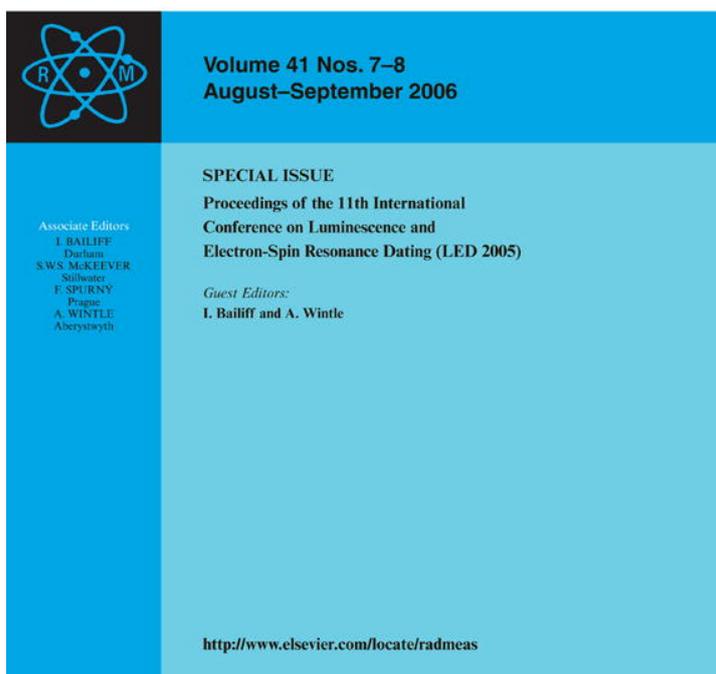




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Comparison of experimental and modelled quartz thermal-activation curves obtained using multiple- and single-aliquot procedures

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Abstract

This paper presents the results of a broad study of the thermal-activation characteristics of three quartz samples of different origin. The thermal-activation characteristics of synthetic, sedimentary and Arkansas quartz are measured as a function of several experimental parameters and over the temperature range 20–500 °C using both multiple-aliquot and single-aliquot techniques. The studies are carried out also as a function of the thermal preparation of the samples, for “as-is” samples, for samples fired at temperatures of 500 and 900 °C. Additional experimental parameters varied in this study include the test dose used in measuring the thermal activation curves and the temperature interval between successive heating of the samples. The results of this experimental study for all three quartz samples are interpreted by using a simple modified Zimmerman model for quartz consisting of 2 electron traps, a luminescence center and three hole reservoirs. The results are also discussed within the recently published complex theoretical quartz model by Adamiec (2005). Investigation of a numerical model of the pre-dose mechanism in quartz. *Radiat. Meas.* 39, 175–189), which is based on a luminescent center, three electron traps and three reservoir hole traps. © 2006 Elsevier Ltd. All rights reserved.

1. Introduction

The study of sensitivity changes occurring in quartz during the application of single- and multiple-aliquot dating techniques is of fundamental importance in TL and OSL. There have been very few comparative studies of the sensitization properties of quartz of different origins, under different “predose” irradiations and/or heating of the samples to various temperatures.

In a recent paper Kitis et al. (2006) presented a comparative study of the predose effect for three types of quartz of different origins. Curves of TL versus dose, and sensitivity S versus predose curves were obtained for the dose range of $0.1 < D < 400$ Gy, as well as for samples which underwent a combined predose irradiation and a subsequent heat treatment to 500 °C. The results of that comparative study were explained by simulating the complete experimental protocol using a modified Zimmerman (1971) model.

The purpose of the present paper is to extend the experimental work by Kitis et al. (2006) to the thermal-activation characteristics (TACs) of synthetic, sedimentary and Arkansas quartz. The TACs are measured as a function of several experimental parameters, namely using multiple-aliquot and single-aliquot techniques, annealing of the samples, different test doses, and various temperature intervals between successive heating of the samples. The experimental results of this study are found to be in agreement with a modified Zimmerman model containing three hole reservoirs.

In a recently published comparative study, Adamiec (2005) studied the thermal-activation characteristics (TACs) of several types of quartz and compared the experimental results with a theoretical model similar to the model by Bailey (2001). Our experimental results are also discussed within the context of this theoretical model.

2. Experimental procedure

The materials used in the present study were high-purity synthetic quartz, natural Arkansas quartz of hydrothermal origin

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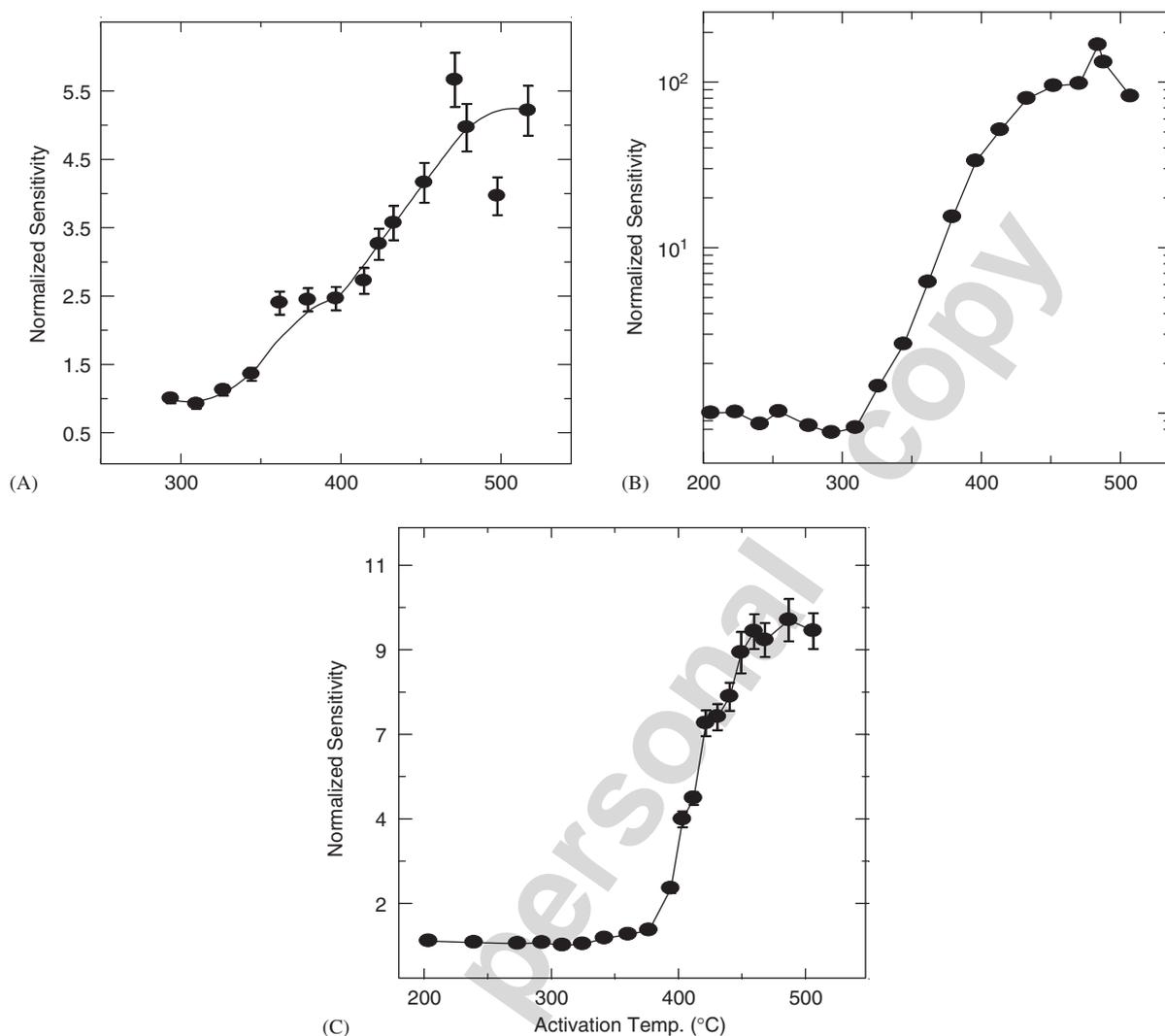


Fig. 1. The multiple-aliquot thermal-activation characteristics (MA-TAC) for untreated quartz samples (A) synthetic quartz (B) sedimentary quartz: note logarithmic sensitivity scale, and (C) Arkansas quartz. Values are normalized to the measurement at the lowest temperature of activation. The test doses used were 2.5, 0.56 and 1.68 Gy, respectively.

and sedimentary quartz. Preliminary descriptions of the quartz samples as well as the details of the TL equipment were published elsewhere (Kitis et al., 2006). All quartz samples were used in powder form with grain size of 80–200 μm , which were obtained by crushing and sieving large amounts of quartz. The mass of each sample was determined using the dispenser of a Harshaw 2000A-B TLD reader. This dispenser has a stable volume, in which the powder is left to flow. The powder drops are attached to a brass disk with an area of 1 cm^2 which was previously covered by a very thin layer of nonluminescent silicon oil. The reproducibility of the dispenser, which has been routinely used for many years, is better than 5%. For the TL measurements a Littlemore 711 TL analyzer was used. The glow oven was first evacuated to 10^{-1} Torr and nitrogen of high purity was allowed to flow during the readout. The light emission was detected by an EMI 9635 QA photomultiplier tube and the glow curves were stored in a computer via a 1024-channel ADC card operating in the MCS mode. A Corning

7-59 blue filter was used during all measurements. The heating strip was nichrome of thickness 0.8 mm, with a Cr–Al thermocouple fixed to it. The heating rate used was $2^\circ\text{C}/\text{s}$. The irradiations were performed with a ^{90}Sr – ^{90}Y beta source delivering 0.56 mGy/min at a sample distance of 15 mm. The time elapsed between the end of irradiation and the readout is in all cases around 40 s.

The protocol used in obtaining the thermal-activation curves using the multiple-aliquot procedure (MA-TACs) is as follows: (i) the “as-is” quartz sample is given a beta dose, (ii) the sample was heated up to an activation temperature T and the TL was recorded. This step yields the sensitivity of the 110 $^\circ\text{C}$ TL peak to the beta dose, which can act as a monitor of the sample reproducibility, (iii) the thermally activated sample is given a second beta dose, (iv) the irradiated sample is heated up to 150 $^\circ\text{C}$ to obtain the activated sensitivity of the 110 $^\circ\text{C}$ glow peak, (v) steps (i)–(iv) are repeated for a higher activation temperature T using another sample.

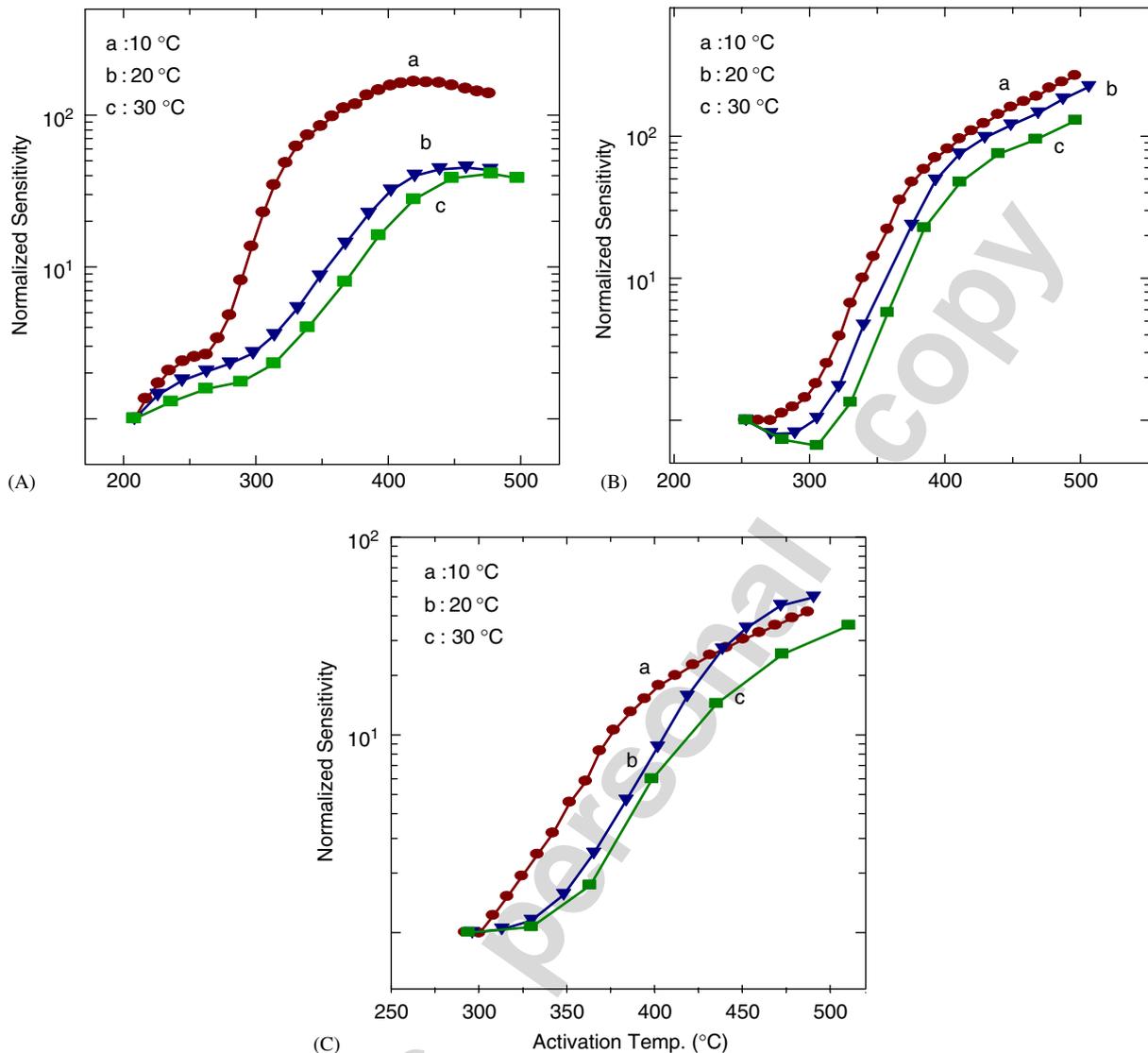


Fig. 2. The single aliquot thermal activation characteristics (SA-TAC) for untreated quartz samples (A) synthetic quartz (B) Sedimentary quartz (C) Arkansas quartz with different temperature intervals $\Delta T = 10, 20, 30^\circ\text{C}$. Note that all sensitivity scales are logarithmic.

In order to measure the TAC for a single-aliquot (SA-TAC), the following procedure is followed: (i) the “as-is” quartz sample was readout up to the first and lowest activation temperature, (ii) the thermally activated sample was given a beta dose, (iii) the irradiated sample was readout up to the next activation temperature, which is higher than the previous one by a temperature step ΔT . The aim of this step is twofold, to obtain the sensitization of the 110°C glow peak due to the previous activation temperature, and secondly additional thermal activation is achieved, (iv) steps (i)–(iii) are repeated for a higher activation temperature.

Additional TACs were measured by delivering a predose of 20 Gy to the samples and then following the MA or SA protocols described above. The effect of annealing on the three samples was studied by using untreated samples as well as samples pre-annealed for 1 h at 500 and 900°C , and immediately cooled to room temperature.

It is noted that throughout the measurements, the integral of the 110°C TL peak is taken as a measure of the sensitivity of the quartz samples. Also, different test doses were used for each quartz sample, and the values of the test doses are given in the legends of Figs. 1–3.

3. Experimental results

3.1. MA-TAC and SA-TAC measurements for untreated samples

The MA-TAC and SA-TAC for the three untreated quartz samples are shown in Figs. 1 and 2. By comparing the MA-TAC and SA-TAC behavior one observes that although the general behavior is the same, there are great differences in the respective values of the sensitization factors. For the MA-TACs the maximum sensitization factors at 500°C for the untreated

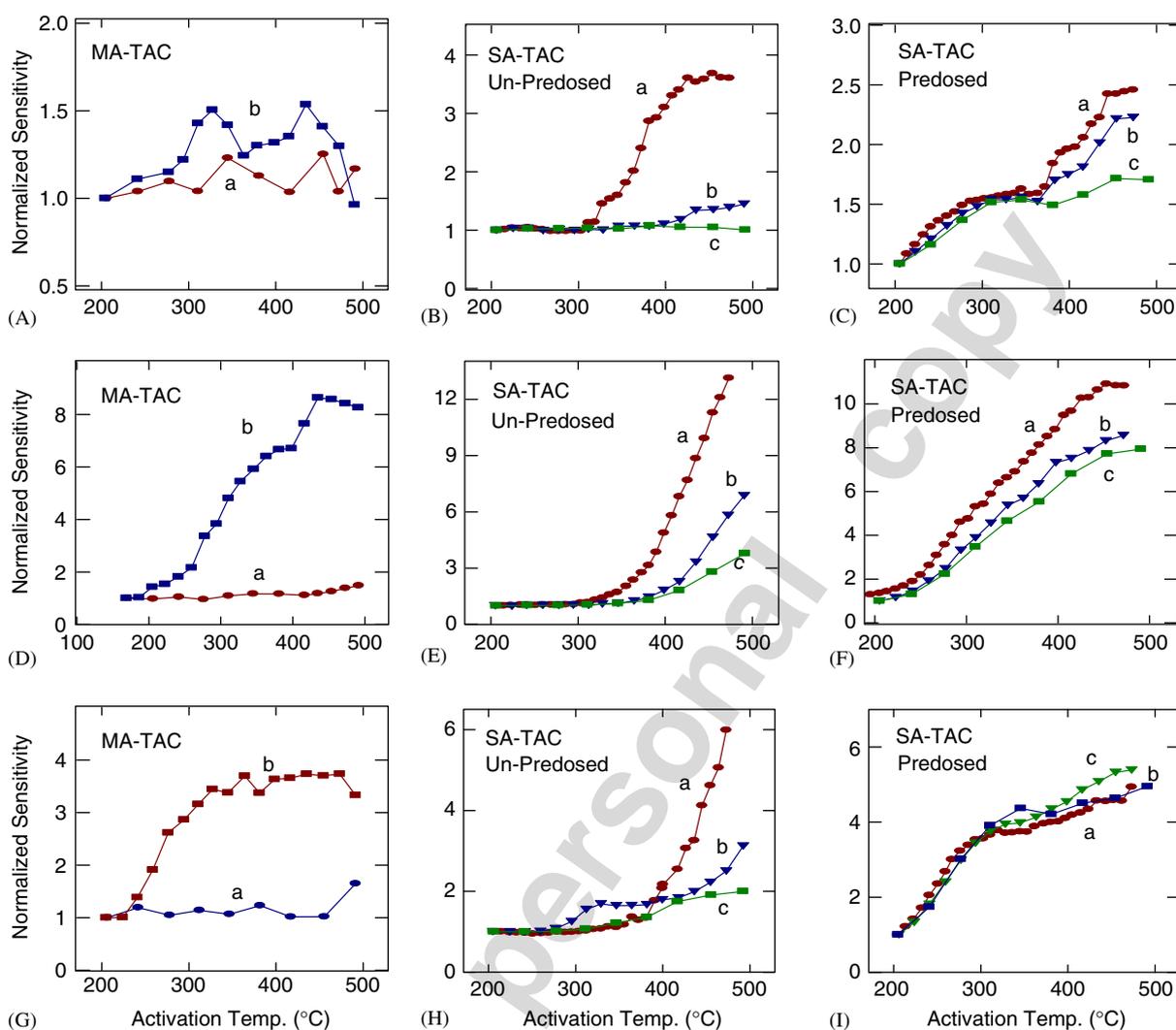


Fig. 3. The MA-TAC and SA-TAC for the three quartz samples annealed for 1 h at 900 °C: (A)–(C) synthetic quartz, (D)–(F) sedimentary quartz, and (G)–(I) Arkansas quartz. The samples on the right hand side were given a pre-dose of 20 Gy before measurement of the TAC. The test dose used was 0.00356 Gy for all measurements shown. Note that all sensitivity scales are linear, but not all start at zero. The curves labeled (a)–(c) in Fig. 3 correspond to measurements with different temperature intervals $\Delta T = 10, 20$ and 40 °C, respectively.

synthetic, sedimentary and Arkansas quartz samples are correspondingly 6, 100 and 10 relative to the initial values (Fig. 1), i.e. they show values ranging over one order of magnitude.

On the other hand, Fig. 2 shows that the maximum sensitizations reached at 500 °C for the three samples using SA-TAC are similar to each other, with the corresponding maximum sensitization values being 200, 150 and 50 relative to the initial values.

For each sample these measurements were made using different temperature intervals (10, 20 and 30 °C). From Fig. 2 it can be seen that the sensitization due to thermal activation depends strongly on the temperature step ΔT used for the activation temperature in SA measurements.

Another important feature of the SA-TACs is that they have three steps at about 240, 340 and 450 °C. These three distinct steps correspond to the three postulated hole reservoirs R_1 , R_2 and R_3 in the modified Zimmerman model and are discussed

later in this paper. Fig. 2 provides direct experimental evidence for the existence of these three distinct hole reservoirs which are activated at different temperatures. The existence of these three distinct hole reservoirs was previously postulated by Bailey (2001) and Adamiec (2005) from analysis of their quartz data.

The data presented in Figs. 1 and 2, as well as additional data not shown here, show that for the SA-TAC curves sensitization start at 300 °C or higher, with the only exception being the SA-TAC for synthetic quartz which starts at ~ 200 °C and has a peak at ~ 240 °C (Fig. 2a). We attribute this difference to the fact that the Arkansas and sedimentary quartz samples possess a clear geological TL signal above 200 °C, while the synthetic quartz samples show no initial TL signal. By applying the additive-dose method, the equivalent dose (ED) values for the Arkansas and sedimentary quartz were found to be 31 and 16 Gy, respectively, while in the case of synthetic quartz the ED value was zero for all practical purposes. These ED

Table 1
The parameters used by Pagonis et al. (2003), and in this paper

Parameters used in Pagonis et al. (2003)	Additional and modified parameters used in the present simulation for the three hole reservoirs R1, R2 and R3
E_t	1.0 eV
s_t	10^{13} s^{-1}
E_r	1.4 eV
s_{r1}	10^{13} s^{-1}
x_t	$5 \times 10^{10} \text{ cm}^{-3}$
A_{r1}	$10^{-10} \text{ cm}^3 \text{ s}^{-1}$
N_{r1}	10^{14} cm^{-3}
M	10^{14} cm^{-3}
A_s	$0.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$
A_m	$10^{-12} \text{ cm}^3 \text{ s}^{-1}$
A_t	$10^{-12} \text{ cm}^3 \text{ s}^{-1}$
N_t	10^{13} cm^{-3}
N_s	$1.01 \times 10^{13} \text{ cm}^{-3}$
A_1	$10^{-12} \text{ cm}^3 \text{ s}^{-1}$
	E_{r1} 1.2 eV
	N_{r1} 10^{12} cm^{-3} (Hole reservoir R ₁)
	E_{r2} 1.5 eV (Hole reservoir R ₂)
	N_{r2} 10^{12} cm^{-3}
	s_{r2} 10^{13} s^{-1}
	A_{r2} $10^{-10} \text{ cm}^3 \text{ s}^{-1}$
	E_{r3} 1.8 eV
	N_{r3} 10^{12} cm^{-3} (Hole reservoir R ₃)
	s_{r3} 10^{13} s^{-1}
	A_{r3} $10^{-10} \text{ cm}^3 \text{ s}^{-1}$

The numbers in the second column show the modified and additional parameters used in this paper, when they are different from those of Pagonis et al. (2003).

values represent, of course, a low limit on the actual geological doses received by the samples, due to their unknown history of exposure to sunlight. Our synthetic quartz SA-TAC data in Fig. 2a show therefore directly the existence of reservoir R₁, which is activated by heating between 200 and 300 °C. This reservoir is assumed to be “full” for the younger synthetic quartz which has ED ~ 10 Gy, while it is empty for the older Arkansas and sedimentary quartz (which have ED values of 31 and 16 Gy, respectively).

3.2. MA-TAC and SA-TAC measurements for annealed samples

Fig. 3 shows how annealing at 900 °C causes the relative MA and SA behavior to become the same, while the untreated sample behavior shown in Fig. 1 is very different for each of the three samples. Specifically, Fig. 3 shows that after annealing at 900 °C, the ratio of maximum sensitizations in the MA-TAC and SA-TAC for the three types of quartz becomes the same, namely a ratio of 1.5:3.5:2.5 for Figs. 3(A)–(C) in the case of synthetic quartz, a ratio of 8:12:12 for Figs. 3(D)–(F) and for sedimentary quartz, and a ratio of 4:6:5 for Figs. 3(G)–(I) for Arkansas quartz. The curves labeled (a)–(c) in Fig. 3 correspond to measurements with different temperature intervals $\Delta T = 10, 20$ and 40 °C, respectively.

This behavior of the three quartz samples is very similar to our previous results on the TL versus dose and sensitivity versus dose curves for these quartz samples (Kitis et al., 2006). These previous results showed that annealing at 900 °C removes the

differences in superlinear behavior and in the measured shapes of the TL versus dose and of the sensitivity versus predose curves.

3.3. Numerical simulation

The complete experimental protocol employed in this study was simulated using the modified Zimmerman kinetic model introduced by Chen and Leung (1999). Chen and Pagonis (2003) explained the shape of experimentally observed TACs by using the model of Chen and Leung (1999). In order to reproduce the experimental behaviors of Figs. 1 and 2, it is necessary to modify the model of Chen and Pagonis (2003) by introducing two additional hole reservoirs, thus the three reservoirs are labeled R₁, R₂ and R₃.

It is noted that working along similar lines, Adamiec (2005) introduced a quartz model consisting of three electron traps, three reservoir hole traps and a luminescence center. Specifically the Adamiec model consists of an electron trap T₁ responsible for the ‘110 °C peak’, a second electron trap T₂ responsible for OSL emission and the TL peak around 320 °C, a thermally disconnected electron trap M, three nonluminescent hole centers R₁, R₂, and R₃ (corresponding to reservoir centers in the Zimmermann model) and a luminescence center L. In this model, recombination of electrons with holes trapped in the R centers is allowed unlike in the original Zimmerman model. Reservoir R₁ is a shallow hole reservoir, R₂ is a reservoir center equivalent to the one described by Bailey (2001) and similar to the reservoir center in the Zimmerman model, and R₃ is responsible for the sensitivity increase observed experimentally above 500 °C.

In our simulation, the activation energies for the three hole reservoirs are taken to be $E = 1.2, 1.5$ and 1.8 eV and the corresponding concentrations are taken as $N_1 = N_2 = N_3 = 10^{12} \text{ cm}^{-3}$. The rest of the parameters in the model are taken to be identical to our previously published model on the superlinearity of quartz samples (Pagonis et al., 2003). Table 1 shows the parameters used in the present model.

The model of Chen and Pagonis (2003) consists of an active trapping state T having a concentration of N_t (m^{-3}) and an instantaneous occupancy n_t (m^{-3}); the activation energy is E_t (eV) and the frequency factor s_t (s^{-1}). S is a thermally disconnected trapping state with concentration N_s (m^{-3}) and occupancy of n_s (m^{-3}). A_t ($\text{m}^3 \text{ s}^{-1}$) and A_s ($\text{m}^3 \text{ s}^{-1}$) are the trapping coefficients into T and S, respectively. L is the luminescence center with concentration M (m^{-3}) and instantaneous occupancy of m (m^{-3}). The transition coefficient of the free holes from the valence band into L is A_1 ($\text{m}^3 \text{ s}^{-1}$) and the recombination coefficient of free holes is A_m ($\text{m}^3 \text{ s}^{-1}$). The modified version of the model includes the three hole reservoirs R₁, R₂ and R₃ having concentrations of N_{r1} , N_{r2} , N_{r3} (m^{-3}) and instantaneous occupancies of n_{r1} , n_{r2} , n_{r3} (m^{-3}) correspondingly; E_{r1} , E_{r2} , E_{r3} are the activation energies (eV) of free holes into the valence band and s_{r1} , s_{r2} , s_{r3} the relevant frequency factors (s^{-1}). The rate at which electron–hole pairs are produced by the irradiation is x ($\text{m}^{-3} \text{ s}^{-1}$) which is propor-

tional to rate at which the dose is given to the sample. The total dose given to the sample is proportional to $x t_D (m^{-3})$ where t_D is the irradiation time.

The set of equations governing the process during the excitation stage is

$$dn_t/dt = A_t n_c (N_t - n_t), \quad (1)$$

$$dn_s/dt = A_s n_c (N_s - n_s), \quad (2)$$

$$dn_v/dt = x - A_1 n_v (M - m) - A_r n_v (N_r - n_r), \quad (3)$$

$$dm/dt = A_1 n_v (M - m) - A_m m n_c, \quad (4)$$

$$dn_{r1}/dt = A_{r1} n_v (N_{r1} - n_{r1}), \quad (5)$$

$$dn_{r2}/dt = A_{r2} n_v (N_{r2} - n_{r2}), \quad (6)$$

$$dn_{r3}/dt = A_{r3} n_v (N_{r3} - n_{r3}), \quad (7)$$

$$dn_c/dt = dm/dt + dn_{r1}/dt + dn_{r2}/dt + dn_{r3}/dt + dn_v/dt - dn_t/dt - dn_s/dt. \quad (8)$$

Eqs. (6) and (7) are the new equations describing the kinetics of the additional hole reservoirs R_2 and R_3 . This set of equations has been solved for certain sets of the parameters using the Mathematica differential equations solver.

The rate equations governing the heating process here are

$$dn_t/dt = A_t n_c (N_t - n_t) - s_t \exp(-E_t/kT), \quad (9)$$

$$dn_s/dt = A_s n_c (N_s - n_s), \quad (10)$$

$$dn_v/dt = n_r s_r \exp(-E_r/kT) - A_r n_v (N_r - n_r) - A_1 n_v (M - m), \quad (11)$$

$$dm/dt = A_1 (M - m) n_v - A_m m n_c, \quad (12)$$

$$dn_{r1}/dt = A_{r1} n_v (N_{r1} - n_{r1}) - n_{r1} s_{r1} \exp(-E_{r1}/kT), \quad (13)$$

$$dn_{r2}/dt = A_{r2} n_v (N_{r2} - n_{r2}) - n_{r2} s_{r2} \exp(-E_{r2}/kT), \quad (14)$$

$$dn_{r3}/dt = A_{r3} n_v (N_{r3} - n_{r3}) - n_{r3} s_{r3} \exp(-E_{r3}/kT), \quad (15)$$

$$dn_c/dt = dm/dt + dn_{r1}/dt + dn_{r2}/dt + dn_{r3}/dt + dn_v/dt - dn_t/dt - dn_s/dt. \quad (16)$$

Eqs. (14) and (15) are the equations describing the kinetics of the additional hole reservoirs R_2 and R_3 during the heating stage. The intensity of the emitted light is given by

$$I(T) = A_m m n_c. \quad (17)$$

In the simulation, the conventional linear heating function is used, $T(t) = T_0 + \beta t$ where β is the constant heating rate of 2°C/s .

Fig. 4 shows the results of simulating the MA-TAC and SA-TAC experimental procedures for quartz and for three values of the temperature step $\Delta T = 10, 20, 30^\circ\text{C}$. It is seen that the simulation produces qualitatively the experimental behavior of the SA-TAC and MA-TAC in Figs. 1 and 2.

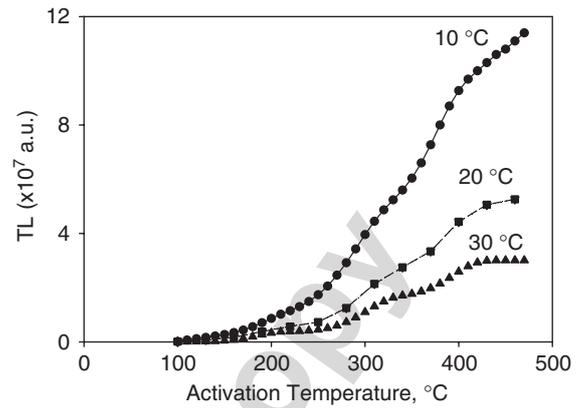


Fig. 4. Simulation of the effect of the annealing temperature step ΔT on the SA-TAC using the modified model of Chen and Leung (1999). The parameters of the model are given in Table 1.

Finally we note the large experimental errors existing for MA-TAC in Fig. 1. Each point is the mean value of several runs made with the same sample. In the cases of SA-TAC the relative errors are for the most part less than 5%, whereas in the case of MA-TACs the error bars are much higher, of the order of 25%. It is possible that the thermal-activation process perturbs the high-temperature region of the glow curve, where the unknown optical, irradiation and grinding history of the samples is accumulated. The large errors in Fig. 1 could be attributed to these unknown histories of the three quartz samples.

4. Discussion and conclusions

In a recently published comparative study, Adamiec (2005) studied the TAC of several types of quartz annealed in air at 1200°C for 10 h; these TACs were characterized by two stages of activation, one occurring between 200 and 300°C and the second one occurring above 500°C . This shape of TAC was also observed in over 30 samples of porcelain. The degree of maximum sensitization varied widely for the 6 samples and was found to range within three orders of magnitude, i.e. between 3.7 and 328.

Additional TAC measurements by Adamiec were performed using untreated sedimentary materials. The TAC of these geological samples presented a very different form to that of the annealed quartz, by exhibiting very small sensitivity changes up to 300°C and with a main activation step starting at $\sim 500^\circ\text{C}$. For these samples, the maximum sensitization factor was found to be between 34 and 251.

Additional TACs for the same geological samples were measured after they were irradiated with a dose of 20 Gy in addition to the natural paleodose and prior to the measurement of the TAC. It was found that these predosed samples display a sensitivity increase after the first heating to 200°C , and this behavior was explained by the existence of a thermally unstable R center that traps holes during irradiation. Adamiec (2005) also analyzed the isothermal sensitization of quartz samples and postulated that there is another hole-trapping site with a lower thermal stability. Bailey (2001) arrived independently at

the same conclusion, namely that there must exist a shallow R center by considering the phenomenon of dose quenching in OSL and TL of quartz samples.

Our measurements give results similar to the Adamiec study and they also include the effects of the temperature step ΔT , as well as a comparison of the multiple- and single-aliquot techniques, and the effect of annealing at temperatures close to the firing temperatures of ceramics in antiquity. Our results show the importance of the details of experimental technique and highlight the improvements in statistics which occur when using the SA-TAC instead of the MA-TAC method. Finally the data presented in this paper provide direct experimental evidence for the existence of the extra shallow reservoir R_1 whose existence was hypothesized previously by Bailey (2001) and Adamiec (2005). More generally, the SA-TAC data presented in Fig. 2 provide direct experimental evidence for the existence of three distinct hole reservoirs which are activated at different temperatures.

Annealing the samples to 900 °C causes the differences in sensitivity between the three quartz samples to disappear and

the sensitivity ratios for the three quartz samples become identical, at least within the accuracy of the experimental data.

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