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THE PARAMETERS OF TRAPS IN K-FELDSPARS AND THE TL BLEACHING EFFICIENCY

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Abstract: The fractional glow technique (FGT) applied to the investigation of optically bleached samples of K-feldspars extracted from sediments reveals the coexistence of various groups of traps which are active in the same temperature region over 300 °C. Significant differences between the trap parameters seem to explain the diversity of TL bleaching efficiency for different trap groups.

1. INTRODUCTION

In the luminescence dating of sediments one assumes that grains lose their thermoluminescence (TL) or optically stimulated luminescence (OSL) signal before deposition as a result of optical stimulation which in this case is caused by sunlight. After such a reset of the TL/OSL signal of the sediment the natural nuclear radiation constantly delivers energy which is accumulated in mineral grains in the form of trapped charge carriers. The natural TL/OSL signal measured in a dating laboratory is then a measure of the time elapsed from the mineral deposition, i.e. from the moment of optical bleaching (Aitken, 1985 and 1998).

For many years the main problem in luminescence dating has been the lack of an objective method which allows one to prove that the sediment TL/OSL signal has been properly reset before deposition. It is believed that in the OSL method only traps which are very efficiently depopulated by light are used but still it is unknown whether the sunlight bleaching was enough long and effective. These "reset problems" have given rise to investigations of bleaching mechanisms and carrier transfer in minerals. The so-called "residual TL" (McKeever, 1994) connected with the difficult-to-bleach fraction of traps, is a particularly interesting object of study.

Feldspars and quartz are the most commonly used minerals in sediments dating. This work presents the results of parameter investigation for those traps involved in the bleaching process in K-feldspars. Optical bleaching changes the shape of the K-feldspar normal glow curve (**Fig. 1**). The sensitivities to bleaching of two TL peaks around 200 °C differ significantly. The 200-400 °C temperature region, being of interest because of its luminescence kinetics, is investigated here by means of fractional glow technique (FGT) (Gobrecht and Hofmann, 1966; Oczkowski, 1978 and 1981).

FGT measurements have been carried out on a K-feldspar sample after various times of optical bleaching. Chruścińska (2001) found that deeper traps over 1.6 eV are much more easily depopulated by light than shallower traps of depth about 1.4 eV. The experiments presented here concentrate on a high temperature edge of the glow curve. Optical bleaching reveals the complex origin of TL in this region.

2. EXPERIMENTAL TECHNIQUE

K-feldspar was separated from sediment from Finland in the usual manner for TL dating and heated to 500 °C before excitation. TL was excited by an X-ray dose of 360 Gy (6 h of irradiation). Bleaching was undertaken in a sunlight simulator using the spectral range of 300-750 nm (Oczkowski and Przegiętka, 1998). Preheat to 310 °C at a rate of 1 °C/s was applied before the FGT measurement. The wave band 390-440 nm, normally used in TL dating, was employed as the spectral window for all measurements. A Schott BG-2 filter was installed in the light detection unit. Fractional TL intensity after 20 h of bleaching in the simulator is still above the sensitivity limit of optical detection when the EMI 6097 B photomultiplier and lock-in technique is used.

The FGT introduced by Gobrecht and Hofmann (1966) consists in registration of the TL intensity during both linear heating and cooling of the sample which are carried out in a cyclic way. The sample heating from temperature T_1 to T_2 and subsequent cooling to temperature $T_1 + \Delta T$ make one cycle. In the next cycle heating is carried out to temperature $T_2 + \Delta T$ and cooling to temperature $T_1 + 2\Delta T$. The direct result of the experiment is the sequence of trap energies E_i (i – numbers of the cycles; symbol plots in Figs 2 and 5), and integrals of the TL intensity, L_i, measured in the cycle. The trap energy is calculated separately for heating (E_{ih}) and cooling (E_{ic}) by means of linear regression applied to dependencies

$$\left[\frac{d\ln I}{d(1/T)}\right]_{ih} = -\frac{E_{ih}}{k}, \tag{2.1}$$

$$\left[\frac{d\ln I}{d(1/T)}\right]_{ic} = -\frac{E_{ic}}{k}, \tag{2.2}$$

where indexes "h" and "c" denote dependence and values obtained respectively for heating and cooling, k is the Boltzmann constant, T is the temperature, I is the TL intensity. E_i is the mean of values E_{ih} and E_{ic} taken with the factors dependent on the heating (w_{ih}) and cooling (E_{ic}) rates in the cycle

$$E_i = E_{ih} + \frac{w_{ic}}{w_{ih} + w_{ic}}\left(E_{ic} - E_{ih}\right). \tag{2.3}$$

The details of reasoning as well as the calculation leading to the above formula are presented in earlier work (Chruścińska, 1994).

The histograms of the trap occupation spectra (histograms in **Figs 2** and **5**) are calculated using the distribution function (Chruścińska, 1994):

$$H_i(E) = \frac{L_i}{\left|E_{i-1} - E_i\right|}, \tag{2.4}$$

where H_i (E) denotes the relative number of traps of energy E emptied during i-th cycle. The final trap occupation spectrum is calculated taking into consideration the possibility of overlapping of H_i (E) obtained for different cycles.

The TL facilities used for FGT with heating-cooling correction (Chruścińska, 1994 and Chruścińska *et al.*, 1996) enables linear heating and cooling with the average rate of about 0.1 °C/s. The trap depth was determined with use of data collected only in that part of the cycle, during which the heating and cooling were linear. The temperature was repeatedly increased by 12 °C and lowered by 10 °C starting at 200 °C, up to 330 °C. It is the high temperature edge of the fractional glow curve. The whole procedure consists of about 40 heating-cooling cycles.

3. MEASUREMENT RESULTS

One complex peak can be observed in the glow curve of an 10 mg aliquot of unbleached K-feldspar after fast preheat (carried out at the heating rate of 1 °C/s) to 310 °C (**Fig. 1**). The TL curve shape changes after bleaching but still only one maximum is detected.

Fig. 2 (upper part) presents the results of FGT measurements carried out after a dose of 360 Gy and preheat to 310 °C. Energy levels of about 1650 and 1800 meV can be distinguished. The lower part of **Fig. 2** shows the results obtained for samples after a dose of 360 Gy, 20 hours of bleaching and preheat to 310 °C. Two trap groups are again observed but their depths are about 1380 and 1460 meV.

The glow curve shown in **Fig. 3** was measured with the heating rate of 0.05 °C/s after a dose of 360 Gy, 20 hours of bleaching and preheat to 310 °C. **Fig. 4** shows the glow curve measured with the lowest heating rate of 0.01 °C/s after a dose of 360 Gy and preheat to 310 °C. The calculated curves were fitted to the experimental glow curves in both cases. The fitted curves were calculated using the trap energy spectrum obtained from FGT. Initially monomolecular kinetics and a quasi-continuous trap depth distribution were assumed. However, the fitting results were highly disappointing.

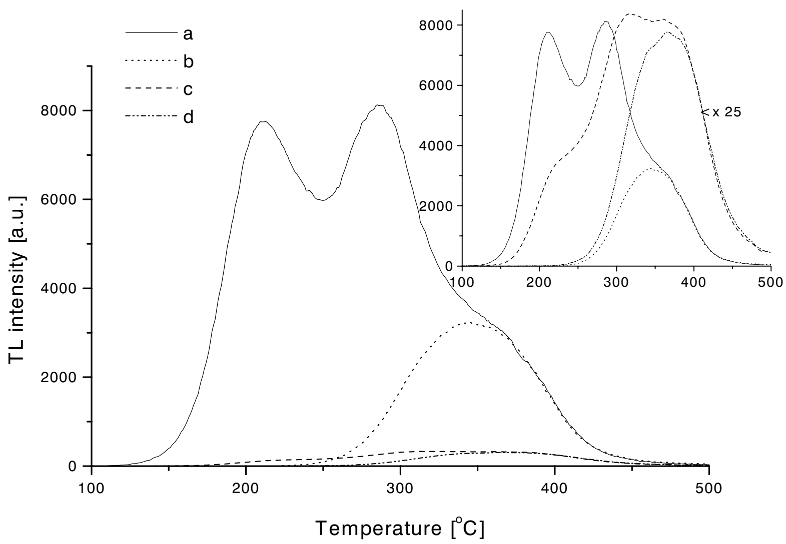

Fig.1. *Glow curves of K-feldspar measured after a dose of 360 Gy: after preheat to 200 °C (a), after preheat to 310 °C (b), after 20 hours of sunlight bleaching and preheat to 200 °C (c) or to 310 °C (d). Heating rate 0.8 °C/s. Inset presents the changes of the curve shape after bleaching more clearly.*

Figs 3 and **4** show the results of fitting, assuming second-order behaviour. A discrete trap spectrum is also assumed. The TL intensity was calculated accordingly to the following formula:

$$I = \sum_{i=1}^{n} \sigma_i \eta_i^2 \exp\left(\frac{-E_i}{kT}\right) \left[1 + \left(\frac{\sigma_i \eta_i}{w}\right) \int_{T_o}^{T} \exp\left(\frac{-E_i}{kT'}\right) dT' \right]^{-2}, \quad (3.5)$$

where i is the trap kind index, σ_i and η_i are numerical parameters related, respectively, to the pre-exponential factor s' and to the initial trap occupation, E_i is the trap depth, k is the Boltzmann constant, T is the temperature, T_0 is the initial temperature and w is the heating rate.

In the case of bleached curve (**Fig. 3**) the calculated curve is the sum of two bimolecular curves (n=2 in Eq. (3.5)) calculated for the energy values of 1380 meV and 1460 meV in accordance with two energy levels marked in the FGT histogram (**Fig. 2B**). The parameters σ and η used for fitting are presented in Table1.

The question arises whether the shallower (<1500 meV) traps were already occupied after irradiation or, alternatively, they retained a very low population, but the bleaching process caused the carrier transfer from other traps. The second possibility seems to be rather unrealistic. The glow curve characteristic for long optical bleaching is very similar to the glow curve after a small dose –

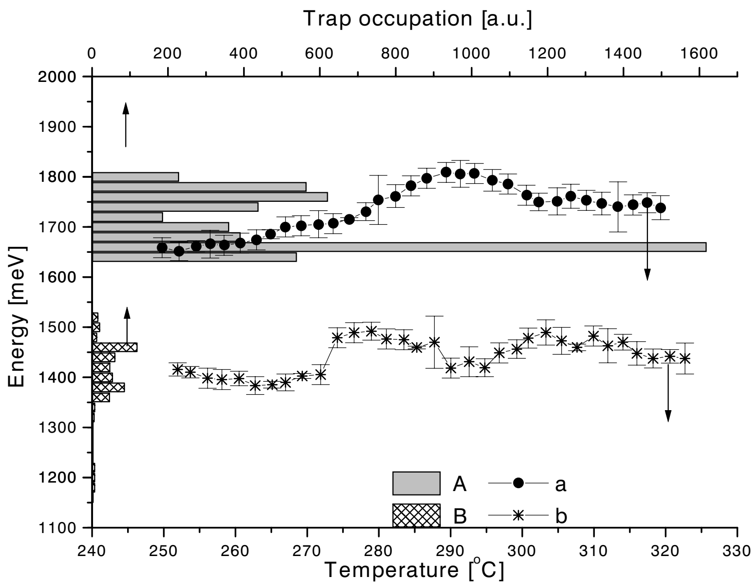

Fig.2. The FGT results. Symbol plots (small letters) present the energy dependence on the maximum temperature in the cycle. Histograms (capital letters) are the trap occupation spectra. The samples of K-feldspar were first given a 360 Gy dose. Then sample: a, A was preheated to 310 °C; sample b, B was bleached for 20 hours and preheated to 310 °C.

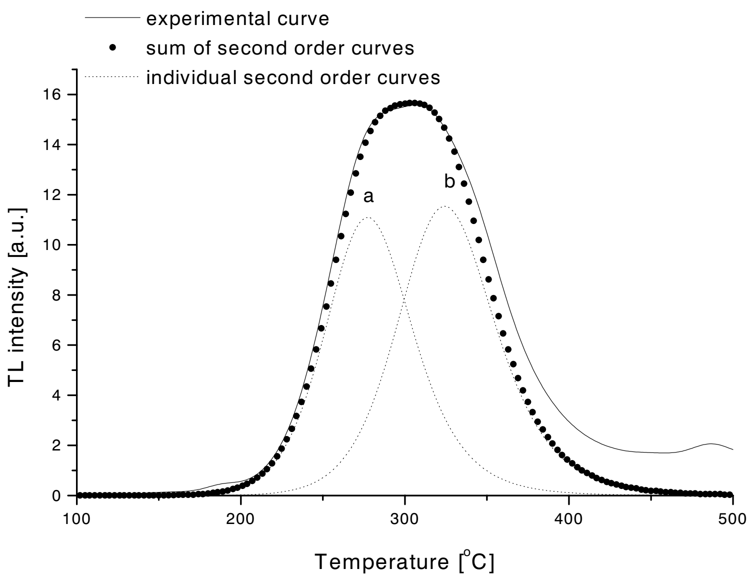

Fig.3. The experimental and fitted glow curves for K-feldspar. The experimental curve was measured after a dose of 360 Gy, 20 hours of bleaching and preheat to 310 °C. Heating rate was 0.05 °C/s. The energy values taken from the FGT measurements were 1380 (a) and 1460 meV (b) The respective fitting parameters are presented in Table1.

the results of FGT after a ~15 Gy dose (**Fig. 5**) do not show the existence of the deeper traps. This indicates that the shallower traps (<1500 meV) are populated efficiently during the first stage of the trap filling process and it is unlikely that they are empty after long irradiation, although the FGT measurements (**Fig. 2A**) do not detect them.

For this reason four individual second-order curves (n=4) were fitted to the glow curve obtained after long irradiation and without bleaching (**Fig. 4**). Two second-order curves were calculated for two energy levels – about 1650 and 1800 meV – distinguished in the FGT results presented in the upper part of **Fig. 2**. The other two were calculated for the E and s parameters used previously to fit the TL curve obtained after long bleaching (**Fig. 3**). The value of h_i (i=3, 4) representing the initial trap occupation of the two shallower traps, were the only fitting parameters in these cases.

4. DISCUSSION

The results of our previous work (Chruścińska, 2001) showed that the shallower traps (~1380 and 1460 meV) are the most resistant to optical emptying. The bleaching experiments presented here and the results of FGT measurements simulation (Chruścińska, 2001a) show clearly that in this K-feldspar there are traps which are active in the same temperature region 250-450 °C (heating rate ~1 °C/s) but they have significantly different parameters. These traps are also filled at different rates during irradiation. As is clear from the FGT measurements for low dosed samples (**Fig. 5**), the shallower traps with energy of 1380 and 1460 meV are filled much more efficiently than the deeper ones with energy of about 1650 and 1800 meV. For the latter traps (1650 and 1800 meV) the TL signal is also detected above 300 °C, but only after a large dose (360 Gy).

Ahmed and Gartia (1985) also determined the kinetics of the TL in microcline as bimolecular and they obtained trap depth values of 1.36 and 1.44 eV for the high temperature edge of TL curve. They measured the TL following a relatively small dose. Much larger doses were used by Visocecas *et al.* (1996) who investigated K-feldspar using a simple initial rise method. The energy values obtained by them are comparable with those presented here for high-dosed samples. In combination, those previous results indicate that after low dose the shallower traps are occupied, and the deeper traps are populated by a higher dose.

The efficiency of trapping and bleaching for a particular kind of a trap is proportional to the ratio of the recombination coefficient b to the retrapping coefficient A. If one includes the ratio b/A in the second-order equation, the value of the bimolecular pre-exponential factors

$$s' = s\,\beta / N\,A \qquad (4.6)$$

is obtained, where N is the trap concentration (Chen and McKeever, 1997). Low values of β/A indicate the predominance of retrapping over recombination (for a particular type of trap). If traps of several kinds take part in the filling process during excitation, the fastest populated one is that with the smallest β/A ratio. Similarly, carriers optically released from the traps during bleaching process repopulate the traps with the smallest β/A ratio most efficiently. Hence, these traps are the most resistant to bleaching. This model is confirmed by the results shown in table1, for the K-feldspar studied here.

In Table 1 the product σ η has the dimension of [s^{-1}] and, according to Eq. (4.6), is equal to sA/β for the fully occupied traps. The values of 10^{12} and 10^{10} obtained here for this product, for the deeper and shallower traps respectively, seem to be realistic. The values of η for fully occupied traps are those determined after a 360 Gy dose.

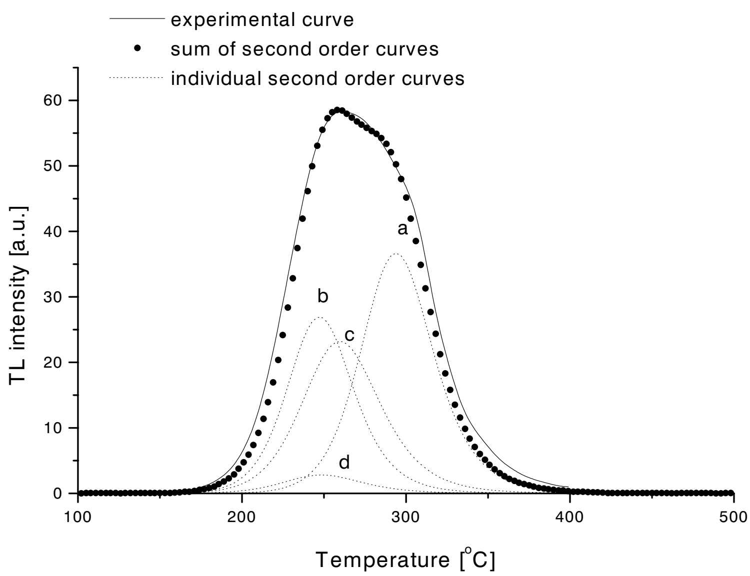

***Fig.4.** The experimental and fitted glow curves for K-feldspar. The experimental curve was measured after a dose of 360 Gy and preheat to 310 °C. Heating rate was 0.01 °C/s. The energy values taken from the FGT measurements were 1800 (a), 1650 (b), 1460 (c) and 1380 meV (d). The respective fitting parameters are presented in Table1.*

The TL intensity dependence on a dose implies that after a dose of 360 Gy the saturation level is reached in the K-feldspar samples investigated here. Hence, the h values determined after a 360 Gy dose can by treated as N, expressed in the arbitrary units of our experiments. **Table 1** includes the initial component of lifetime which is interesting for dating specialist. As one can see from the second-order decay equation (see Chen and McKeever, 1997):

$$I = \frac{I_0}{\left(1 + s' n_0 \exp\left(-\frac{E}{kT}\right) t\right)^2}, \qquad (4.7)$$

where t is time, I_0 and n_0 are the initial luminescence intensity and trap occupation respectively; the presented values are the estimation of minimum values of lifetimes obtained for fully occupied traps.

The ratio β/A for the shallower traps is lower than in the case of other traps for two reasons. The parameter σ (proportional to pre-exponential factor s') is comparatively low (much lower than σ determined for the deeper traps) and η (proportional to N) is not higher than for the deeper traps. The shallower traps are both the most resistant to bleaching and the most easily populated traps. This suggests that the differences between the β/A ratios of individual traps is responsible for the variety of TL bleaching efficiencies observed for this sample.

The TL itself is not a simple reflection of the charge carrier distribution in traps, so investigation of TL bleaching phenomena using a simple comparison of TL curves does not give any direct information about the efficiency of the optical release of carriers from individual types of traps. Two processes could be responsible for the decrease of the TL signal measured after bleaching: the lowered trap population or the reduced recombination probability because of a lack of recombination centres (or excess carriers; McKeever, 1994). The FGT experiments presented here show clearly that different types of traps dominate the TL process before and after bleaching. So emptying of traps is responsible for the optical bleaching of the TL signal from this K-feldspar by visible light, rather than changes in recombination probability. Changes in the initial concentration of excess carriers cannot influence the trap energy value determined by FGT. It only causes a decrease of the total TL intensity.

5. CONCLUSIONS

The light from a broad-band of spectrum was used to bleach the TL signal in a K-feldspar. This non-selective action gives rise to selective effects related to trap features. There coexist two different types of traps giving the TL signal in the same temperature region (over 300 °C) in this mineral. The correlation of low pre-exponential factor with the high filling efficiency and low bleachability

Table 1. *Trap parameters determined by the FGT (E-energy) and fitting procedures (σ and η) using the Eq · (3,5)*

	E [meV]	σ	$\eta \times 10^4$	σ η [s^{-1}]	$\tau = (\sigma\eta)^{-1}\exp(E/kT)$ [years] for T=20 °C
Samples without bleaching	1800	2.9×10^7	21.5	6.2×10^{12}	4.7×10^{10}
	1650	4.5×10^7	14.5	6.5×10^{12}	1.2×10^8
	1460	2.5×10^5	14.7	3.7×10^{10}	1.1×10^7
	1380	6.7×10^5	1.8	1.2×10^{10}	1.4×10^6
Samples after 20h of bleaching	1460	2.9×10^5	1.85	–	–
	1380	6.7×10^5	1.6	–	–

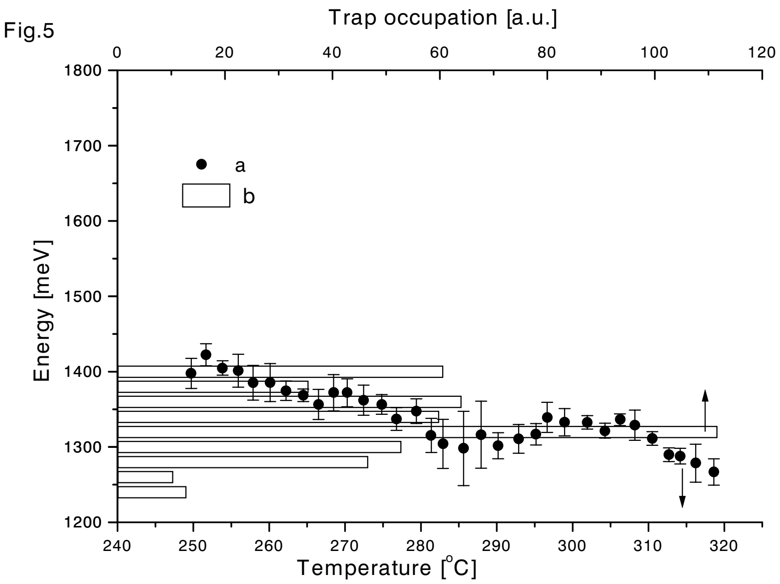

Fig.5. *The sample was given a dose of ~15 Gy and preheated to 310 °C. The symbol plot shows the energy dependence on the maximum temperature in the cycle. The histogram presents the trap occupation spectrum.*

of TL, observed for the traps with energy of about 1380 and 1460 meV, shows that the ratio of recombination to retrapping β/A can be responsible for the selective effects of optical bleaching.

In dosimetric measurements, potential problems arising from the TL intensity dependence on a dose should be taken into account. Traps which contribute to the same glow peak but which have significantly different kinetic parameters can be a source of problems, because in this case a non-linear dose response curve can develop. When the shallower traps are filled faster than the deeper ones, the saturation part of the growth curve for the shallower traps can appear at similar doses as the linear part of the growth curve for the deeper traps.

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