Quartz glow-peaks lifetime analysis : Tl glow-curve deconvolution functions for first order of kinetic compared to Initial Rise Method

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Quartz is a thermoluminescent material which has been used since the 60s for dating samples like potteries, flint, etc., but the method is still subject to some improvement. One of the problem of thermoluminescence dating is the estimation of the lifetime of the used peaks. The application of the glow-curve deconvolution (GCD) technique for the analyses of a composite thermoluminescence glow curve into its individual glow peaks has been applied widely since the 80s. Many functions describing a single glow peak have been proposed. For analysing quartz behaviour, thermoluminescence glow-curve deconvolution (GCD) functions are compared for first order of kinetic. The free parameters of the GCD functions are the maximum peak intensity (Im) and the maximum peak temperature (Tm), which can be obtained experimentally. The activation energy (E) is the additional free parameter. The lifetime (τ) of each glow peak, which is an important factor for dating, is calculated from these three parameters. For lifetime analysis, GCD results are compared to those from initial rise method (IRM). Results vary fairly from method to method.

1. INTRODUCTION

Quartz is one among the different materials used for thermoluminescence dating. One important point of this issue is the estimation of the lifetime of the used peak. Several methods were used, and initial rise method (IRM) is one among these methods. Results with these methods are quite similar and seem to be promising because of the calculated lifetime long enough for dating [1]. Besides, the application of the glow-curve deconvolution (GCD) technique for the analyses of a composite thermoluminescence glow curve into its individual glow peaks has been applied widely since 1980. Many functions describing a single glow peak have been proposed.

The aim of the present work is first of all to compare two different programs for deconvolution, and secondly to compare the glow peaks lifetime calculation results from deconvolution to those from IRM. For the GCD, the program developed by J. M. Gomez-Ros and A. Delgado (CIEMAT, Spain) and the one developed by A. J. F. Ratovonjanahary et al are compared. First-order kinetic is used for both and with second order approximation.

The mineral used as TL material is quartz, and all the TL irradiation and TL reading are performed at "GSF-Forshungszentrum fuer Umwelt und Gesundheit" – Munich – Germany, at the TL-OSL unit of the Radiation protection department.

2. DECONVOLUTION

As well the GCANEW program that GCDMAD uses the first-order kinetic with an approximation of the second order. In that condition, the kinetic equation is given by:

$$I(T) = I_m \exp\left[1 + \frac{E}{kT}\frac{T - T_m}{T_m} - \frac{T^2}{{T_m}^2}\exp\left(\frac{E}{kT}\frac{T - T_m}{T_m}\right)(1 - \Delta) - \Delta_m\right]$$

Where $\Delta = \frac{2kT}{E}$, $\Delta_m = \frac{2kT_m}{E}$, I is the glow-peak intensity, E (eV) the activation energy, T (K) the heating temperature, Im the maximum intensity and Tm the temerature at which Im occurs. For fitting glow cuve, GCDMAD uses Marquardt Method.

3. FIGURE OF MERIT (FOM)

A possibility to be taken as a measure of the goodness-of-fit is a figure of merit originally defined by Balian and Eddy [4] and Misra and Eddy [5] which has proven very useful:

$$FOM = \sum_{j_i}^{j_f} \frac{100\left|y_j - y(k_j)\right|}{A}$$

Where FOM = Figure Of Merit (%), j_i = first channel in the region of interest, j_f = last channel in the region of interest, y_j = information content of channel j, $y(x_j)$ = value of the fitting function in channel j,

A = integral of the fitted glow-curve in the region of interest.

Glow-curves with FOM values in excess of 5% are subjected to further investigation to determine the reasons for the poor fit.

4. THE INITIAL RISE METHOD

At the start of a glow-peak the thermoluminescence is proportional to exp(-E/kT), irrespective of whether first-order kinetics are obeyed or not. This temperature dependence continues until the number of electrons remaining trapped decreases significantly. Hence by plotting Log(thermoluminescence intensity) versus T-1 the value of E can be obtained from the slope of the straight line obtained. To avoid error due to a decrease in the number of electrons remaining trapped, it is necessary to restrict the temperature range such that the thermoluminescence intensity reached does not exceed one-tenth of the peak intensity. Of course, overlapping peaks on the lower edge of the peak under study need to be removed by prior thermal treatment.

A drawback with this method is that if the relevant luminescence centres are subject to thermal quenching, too low a value is obtained for E. This can give rise to a value for the lifetime that is totally erroneous.

Tm can be obtained from the TL glow curve intensity by sorting out TL intensity values.

5. GLOW-PEAKS LIFETIME

Prediction of lifetime for the thermoluminescence peak of a mineral is helpful in establishing the likely time range over which it will be useful. The lifetime in the case of first-order kinetics is given by

$$\tau = s^{-1} \exp\left(\frac{E}{kT}\right)$$

Besides checking that a dating peak has adequate stability, determination of lifetime is also relevant with respect to the kinetic methods of annual dose evaluation.

6. QUARTZ GLOW-PEAKS LIFE-TIME ANALYSIS

6.1. Deconvolution

6.1.1. Quartz grains irradiation and read out

The Merck Ltd. Company supplies the used quartz grains. These are pure and natural quartz grains from Brazil. Quartz grains have preliminary been treated: crushed, washed with chlorhydric acid, then heated at 90°C.

For TL measurements, TL/OSL-DA-12 is used. This reader has a turntable containing 24 gap for planchet carrier and where one put the sample. This reader is equipped with incorporated 90Sr for beta source irradiation.

Five samples of nearly the same amount are put on five different planchets. Each of them is preliminary heated 15 minutes at 500°C in order to ensure that all electrons traps are empty. Then, they are irradiated by approximately 10Gy of beta irradiation from 90Sr. After irradiation is the read out with maximum temperature of 500°C and ramp time of 100sec, i.e. of a heating rate of 5°C/sec.

6.1.2. Deconvolution results

Each glow-curve obtained after read out are deconvoluted. For the deconvolution, the program developed by J. M. Gomez-Ros and A. Delgado (CIEMAT, Spain) and the one developed by A. J. Franck Ratovonjanahary (Madagascar-INSTN) are compared. First order kinetic is used for both ad with second order approximation.

The CIEMAT program is called GCANEW and the one performed by Madagascar-INSTN is called GCDMAD.

The results from these different programs are summarised in the following table.

Table 1: Comparison of results from GCDMAD and GCANEW

Peaks positions	Tm (°C)	E (eV)	τ *	FOM (%)
GCDMAD				
Peak1	115.9 ± 0.2	1.0056 ± 0.0008	1.103 ± 0.009 d	
Peak2	146.9 ± 0.3	0.94 ± 0.01	5.6 ± 0.8 d	
Peak3	178.6 ± 0.2	1.044 ± 0.004	161 ± 9 d	1.76 ± 0.03
Peak4	219.8 ± 0.4	0.789 ± 0.005	33 ± 3 d	
Peak5	277.6 ± 0.4	1.03 ± 0.01	70 ± 20 y	
Peak6	397.7 ± 0.3	1.051 ± 0.004	7300 ± 700 y	
GCANEW				
Peak1	116.2 ± 0.2	1.0060 ± 0.0007	1.132 ± 0.007 d	
Peak2	147.2 ± 0.3	0.94 ± 0.01	5.6 ± 0.9 d	
Peak3	178.9 ± 0.2	1.043 ± 0.004	163 ± 9 d	1.64 ± 0.03
Peak4	220.5 ± 0.4	0.788 ± 0.005	34 ± 3 d	
Peak5	278.2 ± 0.4	1.03 ± 0.01	70 ± 20 y	
Peak6	398.7 ± 0.3	1.051 ± 0.004	7600 ± 700 y	

The table1 shows that these two deconvolution results are quite the same. Both of the program use 1st order kinetic second orders approximation, i.e. generally the same kinetic equation. The very slight difference between these results come from the difference of truncation.

This result can also easily be seen in the figure1. Glow peaks from the two programs are quite the same.

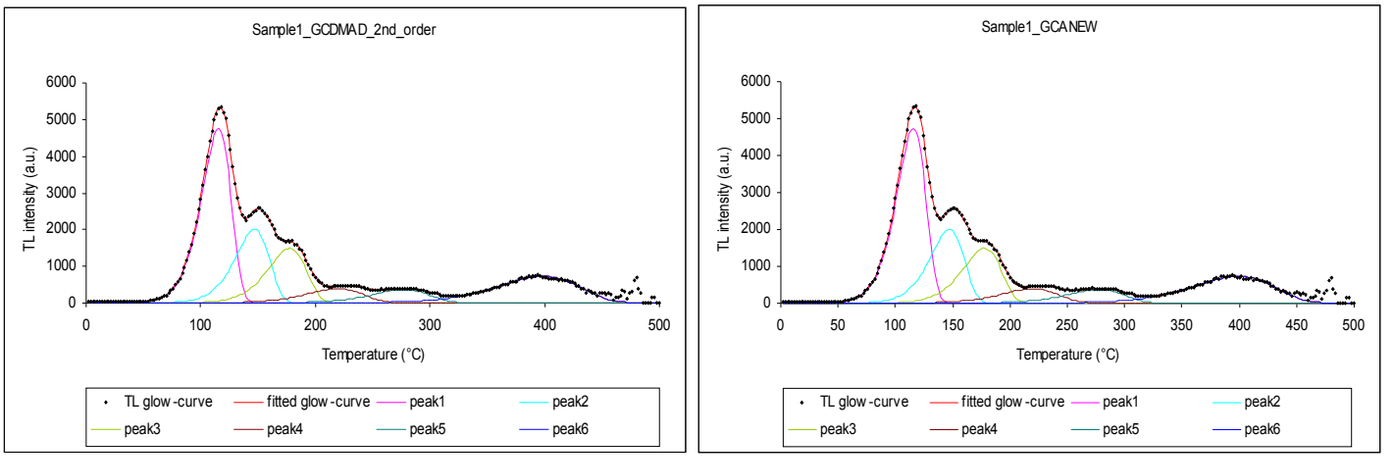

Figure1: An example of TL glow-curve deconvolution. The two figures show the same glow-curve but the one in the left is deconvoluted by GCDMAD and the one in the right by GCANEW. Quartz grains are irradiated by 10Gy of β-source.

6.2. Initial Rise Method (IRM)

Five samples of nearly the same amount are put on five different planchets. Each of them is preliminary heated 15 minutes at 500°C in order to ensure that all electron traps are empty. Then, they are irradiated by approximately 10Gy of beta irradiation from 90Sr.

The peak under study is peak6 appearing at about 400°C because of its half-life higher than all the other peaks.

As overlapping peaks on the lower edge of the peak under study need to be removed by prior thermal treatment, after irradiation is the read out with maximum temperature of 300°C and ramp time of 150sec, i.e. of a heating rate of 2°C/sec. The choice of 2°C/sec is to have a heating rate slow enough for emptying all electrons traps on the lower edge of the peak under study.

After the prior thermal treatment is the read out with maximum temperature of 500°C and ramp time of 100sec, i.e. of a heating rate of 5°C/sec (the same as for the running sequence for deconvolution in order to have the same condition for the best comparison).

By plotting Log(I) versus T-1 the value of E can be obtained from the slope of the straight line obtained.

Table 2: Peak6 lifetime result from IRM. The lifetime is calculated from the mean value of E and Tm.

	E (eV)	**T_m (°C)**	**τ (years)**
Mean values	1.44	402	49 000 000
uncertainties	0.006	1	7 000 000

The table2 shows clearly that the initial rise method gives lifetime value too much greater than the ones calculated by deconvolution. Further analysis showed that the combination of results from IRM and first order kinetic equation is not compatible with the measured glow-peak. Thus, one can say that IRM is not compatible with first order kinetic.

7. CONCLUSIONS

(i) The estimation of the lifetime of the used peak is crucial because it should be long enough for estimating the age of a certain object. IRM seems to be promising because of its long enough lifetime result (table2). However, the latter method is not fully reliable. Firstly, the prior thermal treatment may not be complete because of the overlapping peaks on the lower edge of the peak under study, which is difficult to remove completely. Therefore, at the start of the glow-peak, the thermoluminescence is not really proportional to exp(-E/kT). Secondly, the prior thermal treatment permit to have a single glow-peak which does not follow the first order kinetic.

(ii) GCD is the best way of analysing TL glow-curve. Indeed, This method is proved to be accurate. Firstly, with FOM test which is an accurate testing method, result (table1) shows that the quartz TL glow-curve is really in concordance with first order of kinetics model.

Secondly, the GCD function for first-order kinetics produced in the GCANEW was used to analyse ten reference glow curves. The results were compared with results of the intercomparison presented in [6, 7]. The comparison shows that the proposed first-order kinetic function is among the best of the 13 functions studied in [6, 7] and it is more accurate than other similar approximations previously used [5,8].

(iii) For comparison, results from GCDMAD are very close to the ones from GCANEW. That is normal because these two programs use the same kinetic function. The small difference on the results come from a difference of truncation.

(iv) Peak lifetime from GCD is much shorter than the one from IRM (table 1 and 2). For dating purpose, it is much more convenient to consider IRM results because the high length of used peak lifetime permit to work without any corrections. However, it may lead to misinterpretation if GCD results are considered. In fact, for example for dating an object of around thousand years old, TL dating is possible because the age of the object is less than the used peak lifetime irrespective of whether IRM or GCD is used. However, considering GCD results, some correction on dating estimation are necessary.

(v) Our perspective work is to discover the law followed by the degradation of the used peak with time in order to be able to bring the adequate correction to the dating process.

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