

THE FRACTIONAL GLOW TECHNIQUE AS A TOOL OF INVESTIGATION OF TL BLEACHING EFFICIENCY IN K-FELDSPAR

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Abstract: The fractional glow technique was applied to the investigation of trap occupation in optically bleached K-feldspars separated from sediments. Various bleaching times and two spectra ranges of sunlight simulator were used. Three trap groups exhibit different sensitivities to bleaching. The influence of the spectrum range of the stimulation light on the bleaching efficiency is presented. Results of the fractional glow technique measurements simulations are presented for the case of second order kinetics.

1. INTRODUCTION

K-feldspars are widely used in thermoluminescence (TL) and optically stimulated luminescence (OSL) dating; they are investigated intensively by means of TL and spectroscopic methods. Recently, because of OSL dating, the kinetics of infrared stimulated luminescence is a topical subject for investigations. Both this and the natural bleaching of TL are studied here. The bleaching of the luminescence of minerals before deposition is an essential area of study in both the TL and OSL dating of sediments.

This work presents preliminary first results of applying the fractional glow technique (FGT) (Gobrecht and Hofmann, 1966; Tale, 1981) to the determination of the spectrum of occupied traps after different bleaching procedures. In this way the influence of light on the population of traps in K-feldspar is investigated. Two spectrum ranges of sunlight simulator (Oczkowski and Przegiętka, 1997) were used – 300-750 nm and 375-750 nm (the UV lamps switched off).

Ahmed and Gartia (1985) observed in K-feldspar a shift of TL peak temperature towards high temperature with decrease of trap population. This indicates that the TL of K-feldspars is the process of the second order kinetics. This TL model assumes considerable role of re-trapping during thermal stimulation and the TL intensity dependence on temperature is described by the following formula (see e.g. Chen and McKeever, 1997):

$$I(T) = s'n_0^2 \exp\left(\frac{-E}{kT}\right) \left[1 + \left(\frac{s'n_0}{w}\right) \int_{T_0}^T \exp\left(\frac{-E}{kT'}\right) dT' \right]^{-2}, \quad (1.1)$$

where s' is the pre-exponential factor and n_0 is the initial trap occupation, E 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. Because of some earlier doubts concerning the use of FGT in the case of second-order kinetics (Kierstead and Levy, 1991), computer simulations of FGT experiments were done for this type of TL kinetics before the experimental data were interpreted.

2. FRACTIONAL GLOW TECHNIQUE

The FGT first applied by Gobrecht and Hofmann (1966) was improved mainly in the stage of data handling by taking into account the difference between the heating and cooling ratio in a cycle. The averaged energy of trap emptied in the i -th cycle E_i is described by (Chruścińska, 1994):

$$E_i = E_{ih} + \frac{w_c(E_{ic} - E_{ih})}{w_c + w_h}, \quad (2.1)$$

where E_{ih} is the energy estimated for the heating part of TL curve in i -th cycle, E_{ic} is the energy obtained for the cooling part of i -th cycle, w_h and w_c are, respectively, the heating and cooling rates. In consequence, one can present direct measurement results in the form of trap energy dependence on the maximum temperature in the cycle (called $E(T)$ in the figures presented here) and the dependence of the sum under the TL curve obtained for one cycle on the maximum temperature in this cycle (called the light sum – $L(T)$). The trap occupation spectrum (normally presented as a histogram) $H(E)$ is taken as the sum over all H_i for which $E < E_i < E + \Delta E$, where:

$$H_i = \frac{L_i}{|E_i - E_{i-1}|}, \quad (2.2)$$

L_i is the sum under the TL curve obtained for i -th cycle, the so-called partial light sum. ΔE is the bar width of trap spectrum histogram. **Fig. 1** presents an example of $E(T)$, light sum and histogram of trap occupation spectrum

obtained in result of computer simulation of FGT measurements.

Additionally the energy values and the histograms of trap occupation obtained separately for the heating and cooling cycles are shown (**Fig. 1B** and **1C** respectively). Taking into account the plateau number of the heating curve in **Fig. 1C** one can find four different traps but the corrected $E(T)$ clearly indicates the existence of only three trap types. This illustrates how erroneous the measurement interpretation can be if it is based on the energy obtained for heating only. The deviation from the actual energy value depends on the heating rate used and can be reduced by applying the heating-cooling correction. It has to be stressed, that although the points of closest

approach of the heating and cooling curves (**Fig. 1B**) give the estimate of the trap depth as good as the maximum of histogram ($H(E)$ in **Fig. 1A**) in the presented case of some very good separated TL peaks, in most cases such clear points do not appear in measurement results. Both the $E(T)$ and the light sum $L(T)$ (Eq. (2.2)) give rise to the final result of FGT measurement – the trap occupation spectrum.

The results of FGT are the base for more detailed analysis. This procedure includes fitting to TL curve in order to determine the values of frequency factors associated with a particular trap depth (Chruścińska *et al.*, 1996).

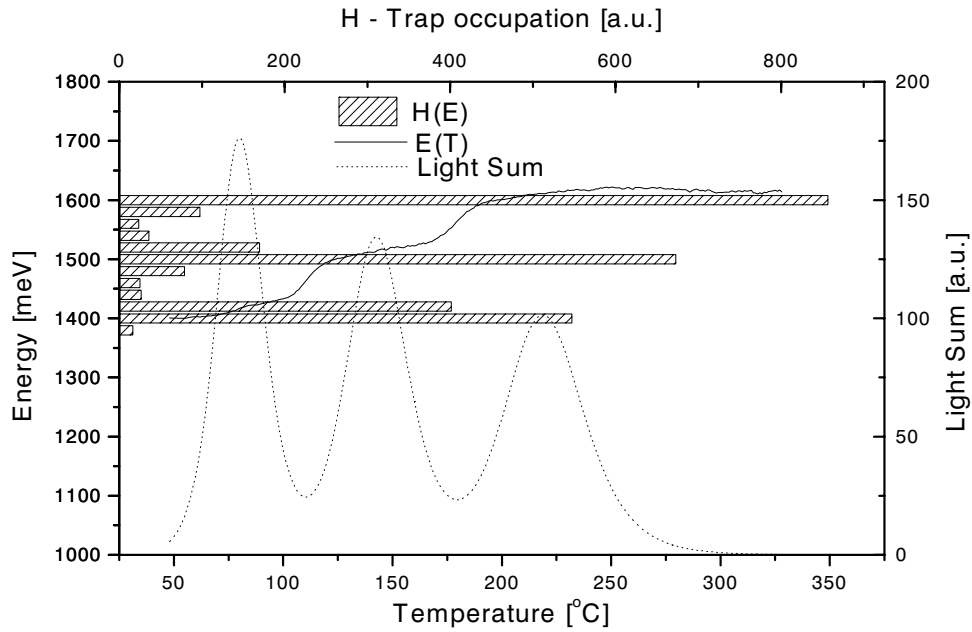


Fig. 1A. FGT simulation: $\Delta T_{\text{heat}}=22K$, $\Delta T_{\text{cool}}=20K$, $T_0=300K$; $E_1=1400meV$, $s'_1=4.5 \times 10^9 m^3 s^{-1}$, $n_{01}=10^6 m^{-3}$, $E_2=1500meV$, $s'_2=4.5 \times 10^7 m^3 s^{-1}$, $n_{02}=10^6 m^{-3}$, $E_3=1600meV$, $s'_3=4.5 \times 10^5 m^3 s^{-1}$, $n_{03}=10^6 m^{-3}$

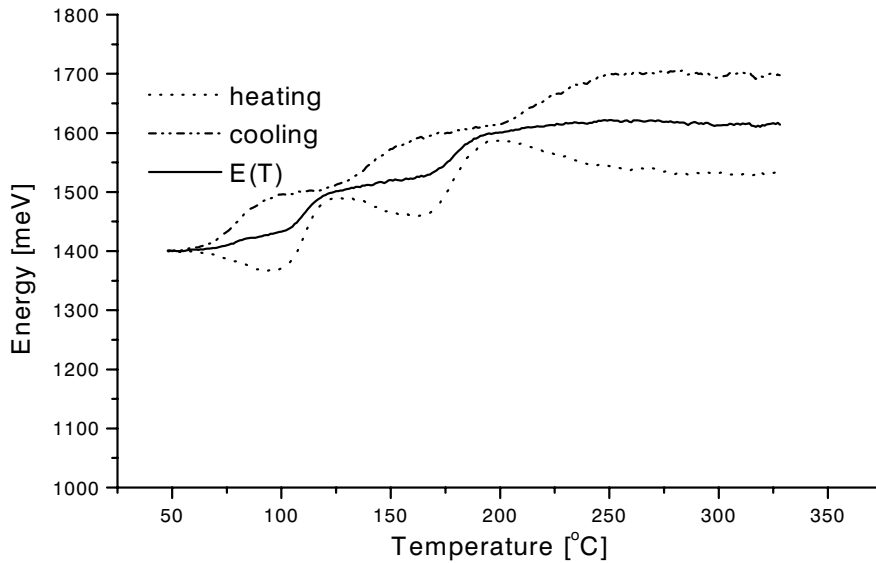


Fig. 1B. FGT simulation: $\Delta T_{\text{heat}}=22K$, $\Delta T_{\text{cool}}=20K$, $T_0=300K$; $E_1=1400meV$, $s'_1=4.5 \times 10^9 m^3 s^{-1}$, $n_{01}=10^6 m^{-3}$, $E_2=1500meV$, $s'_2=4.5 \times 10^7 m^3 s^{-1}$, $n_{02}=10^6 m^{-3}$, $E_3=1600meV$, $s'_3=4.5 \times 10^5 m^3 s^{-1}$, $n_{03}=10^6 m^{-3}$

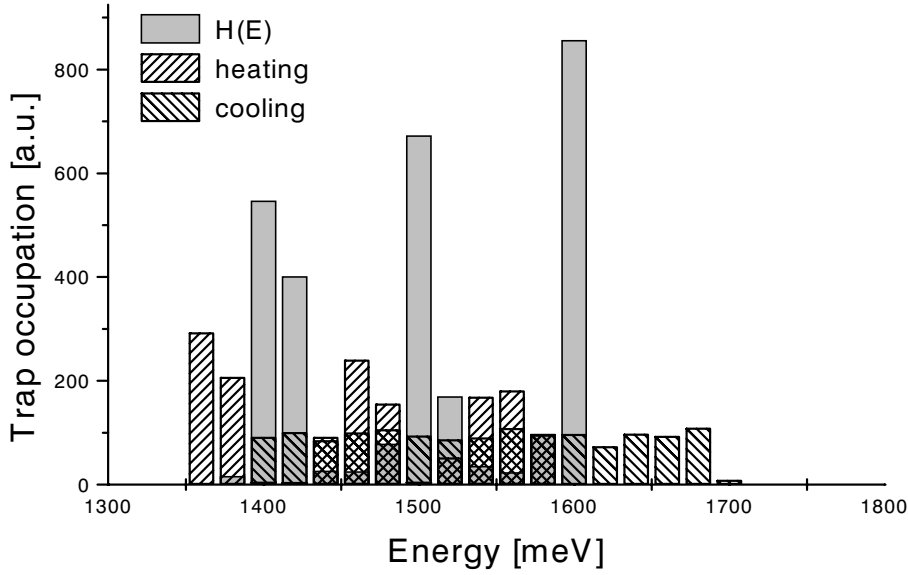


Fig. 1C. FGT simulation: $\Delta T_{\text{heat}}=22K$, $\Delta T_{\text{cool}}=20K$, $T_0=300K$; $E_1=1400meV$, $s'_1=4.5 \times 10^9 m^3 s^{-1}$, $n_{01}=10^6 m^{-3}$, $E_2=1500meV$, $s'_2=4.5 \times 10^7 m^3 s^{-1}$, $n_{02}=10^6 m^{-3}$, $E_3=1600meV$, $s'_3=4.5 \times 10^5 m^3 s^{-1}$, $n_{03}=10^6 m^{-3}$

3. FGT MEASUREMENTS SIMULATIONS

The FGT is applicable to the analysis of complex glow curves and its main advantage is independence of the TL kinetic order. However, it should be stressed that the experimental results always need careful handling and interpretation (Kierstead and Levy, 1991; Chruścińska *et al.*, 1996); the value of activation energy calculated from experimental data in a FGT cycle is the average of the depths of all traps emptied in the cycle.

Computer simulations of FGT experiments for the second-order TL kinetics were carried out assuming values of trap parameters: energy – E , frequency factor – s ,

total trap concentration – N , and initial trap occupation – n_0 . The procedure applied during actual experiments was simulated numerically. For each cycle the second-order TL curve (Eq. (1.1)) was calculated for the heating and cooling of each trap and then all curves were added to create the composite TL curve for the cycle. Many computer experiments were performed for different trap parameters. Figures 2-7 present some exemplary results.

The resolution of the FGT is of great importance. The features of thermal stimulation of luminescence determine the energy range of traps (with close pre-exponent factor values) which are simultaneously emptied in the case of continuous trap distribution and second-order

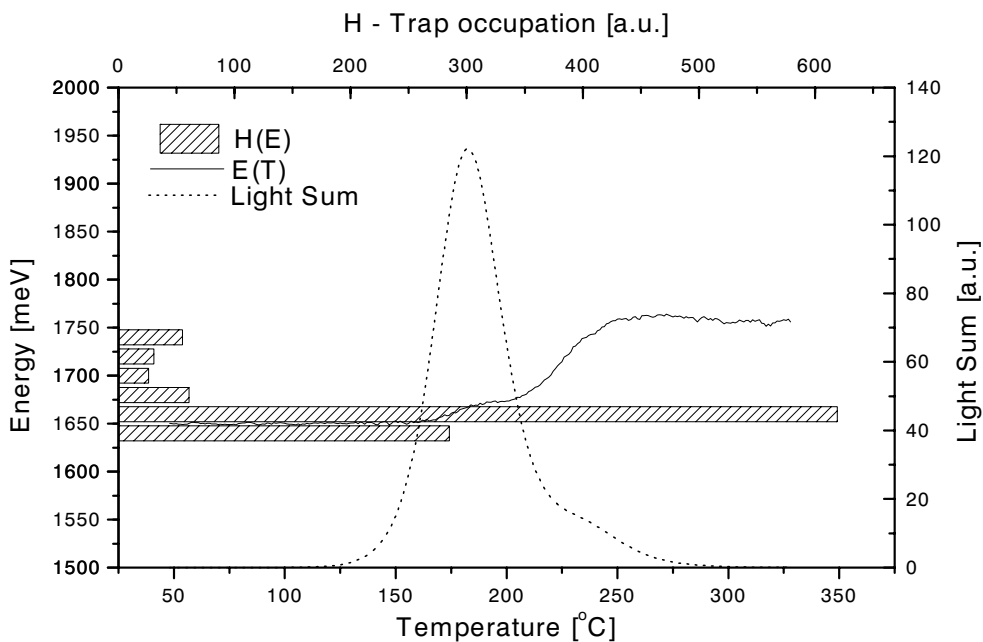


Fig. 2. FGT simulation: $\Delta T_{\text{heat}}=21K$, $\Delta T_{\text{cool}}=20K$, $T_0=300K$

$$E_1=1650meV, s'_1=4.5 \times 10^7 m^3 s^{-1}, n_{01}=10^6 m^{-3}, E_2=1750meV, s'_2=4.5 \times 10^7 m^3 s^{-1}, n_{02}=10^5 m^{-3}$$

kinetics (Gobrecht and Hofmann, 1966) as about $3kT$ (about 150 meV for the temperature range in question). The advantages of the fractional heating is a possibility of distinguishing the traps which have equal s' values and the energy differing by not more than few tens of meV. This is illustrated on **Fig. 2** where the difference in energy value is 100 meV. In spite of the fact that the occupation of deeper traps is ten times lower than the shallower ones, both levels are detected. **Fig. 3** presents results for traps differing in depth only by 50 meV. The trap spectrum extends from the energy of the shallower trap (~ 1650 meV) to the energy value for deeper traps (~ 1700 meV) and only one maximum appears in the middle of this range. The $E(T)$ curve, however, informs that two

different traps are active and their depths are about these assumed for simulation.

The resolution is better for higher difference in pre-exponential factor. This is shown in Fig.4. Two well separated peaks are clear in the trap occupation spectrum. They reproduce the assumed energy values very well. Still closer trap level are good separated in trap spectrum presented in **Fig. 5** which serve simultaneously as an illustration of an effect called reversed trap depopulation. This effect consists in that the deeper traps are emptied before the shallower ones, because the pre-exponential factor, s' value for the latter traps is much higher than the value of this parameter for shallower traps.

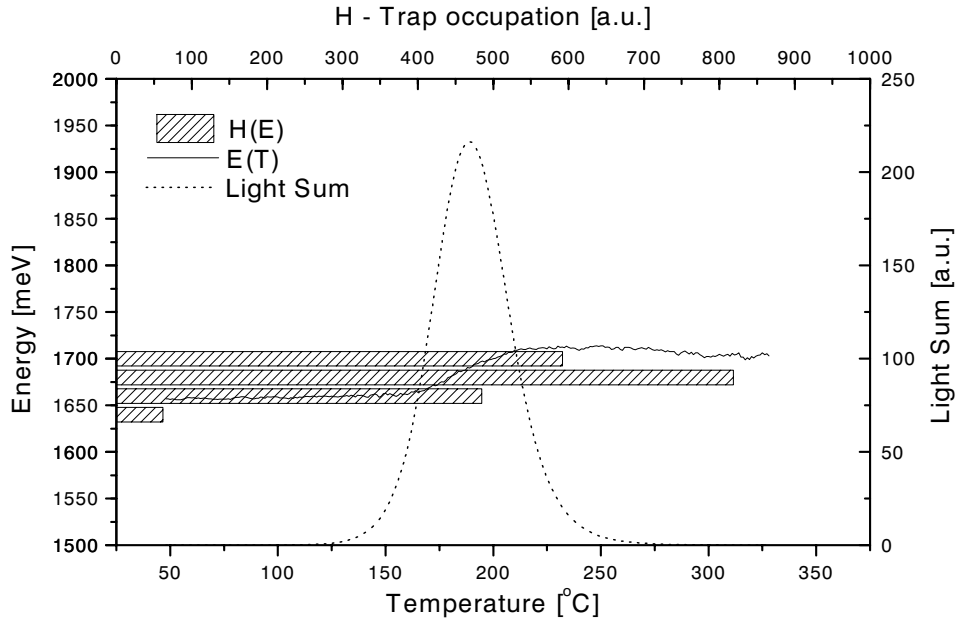


Fig. 3. FGT simulation: $\Delta T_{\text{heat}}=21K$, $\Delta T_{\text{cool}}=20K$, $T_0=300K$

$$E_1=1650\text{meV}, s'_1=4.5 \times 10^7 \text{m}^3 \text{s}^{-1}, n_{01}=10^6 \text{m}^{-3}, E_2=1700\text{meV}, s'_2=4.5 \times 10^7 \text{m}^3 \text{s}^{-1}, n_{02}=10^6 \text{m}^{-3}$$

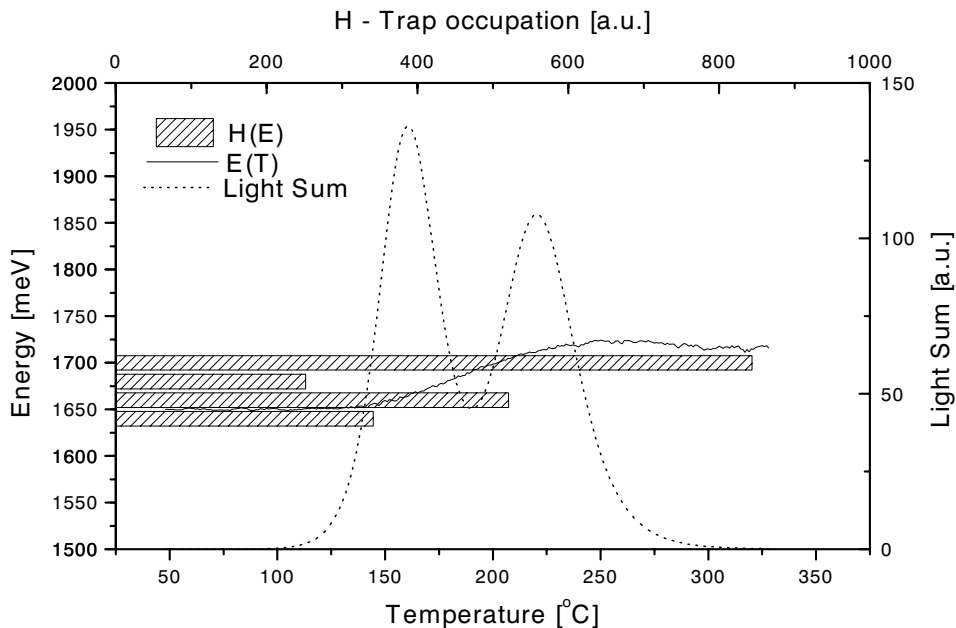


Fig. 4. FGT simulation: $\Delta T_{\text{heat}}=21K$, $\Delta T_{\text{cool}}=20K$, $T_0=300K$

$$E_1=1650\text{meV}, s'_1=4.5 \times 10^8 \text{m}^3 \text{s}^{-1}, n_{01}=10^6 \text{m}^{-3}, E_2=1700\text{meV}, s'_2=4.5 \times 10^6 \text{m}^3 \text{s}^{-1}, n_{02}=10^6 \text{m}^{-3}$$

The effect of reversed trap depopulation can be the reason of uncertainty in the trap depth determination. In **Fig. 5** only a slight shift into the higher energies is observed but much greater discrepancies can appear. The most disappointing results of simulation presented here are observed for simultaneously depopulated traps, one of which – the shallower – has much lower pre-exponential factor than the second, deeper trap, but trap depths are chosen in such a manner that only single TL peak is detected (**Fig. 6**). In this case neither the trap occupation spectra, nor the trap depth curve reflect the assumed data. Nevertheless, even for such an unfavourable parameter set the FGT results clearly indicate that the sharp TL peak, which is observed, has a complex nature. The reason for

this bad result is just the reversed trap depopulation effect. Soon after the beginning of the experiment (when the measured E value is 1300 meV), emptying of the deeper traps starts to prevail and the averaged energy of the depopulated traps increases. The high s' value of the deeper traps causes their fast emptying and the averaged energy of simultaneously depopulated traps again approach 1300 meV. This process is registered by $E(T)$ dependence.

The known feature of second-order TL peaks is their shift to higher temperature with the decreasing initial trap population. So it is reasonable to see how the FGT results depend on this parameter. The additional impulse here is a peculiar regularity observed in experimental re-

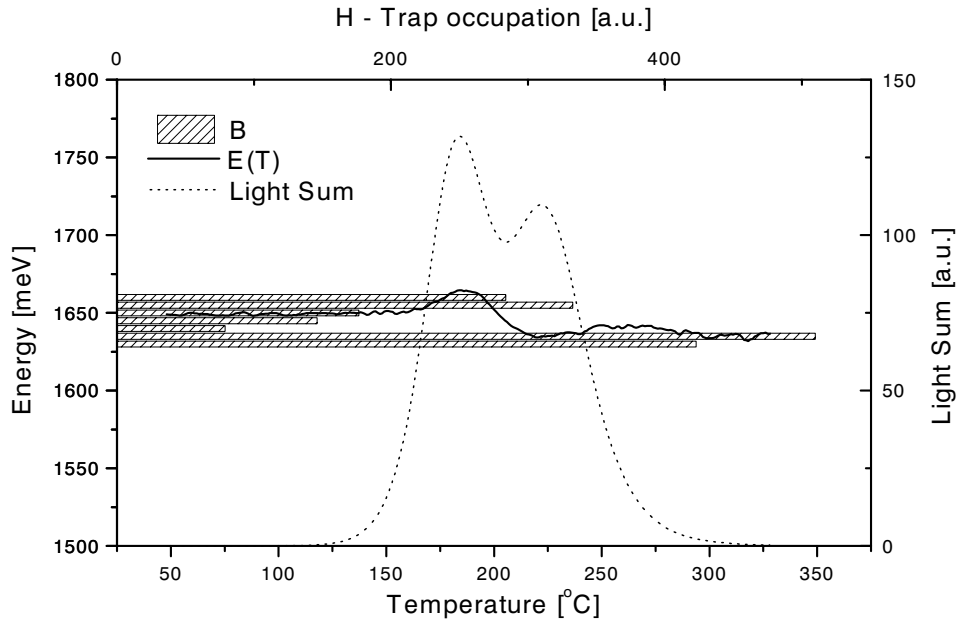


Fig. 5. FGT simulation: $\Delta T_{\text{heat}}=21\text{K}$, $\Delta T_{\text{cool}}=20\text{K}$, $T_0=300\text{K}$

$$E_1=1650\text{meV}, s'_1=4.5 \times 10^7 \text{m}^3 \text{s}^{-1}, n_{01}=10^6 \text{m}^{-3}, E_2=1620\text{meV}, s'_2=4.5 \times 10^5 \text{m}^3 \text{s}^{-1}, n_{02}=10^6 \text{m}^{-3}$$

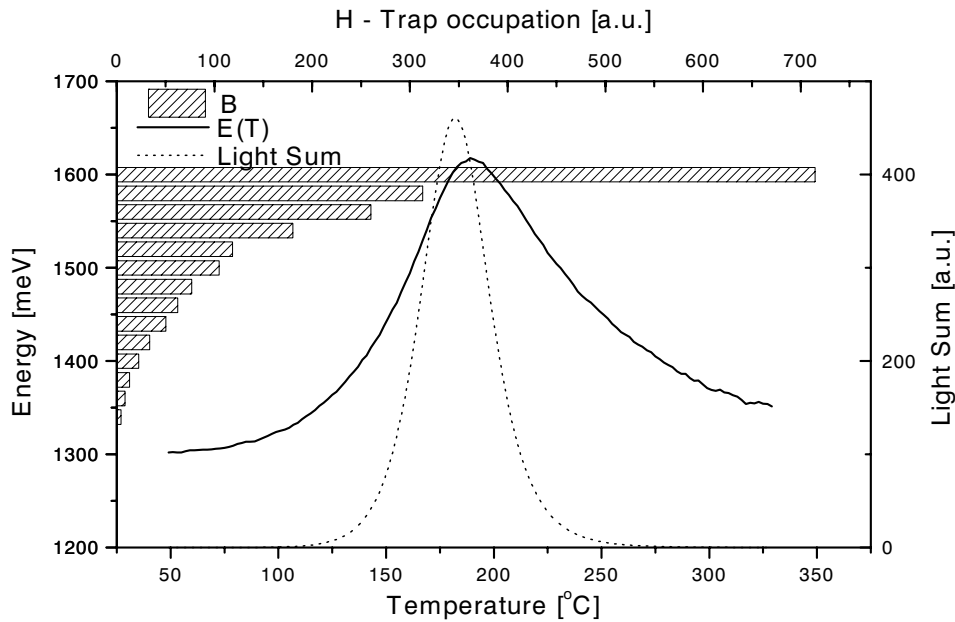


Fig. 6. FGT simulation: $\Delta T_{\text{heat}}=22\text{K}$, $\Delta T_{\text{cool}}=20\text{K}$, $T_0=300\text{K}$

$$E_1=1300\text{meV}, s'_1=4.5 \times 10^7 \text{m}^3 \text{s}^{-1}, n_{01}=10^6 \text{m}^{-3}, E_2=1800\text{meV}, s'_2=4.5 \times 10^9 \text{m}^3 \text{s}^{-1}, n_{02}=10^6 \text{m}^{-3}$$

sults presented in next section – low trap population is associated with low trap energy. This effect gives rise to some concern over the reliability of the FGT. **Fig. 7** shows some exemplary results of the suitable tests. Trap occupation spectra for three different initial trap populations do not show any differences in peak position. The differences in trap occupation are very well reproduced. The change in the relative trap population is also clearly detected (**Fig. 7D**).

Some words concerning the quality of the estimation of relative populations in a single FGT measurement should be added here. It should be remembered that the energy obtained in a cycle is the average of the depths of all traps emptied in the cycle. So the FGT always transforms a discrete level into a band. A problem arises then, which bar of histogram should we connect with one maximum and when should we start to count the occupation of the next maximum. This problem is more serious, because in fact one does not know whether the trap in the measured sample are discrete or whether they have a continuous spectrum. The computer simulation results allow to make the observation that the maximum of the histogram which presents the last emptied level is usually more sharp than the maximum presenting traps which are depopulated earlier (**Fig. 1A** and **5**). The sum of the his-

togram bars which are related to a particular maximum reflect the assumed relative trap populations correctly.

It has to be, however, mentioned that sometimes the maximum in trap spectrum can appear which does not respond to a trap level actually existing in a sample (**Fig. 3**). The detection of such case in particular cases is possible by the measurements of the same trap system with different relative trap populations. Such a test has been done here by measuring the trap occupation spectra before and after bleaching (see section 4).

Summing up, the trap spectra obtained from the FGT analyses for the second-order kinetics are obviously not discrete, this has also been observed in the case of first-order kinetics (Chruścińska, 1994). Nevertheless, the energy values are largely correct. Computer simulations exclude the doubts related to the application of FGT in the case of the second-order kinetics.

4. MEASUREMENT RESULTS

Fig. 8 shows the trap occupation spectra of the unbleached feldspar together with the spectra after two hours of stimulation applied with either spectral ranges. Three trap groups can be distinguished: traps shallower than 1.3 eV, traps with a depth between 1.3 and 1.6 eV

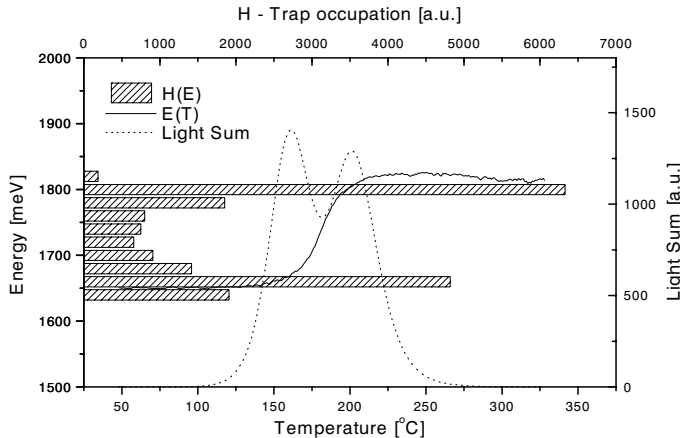


Fig. 7A. FGT simulation: $\Delta T_{\text{heat}}=21\text{K}$, $\Delta T_{\text{cool}}=20\text{K}$, $T_0=300\text{K}$

$$E_1=1650\text{meV}, s_1=4.5 \times 10^7 \text{m}^3 \text{s}^{-1}, n_{01}=10^7 \text{m}^{-3}, E_2=1800\text{meV}, s_2=3.0 \times 10^7 \text{m}^3 \text{s}^{-1}, n_{02}=10^7 \text{m}^{-3}$$

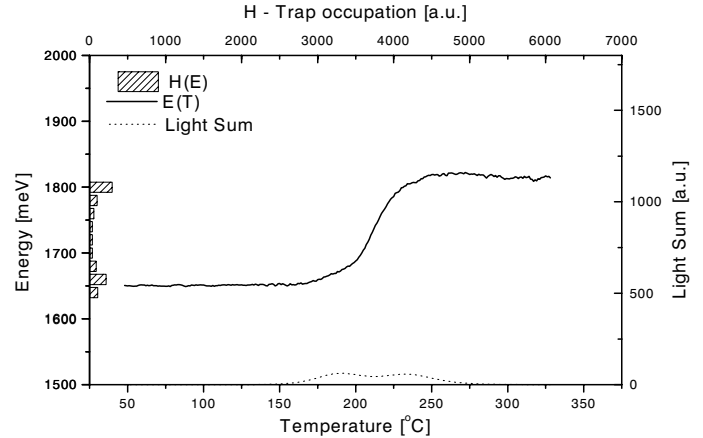


Fig. 7C. FGT simulation: $\Delta T_{\text{heat}}=21\text{K}$, $\Delta T_{\text{cool}}=20\text{K}$, $T_0=300\text{K}$

$$E_1=1650\text{meV}, s_1=4.5 \times 10^7 \text{m}^3 \text{s}^{-1}, n_{01}=10^7 \text{m}^{-3}, E_2=1800\text{meV}, s_2=3.0 \times 10^7 \text{m}^3 \text{s}^{-1}, n_{02}=10^7 \text{m}^{-3}$$

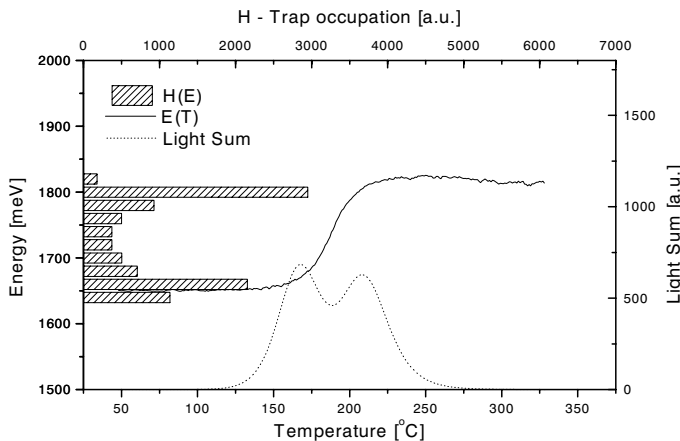


Fig. 7B. FGT simulation: $\Delta T_{\text{heat}}=22\text{K}$, $\Delta T_{\text{cool}}=20\text{K}$, $T_0=300\text{K}$

$$E_1=1650\text{meV}, s_1=4.5 \times 10^7 \text{m}^3 \text{s}^{-1}, n_{01}=5 \times 10^6 \text{m}^{-3}, E_2=1800\text{meV}, s_2=3.0 \times 10^7 \text{m}^3 \text{s}^{-1}, n_{02}=5 \times 10^6 \text{m}^{-3}$$

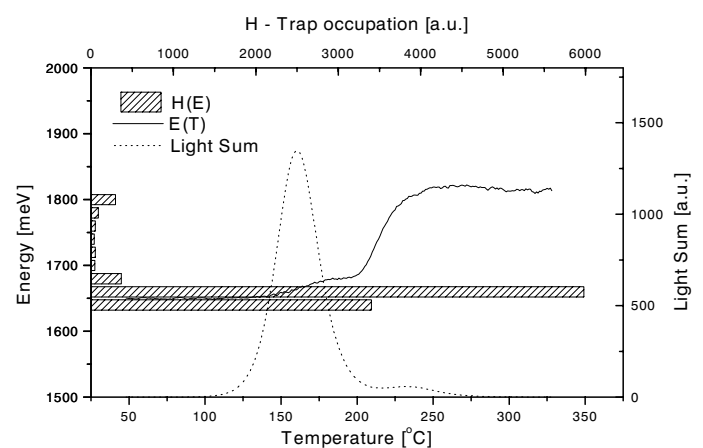


Fig. 7D. FGT simulation: $\Delta T_{\text{heat}}=22\text{K}$, $\Delta T_{\text{cool}}=20\text{K}$, $T_0=300\text{K}$

$$E_1=1650\text{meV}, s_1=4.5 \times 10^7 \text{m}^3 \text{s}^{-1}, n_{01}=10^7 \text{m}^{-3}, E_2=1800\text{meV}, s_2=3.0 \times 10^7 \text{m}^3 \text{s}^{-1}, n_{02}=5 \times 10^5 \text{m}^{-3}$$

and traps deeper than 1.6 eV. The deepest fraction is the most easily depopulated by the light. The shallower traps are somewhat more resistant to optical stimulation but in the case of traps about 1.5 eV both wavelength ranges seem to be still less effective.

There is a tendency for low trap population to be associated with low trap energies. We are confident that this is not an artefact of the analytical procedure, because the computer simulations do not show any relationship between trap energy and population (Fig. 7).

Bleaching reveals the complex nature of the maximum of trap occupation spectrum above 1.6 eV. The shift of this maximum toward lower energy values is observed when the time of bleaching is longer. Fig. 9 and 10 show results of FGT procedure applied after 4 and 20 hours of bleaching. The less effective bleaching with the reduced

simulator spectrum range (Fig. 9A and 10A) gradually changes the relative populations of traps which are emptied simultaneously in the temperature about 300°C (Fig. 11C and D). In result the averaged energy of traps emptied in the same cycle of FGT procedure carried out after altered times of bleaching is different. Because the deeper traps are depopulated much more efficiently, the maximum of trap spectrum shifts towards lower energy values with the increasing time of bleaching. The more effective bleaching with the full simulator spectrum reduces the population of deep traps very quick, so already after 4 hour of bleaching (Fig. 9B) the traps emptied in the temperature about 300 °C have averaged energy below 1.6 eV. 20 hour of this bleaching is enough to depopulate all the deeper traps.

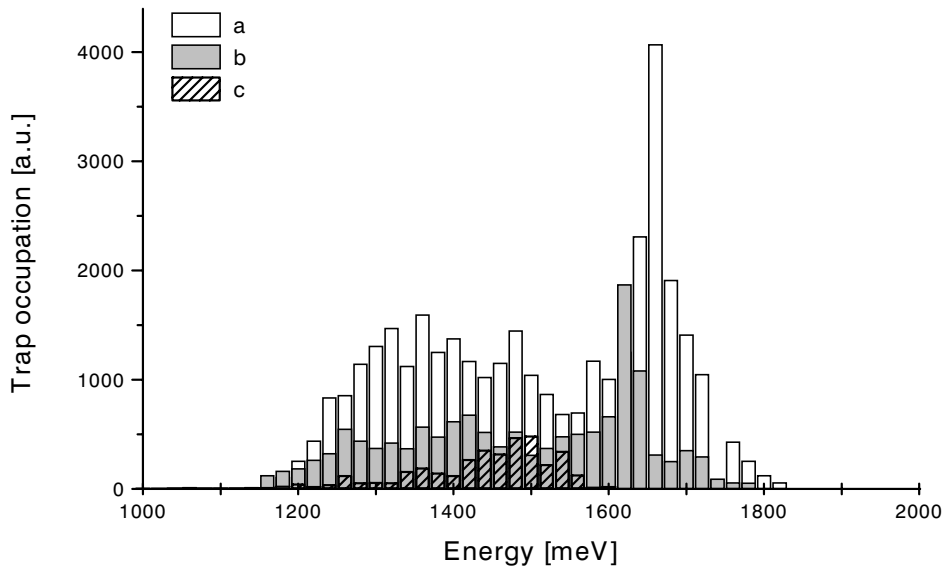


Fig. 8. The trap occupation spectra for (a) unbleached K-feldspar, (b) after 2 h of bleaching by the light without UV part of spectrum, (c) after 2 h of bleaching with full range of simulator light spectrum. FGT procedure: $\Delta T_{heat}=12$ °C, $\Delta T_{cool}=10$ °C, $T_0=125$ °C.

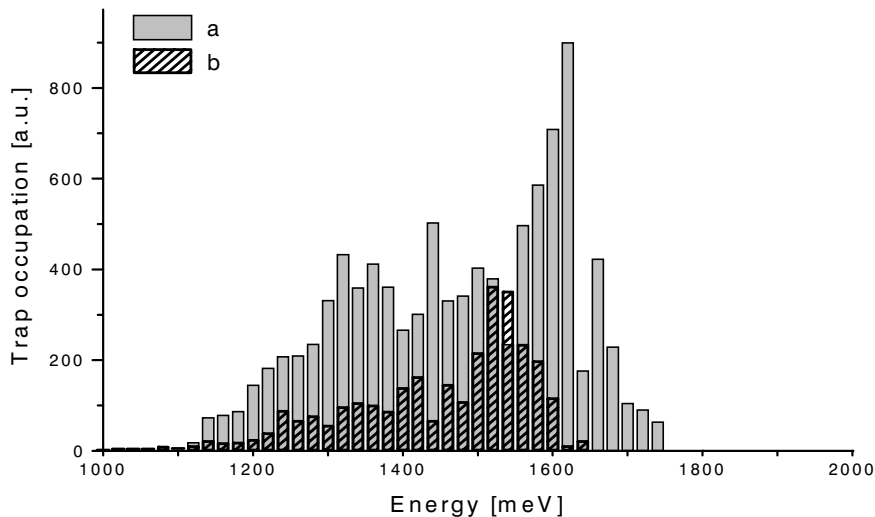


Fig. 9. The trap occupation spectra for K-feldspar after 4 h of bleaching with reduced (a) and full (b) simulator light range. Same FGT procedure as for the results presented in Fig. 8.

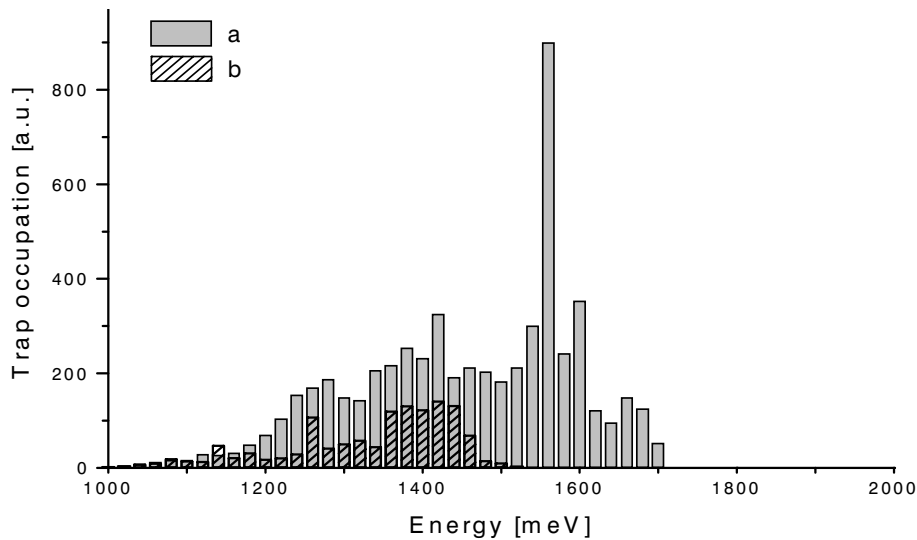


Fig.10. The trap occupation spectra for K-feldspar after 20 h of bleaching with reduced (a) and full (b) simulator light range. Same FGT procedure as for the results presented in Fig.8.

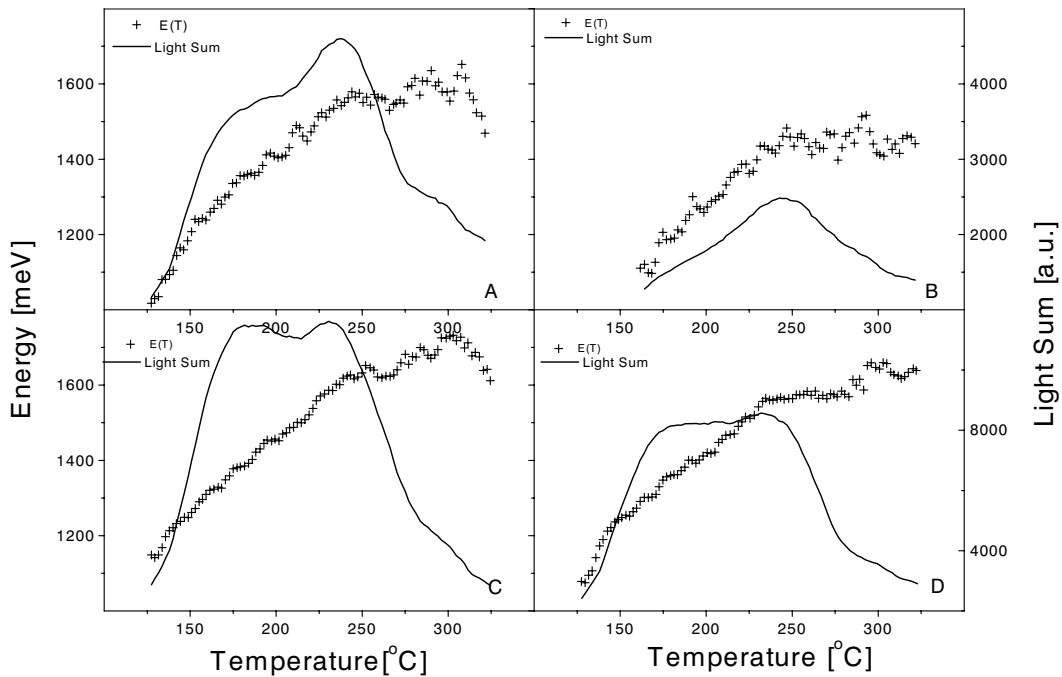


Fig.11. The FGT results for K-feldspar after (A) 4 h and (B) 20 h of bleaching with full range of simulator spectrum, (C) after 4 h and (D) 20 h of bleaching by the light without UV part of simulator spectrum.

It has to be added that the above explanation become obvious after a detailed FGT analysis of the trap occupation carried out after a preheat to 310 °C (Chruścińska *et al.*, 2001). This analysis shows that four traps are active in the temperature region in question. Parameters of these traps differ significantly.

Traps in the energy range 1.3-1.6 eV seem to be responsible for the residual TL observed even after many hours of bleaching. This residual TL presumably also exists in nature in sediments after day light bleaching. Thus, these traps are likely to be the source of problems with incompletely bleached sediments.

5. CONCLUSIONS

These preliminary results show that FGT with the heating-cooling rate correction can be an useful tool to investigate bleaching processes. The changes in trap occupation after bleaching and the influence of the wavelength range of the stimulation light on the occupation spectra are clearly demonstrated.

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