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The combined application of PIXE analysis and thermoluminescence (TL) dating for elucidating the origin of iron manufacturing in Japan

N. Hagihara [a,*], S. Miono [a], Z. Chengzhi [a], Y. Nakayama [b], K. Hanamoto [b], S. Manabe [c]

[a] *Faculty of Science, Osaka City University, Osaka 558-8585, Japan*
[b] *Ritsumeikan University, Kusatsu, Shiga, Japan*
[c] *Committee of Education, Katano City, Osaka, Japan*

Abstract

For elucidating the origin of iron manufacturing in Japan, the usefulness of PIXE analysis was reconfirmed and a new technique of thermoluminescence (TL) dating was applied. Through reproducing experiments of iron manufacturing and forging, PIXE analysis was tested for classifying the iron slag produced from these two different process. The TL dating method was improved for experiments with the iron manufacturing furnace, burnt at high temperature (about 1300 K) and irradiated with relatively low dose. Utilizing PIXE analysis, the iron manufacturing furnace can be distinguished from the older forging furnace used for the imported iron plate. Adopting TL dating, the oldest iron manufacturing furnace can be found out. Some ancient samples in Japan were used as a test of this combined application, and the results were positive, thus proving the suitability of the method.

Keywords: PIXE; TL dating

1. Introduction

PIXE analysis is useful for evaluating the origin of iron manufacturing in Japan. Our previous study illustrated the application of PIXE technique for classifying the iron manufacturing slag [1]. In addition to this proposal, we tried to define the original process of slag with PIXE analysis. For testing this proposal, we participated in the reproducing experiment of iron manufacturing and forging. The experiment was sponsored by the committee of education in Katano city, and operated by Mr. Kihara, an officially recognized special technician of the skill concerned to the traditional iron manufacturing of Japan. Based on the PIXE analysis of the iron slag, the stage of the manufacturing or forging can be identified. The classification process is useful in classifying the sort of site clear. And the combined search with thermoluminescence (TL) dating sheds some light on the origin of iron manufacturing in Japan [2].

* Corresponding author. Fax: +81-6-692-1190.

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2. Reproducing experiment

2.1. Reproducing experiment

An ancient type of smelting furnace was built with clay (height of about 1.2 m and width of about 0.6 m). The furnace was operated for about 10 h. Throughout the operation, iron sand (magnetite and few hematite) and charcoal were added intermittently. The gross weight of iron sand and charcoal were 43.5 and 70.4 kg, respectively. Rough iron had a gross weight of 14.5 kg, and refined iron had 11.8 kg. The slag from the stage of iron manufacturing, (called "NORO" in Japanese) was exhausted when the bottom of furnace was filled (Figs. 1 and 2). NORO contained Fe and other elements such as Ti, V, Cr and Mn. The ratio of these elements to Fe changed with refining. In ancient technique, iron refining was made by annealing, striking, and hardening. The slag from iron refining was very small and had peculiarity in elemental concentration distribution.

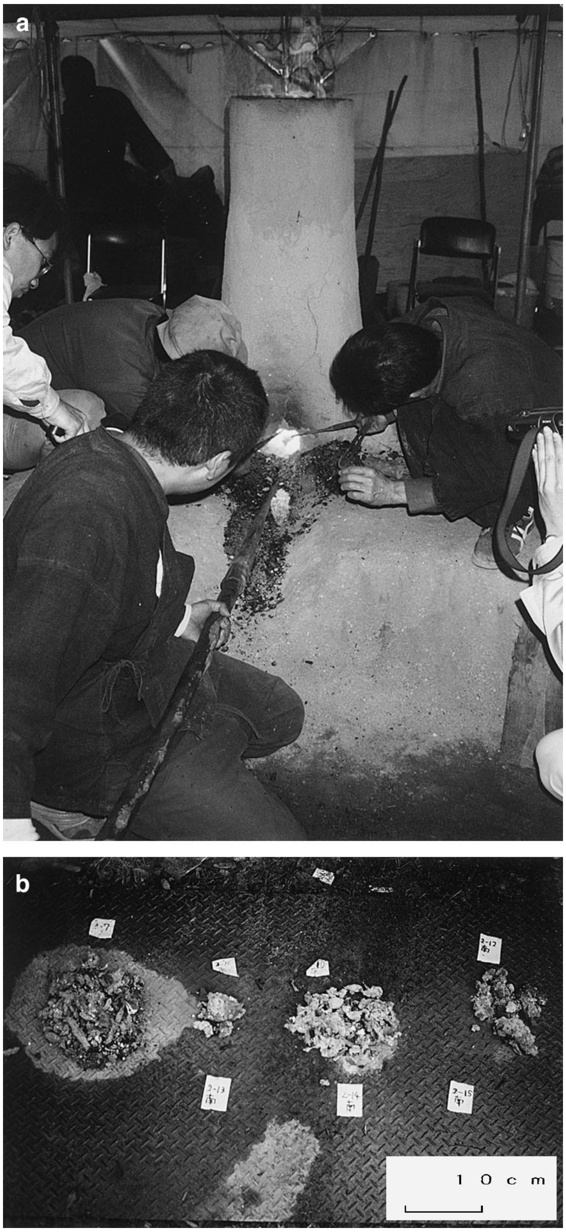

Fig. 1. (a) Raking the slag from the iron manufacturing furnace in the reproducing experiment of ancient iron manufacturing. (b) The slag from iron manufacturing process. With the progress of the process, the ingredient changes.

2.2. PIXE experiment

After the reproducing experiment, some slag samples were furnished for PIXE measurement by the sponsor. In addition to these samples, archaeological slag samples were offered for the trial estimation of raw materials and the source process. In PIXE measurement, for backing the samples, very thin carbon fibers were used, and for fastening the samples little conductive glue was put on them [3]. These factors attributed to minimize the background. PIXE experiments were carried out using 1.2 MeV proton beam in an accelerator housed at the Ritsumeikan University, Japan. The proton beam collimated, 2 mm in diameter, hit with the sample in a scattering chamber. The induced X-ray was detected using a Si(Li) detector. The irradiation time was adopted 1–2 min.

2.3. TL experiment

For the dating of iron manufacturing furnace, TL dating method was adopted. This method is useful for the sample containing the quartz once burned in high temperature (about 800–1200 K), as furnaces. Natural TL and natural + artificial TL of quartz give an archeological acquired dose (paleo dose). Annual dose from the surroundings is measured by TLD (as $CaSO_4$:Tm), or calculated

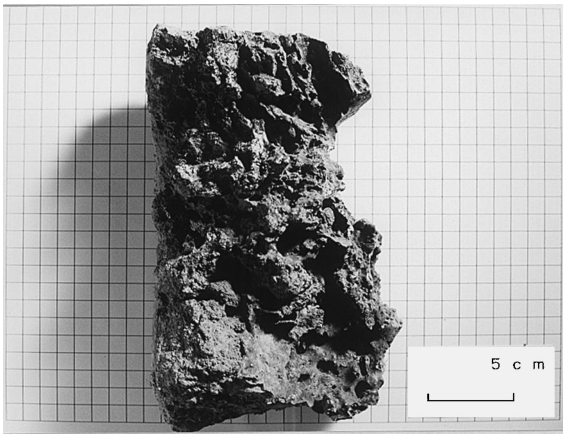

Fig. 2. A piece of burnt wall of melting furnace at Kanakuso-ike. This sample contained quartz burnt with the temperature of not more than 1300 K. This sample was offered for TL dating.

by the concentration of radionuclide (as K, Th, U). The TL age is given as a ratio of paleo dose and annual dose.

Namely, in TL dating, the age relation is given by the following equation [4]:

$$\text{age} = \frac{\text{archaeologically acquired thermoluminescence}}{(\text{thermoluminescence per unit dose of relation}) \times (\text{annual dose from radioactive impurities})}.$$

In the quartz inclusion technique, the surface of quartz grain is removed with the HF treatment(10%, 60 min). As a result of this treatment, the effect of alpha particles was taken away. The age equation is rewritten with absorbed dose, as

$$\text{age} = \frac{\text{paleodose(the dose that the sample received during antiquity)}}{\text{annual dose}} = \frac{\text{paleodose}}{0.9D_\beta + D_\gamma + D_c},$$

where D is the annual dose from the radiations indicated and the subscript c denotes cosmic radiation.

Five furnace wall samples from Okayama prefecture in the Chuugoku region were tested for their TL. Among these one sample contained little quartz, and three samples showed remarkable sublinear phenomenon. The remarkable sublinear phenomenon appears in low dose range, in contrast to general saturation of TL in high dose range. Authors suppose that the high temperature as over 1300 K caused some decrease of traps. In the case of the sample from "Kanakuso-ike" site, it is 5–8 cm thick, and so, the first annealing temperature would be lower than others ones. As a result, only one sample from "Kanakuso-ike" was suited for the TL dating (Fig. 2). In the case of "Kanakuso-ike" sample, paleodose was estimated from natural TL and TL due to the artificial dose of 250 and 500 R, respectively. The correct value for sublinearity was estimated from the TL of re-annealed (1300 K, 1 min) sample. The second annealing temperature was determined by the reproducing experiment. First annealing at high temperature maybe caused due to the denaturation of the quartz. This would make difficult the dating of other three samples. The burnt wall of melting furnace at "Kanakuso-ike" site was 5∼8 cm. Therefore, the sample would contain the annealed quartz with temperature lower than 1300 K. Probably this made the dating about "Kanakuso-ike" sample possible. Annual dose was estimated from the concentration of K, Th, U and Rb. Each concentration was mesured by using the data of activation analysis. However, the data of burnt wall was not considered and hence it was assumed from the slag. The procedure for this is first, the change ratio between burntwall and slag from near site is determined, and second, this ratio is applied to "Kanakuso-ike" sample of slag. Considering the transmissivity, the dose of beta radiation was calculated from the elemental density of the burnt wall, and for the dose calculation of gamma radiation, the average value of slag and burnt wall was used.

3. Results and discussions

3.1. PIXE measurements

The PIXE analysis is useful for estimating the source process of iron slag. The relative concentration of Ti, V, Cr and Mn to Fe changed characteristically as the iron manufacturing and forging process progressed. In the reproducing experiment, the relative concentration of these elements decreased as in Table 1. Especially, Ti and V decreased remarkably, but Cr was not always contained. If this tendency does not reverse, the source process of slag can be estimated from the relative density of Ti and V. The tendency was checked by the slag of reproducing experiment. This way of estimation was applied to some piece of slag from the site of Okayama prefecture. The result added to our former data is shown in Fig. 3. In the last slag could not be plotted. In the last slag, V could not be detected. This constitutes the characteristic point of last slag.

3.2. TL dating

"Kanakuso-ike" sample showed a little sublinearity as shown in Fig. 4. The correction for sublinearity was added by the second-glow measurement. The correction value for sublinearity was 0.591 Gy. The value was measured by the characteristics of 2nd TL after re-annealing and irradiation. The paleodose was estimated at 2.428 Gy. Annual dose was evaluated from the concentration of radioactivities, the value was 2.598 mGy. These data gave a result of 935 yr (B.P.). This result is included within the limits of archaeological presumed age (11–12th century), and within the youngest limits of TL dating (see Table 2).

Table 1
The results of PIXE analysis

Sample	Ti/Fe	V/Fe
Iron sand (□)		
A	0.0069	0.0015
B	0.015	0.0038
Iron manufacturing slag (○)		
No. 1	0.022	0.010
No. 5	0.021	0.0078
No. 12	0.016	0.0053
No. 16	0.015	0.0055
No. 21	0.013	0.0033
Iron forging slag (▽)		
1st	0.013	0.0060
2nd	0.0074	0.0038
last	0.00037	N.D.
Archaelogical sample (◇)		
Kanayama-ike	0.12	0.032
Taishou-like	0.12	0.030
Akimune	0.086	0.011
Hironishi	0.099	0.0088
Yahikida	0.0046	0.0017

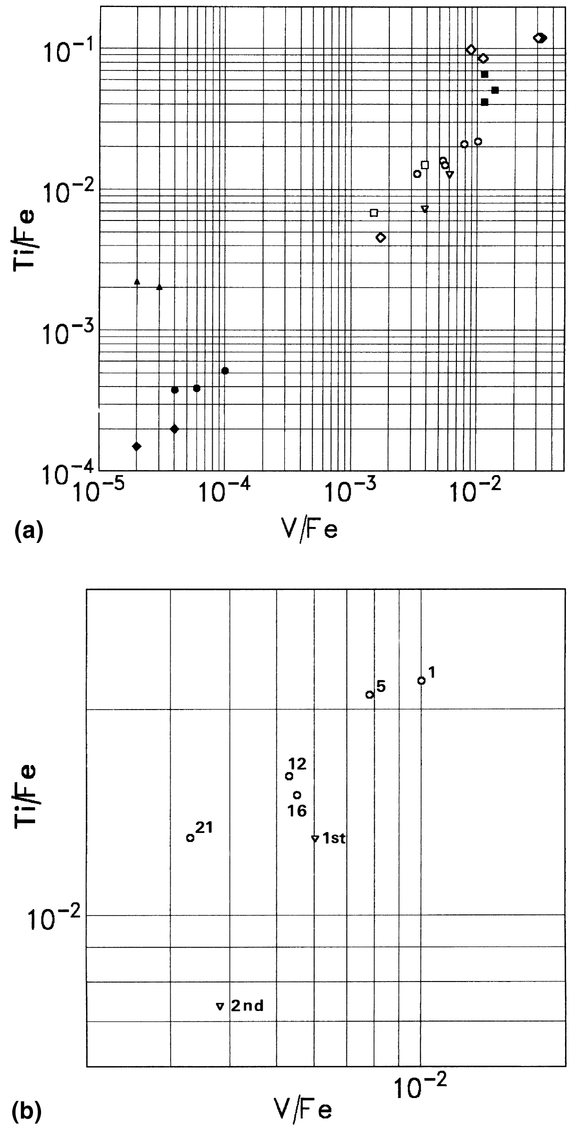

Fig. 3. (a) The vacant dot is added to former data [1], □ is iron sand, ○ is manufacturing slag, ▽ is forging slag, and ◇ is application for archeological sample of iron manufacturing slag. (b) The magnification of manufacturing slag and forging slag. The numbers show the context of formation. With the progress of iron manufacturing and forging process, Ti and V got out of raw materials.

3.3. Discussion and conclusion

Generally speaking, iron manufacturing site is older than forging site. However, in Japan, it is

Table 2
The result of TL dating

Sample	Δ(Gy)	Paleo dose (Gy)	D_β (mGy)	D_γ (mGy)	D_c (mGy)	Annual dose (mGy)	Age
Kanakuso-ike	−0.591	2.428 ± 0.16	1.753	0.870	0.150	2.598	935 ± 62

possible that the forging to imported iron plate began before manufacturing. Therefore, in order to search for the origin of iron manufacturing in Japan, it is necessary to discriminate the slag before dating. The former report by us showed the ability to distinguish raw materials as iron sand and iron ore from the PIXE data of slag. The iron sand used in this reproducing experiment contained less Ti. As in Fig. 3, the data of the slag were divided two groups. The slag from iron sand constitute the higher group on the figure. And the slag from iron ore correspond to the lower group.

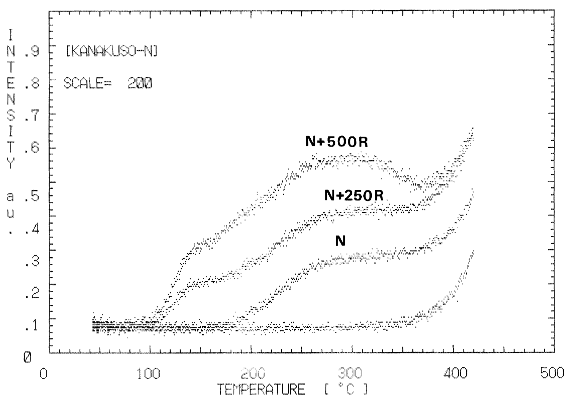

Fig. 4. The thermoluminescence of Kanakuso-ike sample. N is TL due to natural dose. N+250 is TL due to natural and artificial dose of 250 R. N+500 is TL due to natural and artificial dose of 500 R. 598 K peak was used for the estimation of paleodose.

This is the definitely important point to distinguish the raw materials. The data of the slag from reproducing experiment were distributed on the line linking the two group. In the reproducing experiment, iron sand containing less Ti was used for making the iron manufacturing easy. Ti in the iron sand makes the melting point higher. Besides this, the fact that V could not be detected in the last slag proved the effectiviness of PIXE analysis to search the original process of slag. From a chain of PIXE experiments with slag, it was possible to suggest two discrimination criteria, one is to classify the iron sand and iron ore, another is to distinguish iron manufacturing from forging.

At the beginning of iron manufacturing, the technique would be rudimentary. If so, to search the beginning of iron manufacturing in Japan, we have to find out the iron manufacturing slag from iron ore, using PIXE analysis. And regarding the time TL dating method with burnt furnace wall constitute an effective method.

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