Dating of Ancient Ceramics by Thermoluminescence. II

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The colourless fraction from ancient ceramics, i. e. the grain prepared by washing and separating, was used as sample. The measurement of the natural glow and artificial glow signals was performed under nitrogen atomosphere to be free from the oxygen effect. Thus, both of these glow-curves showed nearly the same shape in the part of the high temperature region, so that the absorbed dose of the specimens could be estimated in an available accuracy and it was corrected for rate of alpha bombardment to obtain the specific thermoluminescence. As a result, we have obtained good age correspondence for series of ancient ceramics from Japan. However, in the samples with higher in alpha contents the values of the specific glow were lower than the other samples.

INTRODUCTION

Thermoluminescence dating of ancient pottery has been studied by several groups of workers in recent years, but it has not revealed such a remarkable success as radio-carbon dating. The thermolumineseence dating is based upon a simple principle,[1-3] but the samples to be used are ancient ceramics with complicated mineral composition. Furthermore, the radiation subjected to the specimen comes from various radioactive impurities occuring in the ceramic and from external sources. Some complicated practical problems in thermoluminescence age-determination measurements are resulted from the above facts. In a previous paper[4] dealing with the samples prepared by washing and separating the grain, it was found that the natural glow-curves resulting from ceramics and the artifical glow-curves after Co^{60} gamma-ray irradiation are similar in the shape through the high temperature region for the Yayoi pottery. The advantage of this sample preparation technique for absorbed dose-determination is to be able to avoid difficulties due to heterogeneity of the samples. However, for the Jomon and Sue potteries the deformation of the glow-curve in high temperature region was observed even in the samples prepared by this technique, because they contained some amount of changeable or organic material. We have also suggested that the nitrogen technique adopted by Aitken and his collaborator[5] was useful to avoid this oxygen effect.

The present investigation was undertaken to determine the age of ancient ceramics using these techniques, where the colourless fractions separated from ceramics were used as the samples, and the measurements were performed under nitrogen atmosphere. The age-determination has been made on a selection of

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sherds ranging in age from 600 A. D. to 7300 B. C.

RESULTS

The samples used in the present work are the ancient ceramics of the Jomon, Yayoi, Tumulus, and Asuka era in Japan, as was shown in Table 1. The samples ranging from No. 1 to No. 10 are potsherds, Nos. 11 and 12 are Haniwa, and No. 13 is a roof tile.

Table 1. Samples.

No.	Sites	Materials	Age
1	Natsujima, Kanagawa	Potsherds of Jomon Period	7300 B. C.
2	Kotsutajima, Kagawa	Potsherds of Jomon Period	7000 B. C.
3	Kitashirakawa, Kyoto	Potsherds of Jomon Period	4000 B. C.
4	Akahohara, Kanagawa	Potsherds of Jomon Period	2700 B. C.
5	Sôya, Chiba	Potsherds of Jomon Period	1800 B. C.
6	Shigasato, Shiga	Potsherds of Jomon Period	1000 B. C.
7	Sugita, Kanagawa	Potsherds of Jomon Period	700 B. C.
8	Kôtari, Kyoto	Potsherds of Yayoi Period	200 B. B.
9	Tenjinyama, Osaka	Potsherds of Yayoi Period	100 A. D.
10	Heijô, Nara	Potsherds of Yayoi Period	300 A. D.
11	Ishiyama, Mie	Haniwa of Tumulus Period	400 A. D.
12	Kyozuká, Osaka	Haniwa of Tumulus Period	500 A. D.
13	Asuka, Nara	Roof-tile of Asuka Period	600 A. D.

The experimental apparatus used to measure the thermoluminescence was described in the previous report[3], excepting that a sample box was improved to be airtight with a purpose of heating under nitrogen atmosphere.

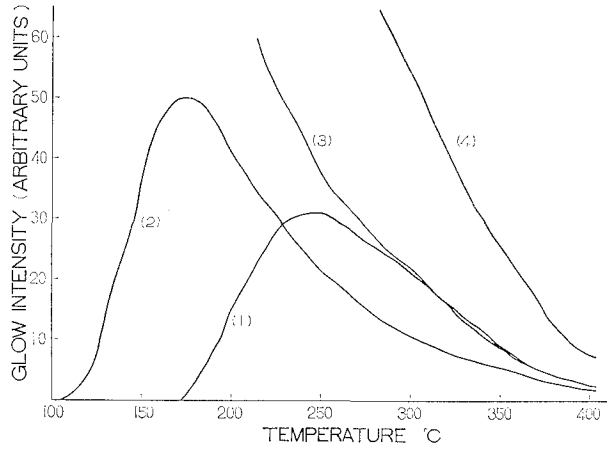

Fig. 1. Glow-curves for the sample No. 2.
(1) Natural glow-curve.
(2) Artificial glow-curves after irradiation with gamma rays from Co^{60} (3×10^3r).
(3) Artificial glow-curves after irradiation with gamma rays from Co^{60} (5×10^3r).
(4) Natural glow plus artificial glow from gamma irradiation (5×10^3r). (From sample irradiated without annealing).

An example of glow-curves for the sample No. 2 is illustrated in Fig. 1, where the glow-curves resulting from the Co^{60} gamma-ray irradiation are superimposed on the natural glow-curve for comparison. All of them show a very broad peak contributed by many groups of trapping levels. A comparison of the two glow-curves, natural and artificial, show that the former decays at the part of the low temperature region. This decay results from the normal temperature after the last heating. As for the part of the high temperature region, all of these glow-curves show nearly the same shape. About some samples of the colourless fractions prepared by washing and separating, the shape of the glow-curves were identical in the high temperature region even in aired condition. As for the rest, the natural glow-curves exhibited characteristic increase contributed by organic impurity. The results of chemical analysis for the samples used in the present work are given in Table 2 for reference.

Table 2. Results of chemical analysis.

Sample No.	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	Ign. Loss	Total	Organic
2	635.2	17.55	4.74	1.08	0.64	2.04	1.53	3.35	2.37	Tr.	0.01	3.97	100.82	0.18
3	60.98	22.67	3.00	1.70	0.42	0.65	0.45	2.33	0.51	Tr.	0.41	7.48	100.60	0.86
6	55.06	24.82	5.14	1.44	0.48	1.90	1.08	2.07	0.54	0.01	0.44	7.91	100.98	0.27
8	65.84	21.29	3.01	0.30	0.40	0.68	0.47	2.60	0.63	Tr.	0.23	5.35	100.80	0.15
9	70.04	21.07	3.54	0.58	0.50	0.42	0.66	1.98	0.63	Tr.	0.03	1.43	100.88	0.02
10	63.92	20.82	4.70	0.65	0.81	1.13	0.98	2.11	0.62	0.04	0.04	5.06	100.88	0.08
11	53.30	24.62	5.73	1.43	0.78	1.56	1.43	2.11	0.39	0.08	2.90	8.09	100.78	Tr.
12	67.46	21.11	4.18	1.30	0.54	0.62	0.83	1.42	0.48	Tr.	0.02	2.90	100.86	0.14
13	56.64	23.93	8.84	1.45	2.17	3.44	1.08	1.18	0.85	0.05	0.01	1.15	100.79	Tr.

The glow intensity of ancient ceramic samples was verified[3] as a linear function of the absorbed dose. Therefore, the absorbed dose is obtained by comparing the natural glow-curve with that from the Co^{60} radiation and by measuring the area ratio of the two curves, when the fading of the thermoluminescence is taken into consideration. It has previously been demonstrated in our study, the thermoluminescence dosimetry of gamma rays from atomic bomb,[6] that the glow signal above 200°C would not decay and could be used for the measurement of the bomb radiation received 20 years ago in Hiroshima and Nagasaki. In the case of ancient ceramics, the elapsed times to be estimated are much larger as compared with those in the case of the bomb radiation, but the natural glow-curves in the former are also in good agreement with the shape of the artificial ones in the higher temperature region. In view of the above facts the most reasonable conclusion to be drawn from the available data is that the glow signal above 280°C or so can be used for the dating of ancient ceramics. As reported in an earlier paper,[4] D, the absorbed dose integrated over the age, can be expressed as $D = Do \times I/Io$, where I is the intensity of the natural glow, Io, the intensity of the artificial glow by irradiation with a standard source and Do, the known amount of irradiation of this source. Also, t, the age of ancient ceramics, can be written as

$t=D/cR$, where R is the natural radiation dose-rate received by the ceramics and c, a constant.

A determination of the effective radioactive content for the natural glow intensity is the important problem which remains unsolved. However, works[7] of the thermoluminescence dating were thus far concerned only with the alpha activity and we also considered tentatively that the natural uranium and thorium radioactive impurities occuring in the ceramic could principally contribute to produce trapped electros. The alpha activity of the sample has been measured using a scintillation counter fitted with special low-background ZnS screens. This is shown

Table 3. Specific glows of the samples.

Sample No.	Age	Natural absorbed dose, D	Relative alpha activity in counts per hr.	Specific glow D/counts per hr.
1	7300 B. C.	3000±300	5.0±0.8	600±113
2	7000 B. C.	5100±300	10.3±1.0	495± 54
3	4000 B. C.	2400±200	5.6±0.7	428± 64
4	2700 B. C.	3300±200	11.3±1.1	292± 34
5	1800 B. C.	1400±150	5.1±0.7	275± 42
6	1000 B. C.	1600±200	55.0±2.3	29± 4
7	700 B. C.	1300±200	8.4±0.8	155± 28
8	200 B. C.	2000±200	17.2±1.5	116± 15
9	100 A. D.	1000±100	8.0±0.7	125± 17
10	300 A. D.	900±100	20.7±1.5	46± 6
11	400 A. D.	800± 50	21.1±1.6	38± 4
12	500 A. D.	410± 70	23.0±1.6	18± 3
13	600 A. D.	350± 20	6.5±0.7	54± 7

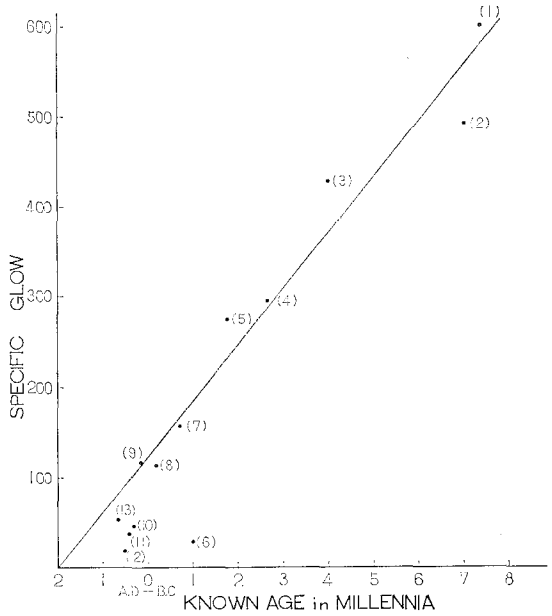

Fig. 2. Specific glows for known-age ancient ceramics.

in Table 3, with the values of D divided by alpha rate, which have been denoted as the "specific thermoluminescence" by Aitken. The preliminary result for the thermoluminescence dating of ancient ceramic, "specific thermoluminescence" plotted against the archaeological age for a series of thirteen samples from Japan, is shown in Fig. 2. From this results, we find that the "specific thermoluminescence" is roughly proportional to age. About the samples of high dose-rate, however, we can not observe the age correspondence. This fact will be discussed in the following.

DISCUSSION

In the measurement of natural glow signals for the ancient ceramics one should use a sensitive detection system and adequate technique to enhance it, such as rapid heating and use of filter to eliminate thermal radiation, since their glow is in general a feeble emitter compared with geological samples. The sample preparation technique utilizing the colourless fraction will be effective for this problem, because the thermoluminescence susceptibility of this fraction is 15 to 20 times larger than that of unseparated powder in our experiment. Thus, for the specimen from Japan we could perform the measurement of the natural glow, without using using the rapid heating method. When sample separation becomes more completed, higher sensitivity would be expected.

Whether the trapped electrons responsible for the natural glow of the samples are caused primarily by alpha bombardment or by a combined effect of alphas, gammas, and betas is one of the major unknown factors in thermoluminescence age-determination measurement. Aitken *et al.*[5] estimated the specific thermoluminescence which varied linearly with age, using the value of the activity for the uranium, thorium and potassium in the pottery. Ralph and Han[7] used also only relative alpha activity in counts per hour as radioactive content. As a result, the plots of specific thermoluminescence *versus* known ages for samples are roughly proportional to age in their studies. From a consideration that the uranium and thorium radioactivity occuring in the specimen are principally effective to produce trapped electrons, we used also the alpha rate for this plot and came to the same results as theirs. However, as showen in Fig. 2, there are the evidences that the specific thermoluminescence for the samples which are rich in alpha content, such as sample Nos. 6, 10, 11, and 12, results in lower values than those of the other samples in significant amount. The present investigation of thermoluminescence dating has dealt exclusively with the alpha rate on the evaluation of effective radioactive content, so that data from the samples which are higher in alpha rate have not proved consistently successful. On the basis of these data, it seemed reasonable to assume that the contribution from potassium in the specimens or external sources must be also examined as the effective radioactive content for the natural glow intensity. Measurements of beta and gamma radiations to which ancient ceramics are exposed are now under study.

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