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Abstract: Laboratory annealing experiments were performed to examine the effect of heating on the thermoluminescence (TL) of quartz phenocrysts from dacite. The total number of photons emitted in the temperature range 100-450°C was counted using a highly-sensitive TL system in order to characterize the decay of TL normalized to natural quartz. Fitting the results at each heating temperature gave a power function that can be used to calculate the TL reduction ratio for arbitrary annealing temperatures and times. The TL reduction lines are curved in an Arrhenius plot, indicating that the activation energy varies even within the experimental temperature range. The plot shows that TL emission decays by up to 50% when heated at 50°C for less than tens years without the generation of luminescence traps. In addition, during the process of annealing, the peak position in the glow curves shifts linearly to higher temperatures with decreasing TL intensity, implying that it is possible to estimate the initial intensity and that such samples are datable by conventional TL methods.

1. Introduction

The thermoluminescence (TL) dating method for quartz is used in various fields of geoscience, including volcano-stratigraphy (Shimao et al., 1999), fault movement (Lin, 1989), and geothermal exploration (Takashima, 1985). However, the obtained ages themselves have proved difficult to interpret, and in some cases differ from those determined by other techniques. One of the reasons for this is probably due to the susceptibility of the TL signals to heating. Aitken (1967) showed this through an analysis of the mean lifetime of trapped electrons as a function of the glow peak temperature. At a 20°C ambient temperature, the mean lifetime for glow peak at 300°C, the common temperature of natural quartz, is 10 ka. Takashima and Reyes (1990) estimated the thermal history of a Philippine geothermal area based on annealing experiments at 200°C using dated quartz. Tsuchiya et al. (2000) divided the TL glow curves of quartz from a geothermal field into L (low), M (medium) and H (high) bands in relation to surface geothermal manifestations. They showed that the total TL intensity of quartz is reduced by geothermal events, seen as a weakening of the L peak in active areas and suppression of H peak emission towards the center of geothermal activity.

To determine quantitatively the stability of trapped electrons, the present authors performed annealing experiments on quartz phenocrysts from dacite. The mineral was heated at 100, 125, 150, 175 and 200°C, for $10^{-1}$ to $10^{3}$ h (6 min to 40 days), and rate of total TL emission reduction at the different heating temperatures was fitted using a power function. This approach proved useful for obtaining a general function that can be used to calculate the reduction ratio for arbitrary heating times and temperatures. Through this analysis, it was

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found that the peak of the glow curves shifts linearly to higher temperatures with decreasing TL reduction ratio. This may assist in the estimating of initial TL intensity before annealing, allowing samples to be dated using conventional TL dating methods.

2. Samples and experimental methods

Quartz phenocrysts were separated from a dacite sample obtained at Hosenji, Konoe Town, Oita Prefecture, Japan (33°11'05"N, 131°10'35"E). The K-Ar age of the whole rock is 0.69 ± 0.08 Ma (UTO and SUDO, 1985). The rock is a hornblende dacite with quartz phenocrysts of up to 1.5 mm in diameter. About 10 kg of the rock was crushed, performed while immersed in water in order to suppress frictional heat. After drying the crushed rock at below 100°C, the material was sifted to collect grains of 0.5-1.0 mm in diameter. Magnetic grains were removed using a hand magnet. The remaining non-magnetic grains were then treated with HF (48%) at room temperature until feldspar, the major constituent, had dissolved. The remaining quartz was then soaked in the same solution for 1 h, at which the TL emission became strongest due to the disappearance of other materials adhered to the quartz grains.

Three-dimensional spectrograms of TL from the purified quartz were measured using a spectral analyzer (PMA-100, Hamamatsu Photonics). As shown in Fig. 1, the quartz produces a broad TL emission from 200 to 370°C with a wavelength peak at 620 nm. These characteristics support the categorization of this sample as a typical red TL-emitting quartz (HASHIMOTO et al., 1986a). According to the experimental data of SHINNO et al. (2001), the emission at 305°C is caused by Al centers.

About 30 mg of the quartz grains were placed on a platinum plate and heated at 100, 125, 150, 175 and 200°C for 0.1-1000 h using a thermostated hot stage (LK-600PM, Linkam) with heater (THMSG 600, Linkam) attached to the TL-measuring system (Fig. 2).

In order to detect weak TL emissions quantitatively, a highly-sensitive TL-measurement system similar to that constructed by HASHIMOTO et al. (1986b) was developed. The natural and heated quartz grains were set on the heater and heated from room temperature to 450°C at 1°C/s. The emitted TL signals were then detected after passing through an infra-red cut-off filter (IRC-65L, Kenko) by a multialkali photomultiplier tube (R649, Hamamatsu Photonics), which was sensitive to photons with wavelength of 500-700 nm. The photomultiplier tube was cooled to -30°C using a cooling system consisting of an electronic cooler (C4877, Hamamatsu Photonics) and a photomultiplier cooler (C2761, Hamamatsu Photonics). The number of photons per second in the temperature range 100–450°C was recorded by a photon counter (C5410, Hamamatsu Photonics). A personal computer was used to control the system.

Unbroken grains were examined under stereoscopic microscope, avoiding broken grains which may have
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been affected by frictional heat during crushing. TL emissions were measured 10 times for each of the natural and heated samples, and the number of photons emitted in the temperature range 100-450°C was averaged. The TL intensities referred to hereafter represent the total numbers of photons minus the number of incandescent photons emitted in the same temperature range.

3. Results

Natural quartz begins to emit TL at 120°C, with a broad peak at 310°C in the glow curve (Fig. 3). The total number of photons emitted in the 100-450°C range is 1.43×10⁶ per mg. As the annealing temperature and/or annealing time increases, the peak moves to higher temperatures and the total TL intensity weakens (Table 1).

Fig. 4 shows the results of the annealing experiment. The TL intensity reduction rate (R) is expressed by the ratio of TL intensity of the heated sample (I) to that of natural quartz (I₀). Each set of data at a given heating temperature can be fitted with a power function as follows.

\[ R_{100} = 1 - 10^{-0.69 \log(s) + 0.15} \] at 100°C (1)
\[ R_{125} = 1 - 10^{-4.79 \log(s) + 0.24} \] at 125°C (2)
\[ R_{150} = 1 - 10^{-2.27 \log(s) + 0.67} \] at 150°C (3)
\[ R_{175} = 1 - 10^{-3.16 \log(s) + 0.69} \] at 175°C (4)
\[ R_{200} = 1 - 10^{-1.01 \log(s) + 0.49} \] at 200°C (5)

where s is the annealing time in seconds. All the equations have correlation coefficients of greater than 0.99.

The constant \( a \) in the equation \( R = 1 - 10^{a \log(s)} \) becomes larger with increasing heating temperature, as given by the following linear function.

\[ a = 0.0382t - 9.360 \] (r=0.993) (6)
1.0
1h 1w 1m 1yr 10yr

0.8
0.6
0.4
0.2
0.0
0.0
2
4
6
8
10

LOG HEATING TIME (s)

TL INTENSITY REDUCTION (R=ln)

Fig. 5 Extrapolation of TL intensity reduction from experimental data.

where \( t \) is the annealing temperature in degrees Celsius and \( r \) is the correlation coefficient. The constant \( b \) can also be expressed by a linear function that is inversely proportional to the heating temperature:

\[
b = -0.0337t + 9.776 \quad (r=0.992)
\]  

(7)

Finally, an equation for calculating the TL intensity reduction ratio for any annealing temperature and time can be derived as follows.

\[
R = 1 - 10^{0.0382(t-9.360)(\log t)(-0.0337t + 9.776)}
\]

(8)

Using this equation, the relationship between the TL intensity reduction rate and the heating temperature and time (Fig. 5) can be constructed by extrapolating to longer heating times and lower heating temperatures. It can be deduced from the figure that at a constant temperature, the TL intensity reduction proceeds slowly in the initial stage of heating, but later becomes more rapid with an almost constant speed. The heating time required to reach this constant reduction rate becomes longer as the heating temperature becomes lower.

Fig. 6 shows an Arrhenius plot of the 0, 0.50 and 0.75 TL intensity reduction lines (100, 50 and 25% loss, respectively), which were also drawn using the equation (8). It should be noted that the isopleths of TL intensity reduction (for example, \( R = 0.50 \)) are not linear in the Arrhenius plot. All three curves are steep at higher temperatures, and gentler at lower temperatures, with the largest curvature at intermediate values. The \( R = 0.50 \) line passes the points of 100°C/0.6 yr, 50°C/5.6 yr, and 25°C/14 yr, suggesting that considerable heating-induced weakening of TL signals occurs even under natural conditions.

As mentioned above, the peak temperature of the glow curves increases as the total TL intensity decreases. Fig. 7 shows this relationship at different heating temperatures and times giving the following linear function.

\[
R = -0.116t + 4.57 \quad (r=0.991)
\]

(9)
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where $t_p$ is the peak temperature. When the normalized TL intensity decreases to as low as 0.01, the peak disappears to form a shoulder-type glow curve.

**4. Discussion**

In fission track studies, many annealing experiments have been carried out in order to estimate the thermal history of rock formation (e.g., OSAKI et al., 1978; SAINI et al., 1982; YAMADA et al., 1995). All of the results are expressed in straight lines on the annealing time-temperature diagram (Arrhenius plot). In the results of this study, however, the isopleths of the normalized TL intensity are curved, with various curvatures appearing on the plot (Fig. 6). This means that the apparent activation energy is variable, even under the experimental conditions of 100-200°C. Accordingly, the experimental data cannot be extrapolated linearly to lower temperatures, and as such it should be pointed out that linear extrapolation to geological time scales may lead to serious errors in the estimation of heating time.

It was revealed through this experiment that the TL signals of quartz are unstable with regard to heat. For example, the TL signal weakens by 27% when heated at 100°C for just 1000 h (Fig. 3). Extrapolation of this data implies that the TL signal will weaken by 50% when heated at 50°C for several years (Fig. 5) or after just ten years when heated at 25°C (Fig. 6). This period of 50% intensity loss is much shorter than the mean lifetime reported byAITKEN (1967) of 10 ka at 20°C. This discrepancy may be partly due to the variable activation energy with temperature as seen on the Arrhenius plot (Fig. 6).

The weak heat-resistant nature of quartz TL emission implies that the equivalent dose in the TL dating method cannot be precisely determined by irradiation using an artificial source such as $\alpha$, $\beta$ and $\gamma$ rays. The artificial TL signals are measured after a much shorter period of time compared to the age to be dated considering that partial annealing will occur even at ambient temperatures. Accordingly, it is strange that quartz TL ages determined by the conventional method are reasonable in most cases. The weakening and accumulation of TL over geological time must therefore have a more complicated explanation, and the continuous generation of luminescence in nature must be taken into consideration.

One of the applications of these experimental findings is that the TL ages from quartz in altered rock or fault gouges may show the age of thermal events such as hydrothermal alteration and faulting, as the TL signals appear to be easily reset. HAYASHI (1997) indicated that TL ages of quartz phenocrysts appeared to reflect alteration ages even in low-temperature rocks with cristobalite-smectite assemblages. In addition, the glow curves of quartz from steaming ground are shoulder-type curves without a clear peak and with only weak emissions at high temperatures. This suggests that the TL signals had decayed by more than 99%, as estimated from Fig. 7. For quartz in fault gouges, TL and electron spin resonance (ESR) ages may indicate the time of faulting because previously accumulated TL signals will have been reset by frictional heat during the event (TANAKA, 1989). However, the reset might occur at considerable depth where ground temperatures cannot be overlooked from the viewpoint of TL annealing. Most TL and ESR ages of thousands to tens of thousands of years (TANAKA, 1989; LIN, 1989) may reflect such geologic setting.

TSUCHiya et al. (2000) divided the TL glow curves of quartz from the Kakkonda geothermal field into L (low), M (medium) and H (high) bands in relation to surface geothermal manifestations. They insisted that the total TL intensity of quartz is unrelated to the stratigraphy and is weakened by the geothermal event. That is, the L peak is lower in active areas, and H peak emission is reduced towards the center of geothermal activity. These facts support the present results, indicating that the initial TL intensity before heating decreases gradually with increasing temperature and time. Consequently, the TL behavior of minerals can be applied to estimate the paleo-temperature history in the low-temperature range.

As TAKASHIMA and REYES (1990) indicated, another point of interest is the peak shift towards higher temperatures during the annealing process (Figs. 3 and 7). As the peak shift forms a linear relation with TL intensity reduction, the initial intensity of the partially annealed mineral before heating can be calculated. This relation will be useful for dating minerals using the conventional TL methods. However, the peak position of the glow curves varies not only with the mode of electron trapping in crystals but also with experimental conditions such as heating rate, grain size, and the volume of
material. Careful examination will therefore be necessary for dating partially annealed samples.

5. Conclusions

This study showed that the TL emission from quartz decreases gradually during the process of annealing, even under natural conditions. The major findings of this study are summarized below.

1. The quartz sample examined was typical red TL-emitting quartz producing a glow curve with a broad peak at 310°C and emitting about $1.43 \times 10^6$ photons per mg.
2. The peak of the glow curve was found to shift linearly to higher temperatures with decreasing total TL intensity. The initial intensity can then be estimated using this relationship.
3. A power equation was proposed for calculating the normalized TL intensity reduction rate for arbitrary heating temperatures and times.
4. The unstable nature of quartz TL emission implies that the equivalent dose in the conventional TL dating method cannot be precisely determined by irradiation with artificial sources.
5. The isopleths of the normalized TL intensity reduction rate on an Arrhenius plot are curved, with various curvatures, indicating that the activation energy varies with temperature.

References