Preferable use of red-thermoluminescence (RTL)-dating for quartz extracts from archaeologically burnt pottery -comparison of RTL and BTL (blue-TL) measurements using single-aliquot regenerative-dose (SAR) method

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Abstract

Red- (RTL) and blue-thermoluminescence (BTL) dating procedures for quartz aliquots were applied to nine Jomon pottery pieces, which were manufactured and used 3,500-6,000 years ago. Quartz grain extracts from each piece were measured with respects of both RTL and BTL using a new automated luminescence measuring system that included a small X-ray irradiator and a single-aliquot regenerative-dose (SAR) protocol. Equivalent doses from RTL were evaluated to be higher than BTL-doses in most cases. This is due to contamination of feldspar grains and/or to light-bleaching effects. In a few cases, BTL-quartz constituents have not been detected. The TL-age results, obtained using the equivalent doses and annual doses, indicated that the RTL-ages are closer to the predicted archeological ages, giving more reliable results than the BTL-ages. Conclusively, the RTL-dating was recommended for the quartz extracts from the archaeologically burnt materials in the present experiments, probably because of the high impurity contents in the quartz grains. Although the existing BTL-dating could be already applied to the pure quartz grains without much content of impurities, the check of TL-properties, including RTL or BTL, should be considered prior to the practical TL-dating for burnt quartz fractions.

1 Introduction

The blue-thermoluminescence (BTL) from quartz grains has been utilized for the TL-dating before the availability of highly sensitive TL-spectrometry and photographic observation (Aitken, 1985). In the beginning of the 1980s, the red-thermoluminescence (RTL) phenomena have been discovered in addition to the already well-known BTL phenomena within quartz grains of the Niigata dune sand after either natural or artificial exposure of radiation (Hashimoto et al., 1986). Subsequently, both the volcanically originating quartz grains and the artificially burnt ones were found to offer such RTL properties. Especially, in both the volcanically originating and the burnt quartz fractions, RTL measurements are preferable for dating over a period of 1 Ma (Hashimoto et al., 1987, 1993, 1999; Miallier et al., 1994). The causes of the RTL have been investigated by artificial thermal annealing treatments on some natural quartz crystals and by synthesizing quartz glasses with various kinds of impurities along with the aids of the sol-gel method of silica glass (Hashimoto et al., 1991, 1997). As a result, the rapid cooling process after annealing beyond 867°C (β-quartz/tridymite phase inversion temperature) was found to be responsible for the RTL properties as well as the collaboration with the Al-impurity content beyond 100 ppm (Hashimoto et al., 1994, 1996).

In order to evaluate reliable paleo-doses or equivalent doses, a single-aliquot regenerative-dose (SAR) technique has been developed mainly for the optically stimulated luminescence (OSL) measurements, in which luminescence-measurement and irradiation could be repeatedly adopted under the same geometrical conditions (Wintle and Murray, 2000).

In this study, the RTL and BTL methods were applied to the evaluation of naturally accumulated doses (or paleo-doses) for the quartz extracts from pottery pieces. The SAR-protocol was employed using a new automated luminescence measuring system equipped with a small X-ray irradiator (Hashimoto et al., 2002a,b). The both RTL- and BTL-ages were determined from the relationship between the paleo-doses and the annual doses, which were estimated from the natural radioactivity of the ambient soil of the buried pottery pieces and crushed pottery material. The results were compared to each other as well as with the ages predicted from the mode of pottery and the stratigraphic viewpoints.
2 Experimental

2-1 Sample pieces of pottery
Pottery pieces from the Okumimote site, situated in the northern district of Niigata, Japan, were used in this study. Nine pottery pieces were collected, together with related soil samples from four ruin sites: Achiyadaira, Shimozori, Miyasori, and Motoyashiki areas. From the archaeological view, the pottery samples were assumed to be manufactured and used about 3,500-6,000 years ago. During these periods, almost all pottery surfaces were decorated with some rope-shaped patterns, so that we called them Joumon (rope-pattern decorated) pottery. Soil samples of the sites where the pottery pieces were excavated were also collected to estimate the annual doses.

All procedures for the isolation of coarse quartz grain fractions have been done under the red light to avoid bleaching effects as low as possible. The samples were gently crushed in an agate mortar. Fine soil or clay constituents were washed out with water to allow relatively heavy and coarse grain parts to be collected. All grain fractions were treated with HCl solution. The etching procedure with concentrated HF for 6 hours followed to remove surface layer; then the surfaces were washed with water. After drying, heavy liquid separation (2.64-2.66 g/cm$^3$) with sodium polytungstate solution was carried out to purify the quartz fraction. Finally, quartz grains were sieved into 125-250 µm-sized particles.

2-2 Thermoluminescence color imaging and on-line TL-spectrometry
The characteristics of TL-coloration from quartz extracts were examined with a qualitative thermoluminescence color image (TLCI) technique and subsequently with an on-line TL-spectrometry (Hashimoto et al., 1997a).

Each TLCI was taken in the temperature range of 80 to 450°C. Because further quantitative information of detection wavelengths was needed, the on-line TL-spectrometry was carried out for the grain samples using a highly sensitive spectrometric system that included an image-intensifier photo-diode array (IPDA) detector. Based on both TLCI and TL-spectrometric results, the combination of optical filters and photomultiplier tube could be appropriately selected.

In the practical RTL-measurements, a photomultiplier tube (PMT, Hamamatsu, R-649S) with multi-alkali (Na-K-Sb-Cs) photon detection part was installed together with a filter combination of a red-glass filter (Toshiba, R-60) and an infrared-cut filter (Eagle) to reduce blackbody radiation starting from longer wavelengths. The BTL-measurements were carried out using a PMT (Hamamatsu, R-585S) with bialkali-photon sensitive surface and a blue-glass filter (Toshiba, B-390). The optical transmission properties of these filter combinations are indicated for BTL and RTL measurements in Figure 1.

![Transmittance as a function of wavelength for detection of RTL and BTL using optical filter combinations.](image)

2-3 Luminescence measurements
All of the luminescence measurements were carried out using a new automated TL/OSL-reader system, which has been developed for the SAR-method (Hashimoto et al., 2002a, Fattahi, M. and Stokes, S., 2000). This system was especially focused on the RTL-measurements from minerals, which have been recently expected to provide reliable luminescence dating from both quartz and feldspar grains (Fattahi and Stokes, 2003). In the SAR-method, every luminescence measurement with high sensitivity is required to fulfill the same conditions as well as in the case of the artificial irradiation on mineral samples. The measuring requirement was realized by using a light guide made of a core rod-type glass pipe (68 mm length, 11 mm diameter, manufactured by Nissei Denki Co. Ltd.), inserted between a sample vessel for luminescence and a PMT-surface. The use of a glass light guide also helped the elimination of thermal noise from the heater due to non-thermal conductivity. The artificial irradiations with the desirable doses were obtained using a small X-ray irradiator (Varian, VF-50J tube with W-target, 50kV, 1mA, 50W at maximum operation) instead of a commonly available radioactive-source. The advantages of this X-ray irradiator include the availability of variable dose settings by adjusting both applied voltages and currents of the tube, simple radiation protection without heavy shielding material, and uniformity of irradiated areas ascertained also by Andersen et al. (2003). Additionally, the use of a cooling fan for heater assembly allowed rapid
recycling TL-measurements (Hashimoto et al., 2002a, b).

To minimize the influence of black-body radiation at higher temperature beyond 300\(^\circ\)C, we made the heater area facing the PMT as small as possible. The heater was constructed by assembling four pieces of ceramic heater (heating power of 32Wx4) into one stack, which is readily controllable by a commercially available thermo-control unit (Okura, EC5800S). The background counts accompanied with rising temperature are shown in Fig. 2 in both cases of RTL and BTL-measurements. The present RTL-reader reveals an excellent low noise value (about 20 cps at 300\(^\circ\)C), compared with a reference background of about 75 cps at 300\(^\circ\)C (Fattahi and Stokes, 2000). This means that the present RTL-measuring system is applicable to the lower dose-samples, which leads to the possibility of recent sample dating and/or the necessity of small amounts of quartz grains for precious samples.

On the basis of preliminary experiments, the preheating condition after artificial irradiation was applied for 10 sec at 200\(^\circ\)C. The weight of the measured sample was always fixed to 5 mg. Additionally, the sensitivity changes associated with repeated measurement (heating)/irradiation cycles were confirmed to provide only negligibly small contributions for both RTL- and BTL-measurements (Yawata & Hashimoto, 2004). Therefore, the SAR-method was employed here without any correction of sensitivity changes.

**Figure 2.**
Dark counting rate of a blank silver pan on new automated luminescence measuring system. The photomultiplier tube (PMT, Hamamatsu, R-649S) for RTL was cooled at -20\(^\circ\)C, while the PMT for BTL (Hamamatsu, R-585S) was employed at room temperature. Filter combinations are described in Fig. 1.

**2-4 Estimation of annual doses**
Whenever the annual dose is evaluated from measurements of naturally occurring radioactivity for dried-soil material, the correction of water content in the as-received soil was required (Aitken, 1985). To estimate water contents, we dried the original soil samples on a hotplate. The heating condition was for 48h at 100\(^\circ\)C. The dried soil and crushed pottery samples were packed into a cylindrical plastic container (U-8). The samples were subjected to the \(\gamma\)-ray spectrometry using a germanium coaxial p-type detector connected with a multi-channel analyzer (EGPC 120-210-R, EURISYS Measurrs). By assuming a homogeneous distribution, one can calculate natural annual doses from the radionuclide concentrations in the radioactive equilibrium within uranium and thorium decay chains (Aitken, 1985). The potassium, uranium, and thorium contents were determined by the photo-peaks at 1460 keV of \(^{40}\)K and at 609 keV of \(^{214}\)Bi for the U-series, and by the peak of 583 keV of \(^{208}\)Tl for the Th-series, respectively.

**Figure 3.**
Contour maps of artificially induced TL from quartz extracts from pottery pieces. The quartz extracts of about 10mg were irradiated to X-ray doses of 2.7kGy: (a) No. 5 pottery piece from Achiyadaira, (b) No. 8 pottery piece from Miyasori.

**3 Results and discussion**

**3-1 TL-spectrometric results**
Two typical contour maps are illustrated in Figs. 3(a) and 3(b). A typical single-RTL peak in the
red-spectrometric region, consisting of 620 nm in wavelength and around 330°C, could be recognized in both the contour maps. All other quartz extracts from the present pottery pieces showed similar RTL-properties, in which an intense peak appears around 330-360°C in the red wavelength region of 600-650 nm. These RTL-properties of quartz extracts were excellently concordant with the TL color images photographed by a color-sensitive film, although a few quartz extracts showed blue grain components, probably due to feldspar contamination. The present result has also confirmed that quartz extracts from other burnt relics or pottery pieces have given RTL-properties without almost any exception (Hashimoto et al., 2001). Additionally, this result could support the explanation that quartz slices fired beyond 900°C can change from BTL into RTL, which is consistent with the RTL-nature of quartz grains from the volcanic ash layers (Hashimoto et al., 1996, 1997b). In these pottery pieces, although most RTL might be attributable to the effects of archaeological firing, there remains still now some possibility of contamination of the as-received RTL quartz grains, which were provided from a volcanically originating layer into clay minerals as raw material of the pottery.

In addition to these red-regions of 600-700 nm, the BTL (ranging of 350-500 nm), which has been used appropriately for the TL-dating of quartz extracts, was also employed for the purpose of comparison with the present pottery dating.

3-2 Luminescence measurements and dating results
The changes of both RTL and BTL-glowcurves by applying the SAR-method are shown in Figs. 4(a) and 4(b), for quartz extracts from the pottery piece of Achiyadaira. In the RTL-glowcurves, there exists two intense peaks around 230°C and 350°C. The former was induced by artificial X-ray irradiation, because natural TL (NTL)-glowcurve does not present any peak in this region. Alternatively, the natural RTL-glowcurve offered a broad peak in the high temperature region beyond 300°C. The integration temperature range was determined from 290°C to 360°C by using plateau tests, consisting of ratios of ATL (artificial TL)- to NTL-glowcurve as a function of heating temperature.

On the other hand, the BTL-glowcurves consist of broad spectra over 200 to 400°C. Such glowcurves are often observed in the case of thermally annealed feldspar grains when a preheating procedure was applied with the similar condition of 200°C for 10 sec. We assumed that some proportion of feldspar constituent was contaminated in the quartz extracts. However, the BTL-integration was done in the high temperature regions of 340-380°C. A similar difference between RTL- and BTL-glowcurves has been reported by the RTL-dating of quartz from Quaternary volcanoes by Montret et al. (1992). These authors also suggested that some contamination of feldspar components could be seen in BTL-glowcurves.

Figure 4.
Changes of glowcurves of RTL (a) and BTL (b) associated with artificial irradiation doses. Quartz extracts are obtained from No. 5 pottery piece.

The RTL- or BTL-values integrated over plateau regions as a function of regenerative doses brought on the corresponding response curves as shown in Figs. 5(a) and 5(b). It was noticed that every response curve of RTL from SAR-method gave different gradients from aliquot by aliquot, not only between different pottery pieces but also within the same piece. This means that the RTL-sensitivity properties reflect differently in each quartz grain as well as in each aliquot. In dose-response curves, the curves often give supralinear results over regenerative doses of 10-15 Gy in many cases, so that the growth curves were fitted using a polynomial curve.
Figure 5. Luminescence response curves as a function of regenerative doses. RTL (a) and BTL (b) are measured for a quartz aliquot from No. 5 pottery.

All results from RTL and BTL dating are summarized together with annual doses in Table 1. The experimental errors of equivalent doses are derived from two to four aliquot analyses. From the viewpoint of the equivalent doses, all of the RTL-values are found above 11.6Gy and up to 26.0Gy. On the other hand, the BTL-equivalent doses estimated usually give lower values than the RTL-ones. In four samples, no-BTL was detected even with the highly sensitive luminescence measuring system in our laboratory. It should be emphasized here that the quartz fractions from burnt samples such as pottery pieces tend to give the RTL-property, probably owing to the thermally heating process used during the manufacture of such material. Therefore, the RTL measurements are recommendable to evaluate accumulated dose.

The annual doses were evaluated from both crushed pottery pieces and surrounding soil. The former was used for β-ray contributions, while the latter was employed for γ-ray contributions by correcting water content. All annual doses are used to calculate mean value and standard deviations as indicated by two asterisks. There appears that two samples, including B-8 and B-10, differ greatly from the other pottery pieces. Since the radioactivity contents in the pottery are apparently dependent on the clay materials of pottery, these two pieces of pottery might be tentatively considered to have been manufactured in a different place from where the other pottery pieces were made.

The annual doses were utilized to calculate the TL-ages. The results are presented in the last three columns, together with ages predicted from the mode of pottery surface. Very good agreement exists between RTL-ages and the ones predicted within experimental errors. In advanced analysis, the authors are intending to improve RTL-measuring condition aiming towards the reduction of experimental errors, using the application of a single grain method (Yawata and Hashimoto., 2004). There exists a certain trend of giving shorter ages from BTL, as expected from the results of equivalent doses, in which some accumulated doses of BTL could not be detected. This underestimation of BTL-doses could arise from several factors, including the relatively unstable nature of BTL-source in comparison with the stable nature RTL (Hashimoto et al., 1993), tendency of BTL to bleach easily during sample storage, the presence of concomitant feldspar grains in the purified quartz fraction and so on. In the extreme case, the absence of BTL might introduce no-BTL emission in some burnt quartz. In fact, the BTL in quartz fractions from some volcanic origin has offered two or three orders lower than the RTL (Hashimoto et al., 1987).

The dominant presence of RTL-quartz has been recognized not only in materials of volcanic origin, but also in archaeologically burnt pottery. Consequently, the RTL from quartz grains has been considered a potentially useful dosimeter for the dating of thermal resetting events, such as archaeological burning of pottery, porcelain and stone as well as volcanic eruptions (Montret et al., 1992, Hashimoto and Fujita, 1999).

4. Conclusions

Most quartz grains extracted from burnt pottery pieces have shown strong RTL properties. Thus, the luminescence measurements involving RTL and BTL are applied to the estimation of the naturally accumulated doses for the quartz extracts from archaeologically burnt pottery pieces by applying the SAR-method.

The ages evaluated from RTL have revealed values in excellent agreement with the expected ages, whereas BTL gave relatively lower values or no-information about ages. Conclusively, the RTL-dating will be recommended for quartz extracts from archaeologically burnt pottery.

Some pure quartz grains without so much impurity, that originated from plutonic rocks, could be applied generally to the existing BTL-dating. In fact, Madagascar quartz slices of hydro-thermal
Table 1.
Comparison of equivalent doses and luminescence ages for pottery pieces using RTL- and BTL-measurements of quartz extracts.

<table>
<thead>
<tr>
<th>Pottery pieces</th>
<th>mode of Jomon pottery or Jomon stage</th>
<th>RTL equivalent dose (Gy)</th>
<th>BTL equivalent dose (Gy)</th>
<th>Annual dose (mGy/y)</th>
<th>RTL age (years B.P.)*</th>
<th>BTL age (years B.P.)</th>
<th>Predicted age (years B.P.)</th>
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<tr>
<td><strong>Activated</strong></td>
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<td>A-5</td>
<td>Minamisanjuinaba</td>
<td>13.1 +/- 4.0</td>
<td>6.3 +/- 1.4</td>
<td>3.47 +/- 0.11</td>
<td>3800 +/- 1150</td>
<td>1800 +/- 410</td>
<td>4000</td>
</tr>
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<td>A-8</td>
<td>Shino</td>
<td>17.3</td>
<td>n.d.</td>
<td>3.27 +/- 0.11</td>
<td>5300 +/- 180</td>
<td>n.d.</td>
<td>5000</td>
</tr>
<tr>
<td>A-14</td>
<td>KasoriB3</td>
<td>14.7 +/- 2.1</td>
<td>13.3</td>
<td>3.17 +/- 0.11</td>
<td>4600 +/- 670</td>
<td>4200 +/- 150</td>
<td>3500</td>
</tr>
<tr>
<td>B-8</td>
<td>later period of early stage</td>
<td>11.6 +/- 3.3</td>
<td>4.4 +/- 2.2</td>
<td>2.17 +/- 0.10</td>
<td>5300 +/- 1520</td>
<td>2000 +/- 1000</td>
<td>6000</td>
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<td>B-10</td>
<td>middle period of early stage</td>
<td>14.8 +/- 3.5</td>
<td>9.3 +/- 0.8</td>
<td>2.18 +/- 0.09</td>
<td>6800 +/- 1640</td>
<td>4300 +/- 410</td>
<td>6000</td>
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<td>B-12</td>
<td>early period of early stage</td>
<td>26.0 +/- 2.2</td>
<td>n.d.</td>
<td>3.69 +/- 0.12</td>
<td>7000 +/- 630</td>
<td>n.d.</td>
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<tr>
<td>A-18</td>
<td>later period of late stage</td>
<td>15.9 +/- 2.4</td>
<td>1.47</td>
<td>3.44 +/- 0.11</td>
<td>4400 +/- 710</td>
<td>430 +/- 10</td>
<td>5000</td>
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<td>A-23</td>
<td>Hanadumikasou</td>
<td>22.7 +/- 2.9</td>
<td>n.d.</td>
<td>3.01 +/- 0.12</td>
<td>7500 +/- 1000</td>
<td>n.d.</td>
<td>6000</td>
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<tr>
<td>B-18</td>
<td>later period of late stage</td>
<td>12.2 +/- 1.0</td>
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<td>3.17 +/- 0.13</td>
<td>3800 +/- 360</td>
<td>n.d.</td>
<td>3500</td>
</tr>
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</table>

3.06 +/- 0.51** n.d.: Not determined

*: B.P.: before present (2000)
**: mean and standard deviation

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References


Reviewer
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