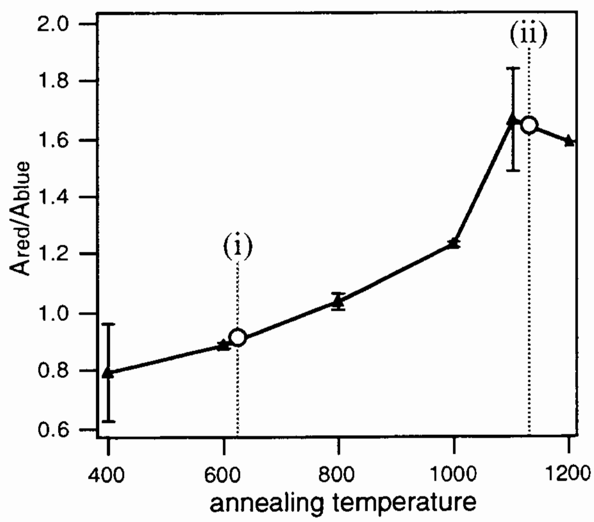

Figure 3.

The results of the color image analysis for the AGCIs from annealed Takidera clay and temperature estimation of kiln relics. The triangles are the A_{red}/A_{blue} ratio in each annealing temperature. (i) and (ii) are 30~40 cm depth from the surface of the kiln and the real surface of the kiln, respectively

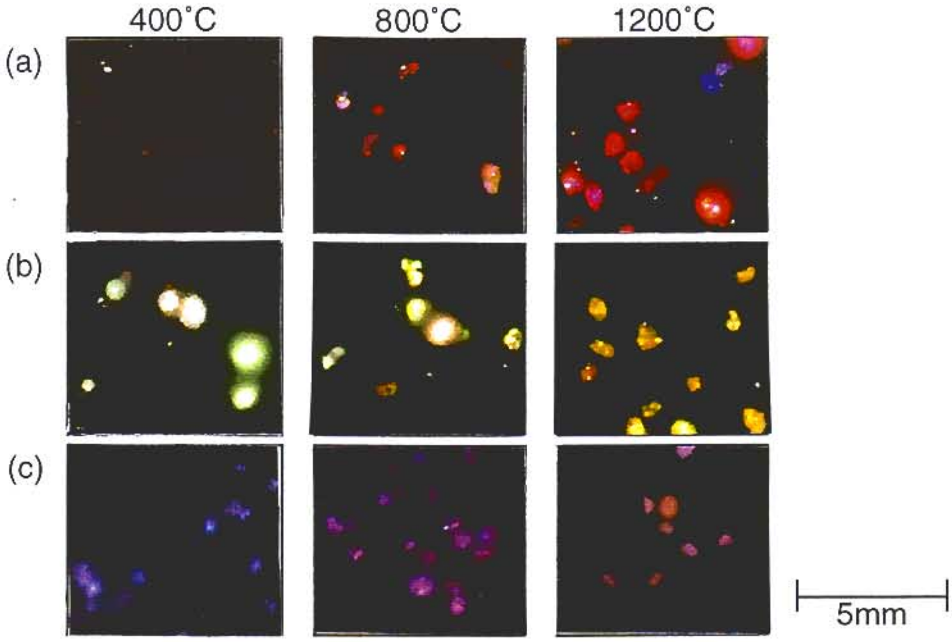

Figure 4.
AGCIs ingredients of ceramics.(a) kaolin clay from Iwate, Japan, (b) kaolin from Hadong, Korea, (c) gaerome-clay from Aichi, Japan. Every photographic condition was the same with FIG. 2.

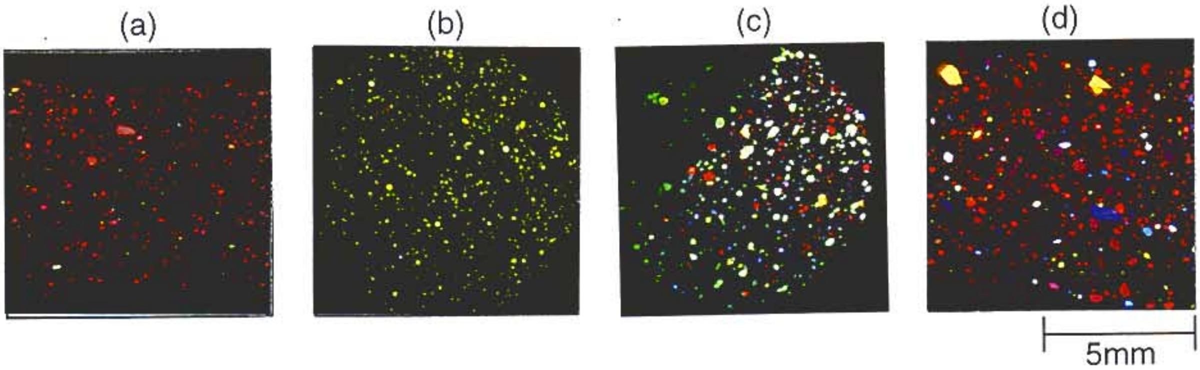

Figure 5.
AGCIs from Sueki pottery pieces.(a) Suemura kiln, Osaka, Japan, (b) Asakura kiln, Fukuoka, Japan, (c) Shoryuji kiln, Chiba, Japan, (d) Takidera kiln, Niigata, Japan. Every photographic condition was the same with FIG. 2.

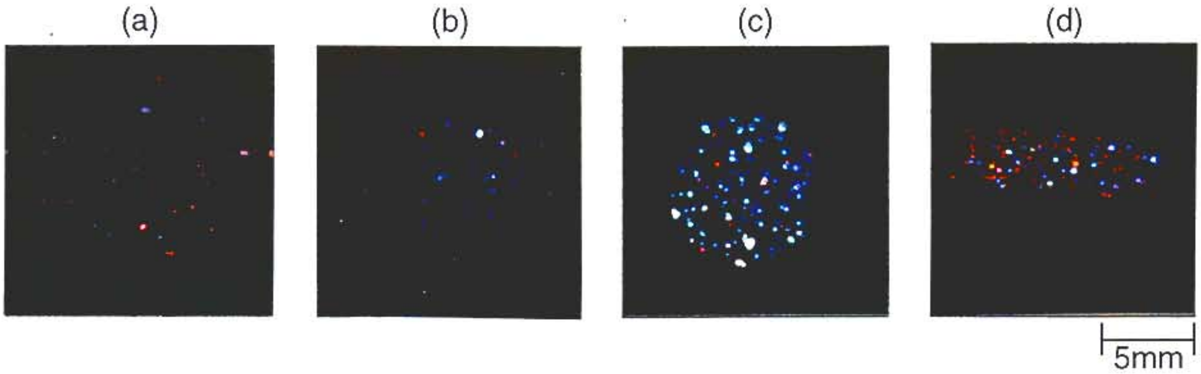

Figure 7.
TLCIs from Sueki pottery pieces.(a) Suemura kiln, Osaka, Japan, (b) Asakura kiln, Fukuoka, Japan, (c) Shoryuji kiln, Chiba, Japan, (d) Takidera kiln, Niigata, Japan. These images were obtained in 120 to 380°C ranges after X-ray irradiation of 7kGy.

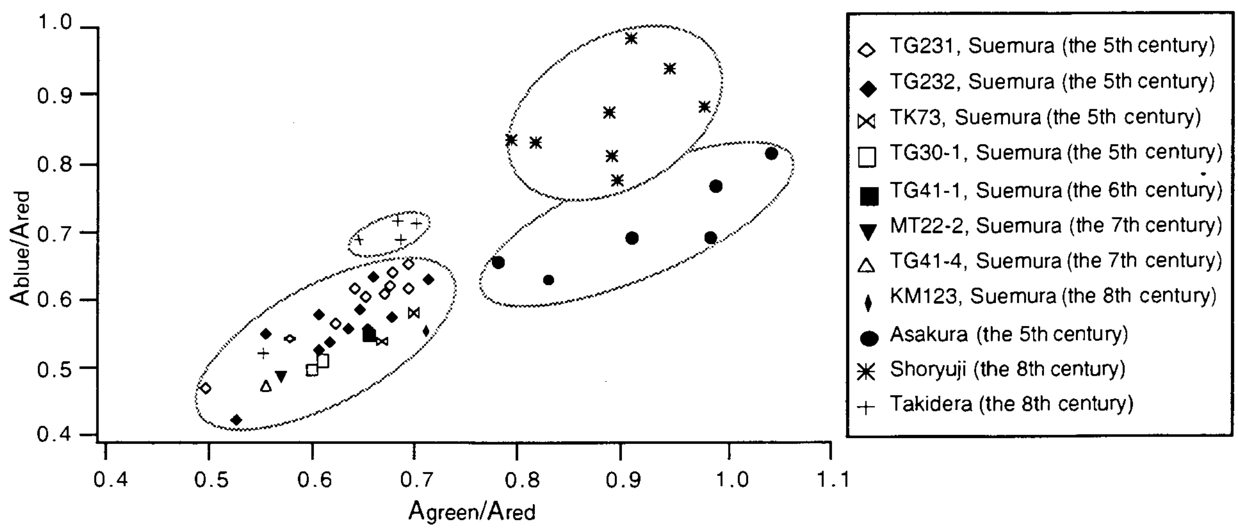

Figure 6.
The grouping results of AGCIs from Sueki pottery pieces using color image analysis.

On the basis of these results, it was verified that the thermal history, including temperatures, could be estimated using AG phenomenon.

Figure 4 shows AGCIs from different pottery ingredients. These AG colors were also changed with annealing temperatures. However, these images apparently differed in respective clays though the samples were applied to the same annealing treatment. This suggests that the AG color from the sample should be affected on mineral constituents if the samples were fired or sintered in similar condition. As mentioned above, the annealing temperature could be useful to the provenance search of the sintered clay or earthenware because of rendering constant value dependent on raw clay materials. The one of the most effective minerals affecting the AG emission color would be remnants of feldspar.

The dependence of AGCI on pottery provenance

The AG emission color of the clay gives some information of the minerals contained when the samples were sintered. This means that the pottery made by the different clays brings on the different color patterns dependent on the provenance.

The AGCIs from Sueki pottery made in the different regions were shown in Fig. 5. The AGCIs from Suemura (a), Asakura (b), Shoryuji (c) and Takidera (d) regions indicate individually, intrinsic color patterns, roughly separable into the color, red, yellow, green and red, respectively. These images give interesting characteristics dependent on the producing centers owing to different ingredients. Almost all of color images are suggestive of the provenance of pottery, though it happens to be hard to distinguish (a) from (d) in Fig.5 because of the similar red color. These AGCI results are in excellent agreement with the provenance search from analysis of chemical elements using the energy dispersive X-ray fluorescence spectrometer by Mitsuji (1994).

Figure 6 shows the results from the color image analysis of these AGCIs. The results from the Suemura region have the same characteristics in spite of difference in both ages and excavated kilns. This figure clearly indicates the grouping distributions dependent on the pottery provenance. The Suemura region is readily distinguishable from the Takidera region. The color image analyses of AGCIs have proven a possibility to classify the images into individual groups of the respective provenance. As a result, it is concluded that the origins of pottery could be presumed using the results of color image analyses from AGCIs based on a simple procedure.

The dependence of TLCI on pottery provenance

The TLCIs from the Sueki pottery pieces manufactured in the different regions were shown in Fig. 7. These images show two color patterns; the main color spots of Suemura (a) and Takidera (d) are red, while Asakura (b) and Shoryuji (c) are mainly blue. These images were too weak to perform the color image analysis even from the samples irradiated artificially. However, the provenance search of dune sands using the color image analyses of TLCIs from quartz grains has been carried out by Hashimoto et al. (1989). The naturally accumulated TL intensities from pottery pieces are now applied to estimate the manufactured ages in the same origins.

Conclusions

The AG emission color patterns from burnt clay were significantly changed with annealing temperatures. The result of the AG color image analysis gave the similar color ratios in the case of completely sintered clay.

The AGCIs from different pottery ingredients apparently reflected the mineral constituents, such as a variety of feldspars, even when the same annealing treatment was applied after keeping at about 1200 °C. If the samples were fired in similar condition or sintered, the AG color from the samples should be affected mainly on respective mineral components. In fact, AGCIs from some Sueki pottery pieces excavated nearby the kiln reflected the clay natures of the manufacturing regions regardless of the ages. The color image analysis of AGCIs was resulted in the grouping of pottery provenance, depending on the clay properties

Finally, it was proposed that thermal history of kilns and the origin of pottery could be interpreted using luminescence color images.

Acknowledgments

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Review :

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