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Simulating comprehensive kinetic models for quartz luminescence using the R program KMS

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HIGHLIGHTS

- New open access R program KMS for simulation of quartz luminescence.
- Compact functions for simulating TL and OSL events in geological history of quartz.
- Practical examples given for sedimentary or fired quartz samples.
- Examples are provided for multiple and single aliquot dating protocols.

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ABSTRACT

Kinetic models have been used extensively for modeling and numerical simulation of luminescence phenomena and dating techniques in quartz. In this paper we introduce the open access R program KMS for kinetic model simulation of luminescence phenomena in quartz. Several handy and compact functions are designed to simulate events in the geological history of quartz: crystallization, irradiation, optical illumination, and heating processes. These R functions provided by program KMS offer useful numerical tools to perform quartz luminescence simulations in a flexible manner. The simulation process can be understood easily by creating transparent programs by creating sequences of these compact R functions. With this contribution, we provide several practical examples of using the R functions in KMS to simulate the geological history of either sedimentary quartz samples, or of quartz samples which were fired in antiquity. In addition, examples are provided for simulations of commonly used dating protocols, like the multiple aliquot additive-dose technique (MAA) and the single aliquot regenerative-dose protocol (SAR).

1. Introduction

Luminescence techniques are well-established experimental methods for dating and retrospective dosimetry. During the past 50 years, several reliable protocols have been developed for determining the equivalent dose (ED) for quartz samples using thermoluminescence (TL) or optically stimulated luminescence (OSL) signals. Modeling provides fundamental answers about the validity of the complex experimental protocols used during luminescence dating (Chen and Pagonis, 2011). Kinetic models have been used to simulate a wide variety of experimental behaviors in quartz, and to elucidate the underlying physical mechanisms. Theoretical and modeling work helps researchers to obtain a better understanding of the various factors influencing both the precision and the accuracy of the experimental protocols (Pagonis et al., 2011a).

Zimmerman (1971) first proposed a pre-dose model to explain sensitization and thermal activation phenomena observed for luminescence emissions of quartz. Chen and Leung (1999) presented a comprehensive version of the Zimmerman model which successfully reproduced several of the experimental features previously observed in the 110 °C peak in quartz. A modified version of this model has been used by Pagonis et al. (2003) to describe the experimentally observed super-linearity of pre-dosed and annealed quartz samples. Pagonis and Carty (2004) used the model to simulate the complete sequence of experimental steps taken during the additive dose version of the pre-dose technique, and showed that the model can reproduce accurately the accumulated dose received by the sample. Adamiec (2005) developed a kinetic model of pre-

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dose sensitization in quartz based on the Zimmerman's model. The experimentally observed thermal activation characteristics and isothermal sensitization of quartz samples were successfully simulated using the model (Adamiec et al., 2004, 2006).

Bailey (2001) presented a comprehensive phenomenological model of quartz, which was developed on the basis of empirical data. The model consists of five electron traps and four hole centers and is able to reliably reproduce a wide variety of TL and OSL phenomena in quartz (Bailey, 2001; Pagonis et al., 2007a,b, 2008a). The original model by Bailey (2001) does not contain traps that describe the experimentally observed slow OSL components in quartz. Bailey (2004) further improved the model by adding three electrons traps that denote the source traps for the charge giving rise to these slow decaying OSL components S1, S2 and S3. In a further improvement, the original model presented by Bailey (2001) was modified by Pagonis et al. (2008b) to include two additional levels in order to simulate the experimentally observed thermally transferred OSL (TT-OSL) signals and basic transferred OSL (BT-OSL) signals. This model was successfully applied for assessing the accuracy and precision of several luminescence protocols for ED determination (Pagonis et al., 2011a,b,c). These comprehensive kinetic models are based on the solution of a set of ordinary differential equations that describe the evolution of the electron and hole populations under a sequence of events. These events include usually quartz crystallization, irradiation, optical illumination, and heating processes.

The past 5 years have seen the development of sophisticated software packages in the open access programming language R (R Core Team, 2015), for the purposes of analyzing experimental data for luminescence dating and luminescence dosimetry applications. Specifically very extensive R-packages have been developed for analyzing OSL and TL luminescence data, and for helping researchers perform the complex operations required in modern dating protocols (Kreutzer et al., 2012; Dietze et al., 2013; Peng et al., 2013; Fuchs et al., 2014; Peng, 2015). While these R-packages cover almost all aspects of TL and OSL data analysis, there is a lack of similar programs for simulating the associated quartz models.

In this paper, the program KMS (Kinetic Model Simulations) is presented, which was also developed in the open source statistical environment R. In the examples provided in this paper, the program KMS is used for modeling quartz luminescence according to the comprehensive kinetic models developed by Bailey (2001, 2004) and by Pagonis et al. (2008b). However, program KMS can be easily modified to simulate any other kinetic model which is based on a set of differential equations to describe the traffic of electrons and holes in a dosimetric material.

The specific goals of this paper are as follows:

(1) To offer an openly accessible and transparent software environment for kinetic model simulation and
(2) To provide easy-to-use flexible code for modeling quartz luminescence phenomena.
(3) To present a small number of handy and compact R functions which simulate events in the history of quartz samples: crystallization, irradiation, optical illumination, and heating processes.
(4) To provide application examples which illustrate the basic functionality of these R functions, by providing several R code templates with the corresponding detailed explanations.

2. Description of the models

Energy level diagrams for the comprehensive quartz models of Bailey (2001, 2004) and Pagonis et al. (2008b) are shown in Fig. 1(A–C). The kinetic parameters used in these models are summarized in Tables 1–3. The original model by Bailey (2001) consists of five electron traps and four hole centers (Fig. 1A). Level 1 in the model represents a shallow electron trapping level, which gives rise to a TL peak at ~110 °C with a heating rate of 5 °C s^{-1}. Level 2 represents a generic "230 °C TL" trap, typically found in many quartz samples. Levels 3 and 4 are usually termed the fast and medium OSL components. They yield TL peaks at ~330 °C and give rise to OSL signals. Level 5 is a deep electron center which is considered thermally disconnected. Levels 6 and 7 are thermally unstable, non-radiative recombination centers (also termed "hole reservoirs"). Level 8 is a thermally stable, radiative recombination center termed the "luminescence center" (L-center). Level 9 is a thermally stable, non-radiative recombination center termed a "killer" center (K-center). Bailey (2004) added levels 5, 6, and 7 to the original model of Bailey (2001) to represent slow OSL components (termed "S1", "S2", and "S3") known to be present in quartz (Fig. 1B). Pagonis et al. (2008b) introduced levels 10 and 11 to the original model of Bailey (2001) to represent the source traps for the TT-OSL signal and BT-OSL signal (Fig. 1C).

The kinetic parameters in Tables 1–3 are as defined by Bailey (2001, 2004): N_i/N_j are the concentrations of electrons traps or hole centers (cm^{-3}), n_i/n_j are the concentrations of trapped electrons or holes (cm^{-3}), s_i/s_j are the frequency factors (s^{-1}), E_i/E_j are the electrons trap depths below the conduction band or hole trap depths above the valence band (eV), A_i are the conduction band to electron trap transition probability coefficients (cm^3 s^{-1}),

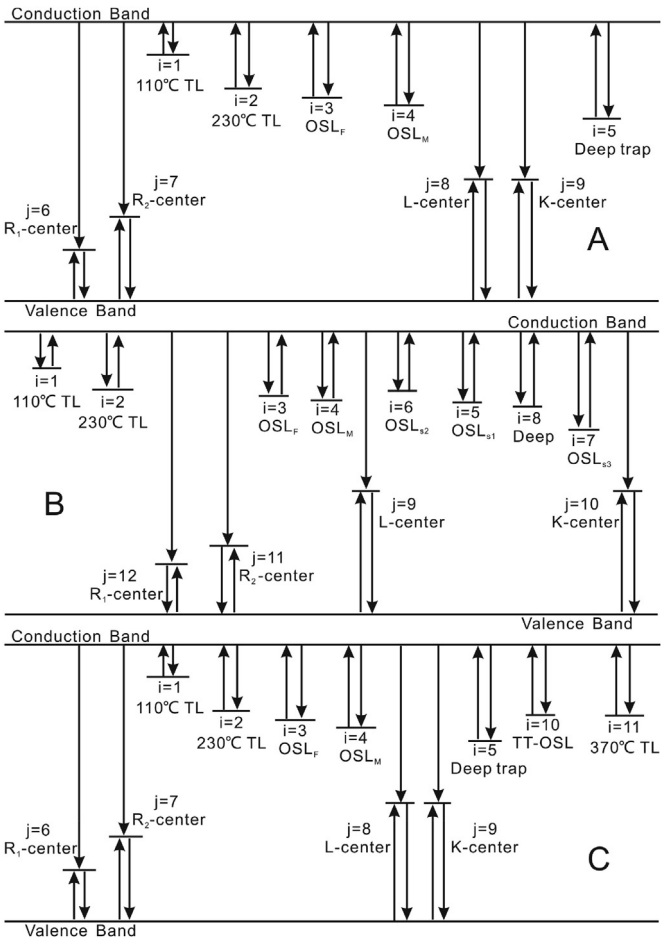

Fig. 1. Schematic diagrams of the comprehensive quartz models of (A) Bailey (2001), (B) Bailey (2004), and (C) Pagonis et al. (2008b).

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Table 1
Parameters used in the kinetic model of Bailey (2001).

Level	Parameter						
	N_i/N_j (cm^{-3})	E_i/E_j (eV)	s_i/s_j (s^{-1})	A_i/A_j ($cm^3\ s^{-1}$)	B_j ($cm^3\ s^{-1}$)	θ_{0i} (s^{-1})	E_i^{th}(eV)
i = 1	1.5e7	0.97	5e12	1e-8	–	0.75	0.1
i = 2	1e7	1.55	5e14	1e-8	–	0	0
i = 3	1e9	1.7	5e13	1e-9	–	6.0	0.1
i = 4	2.5e8	1.72	5e14	5e-10	–	4.5	0.13
i = 5	5e10	2.0	1e10	1e-10	–	0	0
j = 6	3e8	1.43	5e13	5e-7	5e-9	–	–
j = 7	1e10	1.75	5e14	1e-9	5e-10	–	–
j = 8	1e11	5.0	1e13	1e-9	1e-10	–	–
j = 9	5e9	5.0	1e13	1e-10	1e-10	–	–

Table 2
Parameters used in the kinetic model of Bailey (2004).

Level	Parameter						
	N_i/N_j (cm^{-3})	E_i/E_j (eV)	s_i/s_j (s^{-1})	A_i/A_j ($cm^3\ s^{-1}$)	B_j ($cm^3\ s^{-1}$)	σ_i (cm^2)	E_i^{th}(eV)
i = 1	1.42e10	0.97	5e12	1e-8	–	1e-19	0.1
i = 2	1.5e9	1.55	5e14	1e-8	–	0	0
i = 3	2.05e11	1.7	5e12	1e-9	–	1e-16	0.1
i = 4	7.04e10	1.72	5e13	8e-10	–	3e-17	0.13
i = 5	1.77e11	1.8	5e13	8e-10	–	4e-18	0.2
i = 6	2.53e11	1.65	5e13	5e-10	–	3e-19	0.2
i = 7	3.58e12	2.6	5e13	2e-10	–	2e-21	0.2
i = 8	1.28e13	2.0	1e10	1e-10	–	0	0
j = 9	8.83e13	5.0	1e13	1e-9	1e-10	–	–
j = 10	1.15e14	5.0	1e13	1e-10	1e-10	–	–
j = 11	4.16e12	1.75	5e14	1e-9	5e-10	–	–
j = 12	4.2e11	1.43	5e13	5e-8	5e-9	–	–

Table 3
Parameters used in the kinetic model of Pagonis et al. (2008b).

Level	Parameter						
	N_i/N_j (cm^{-3})	E_i/E_j (eV)	s_i/s_j (s^{-1})	A_i/A_j ($cm^3\ s^{-1}$)	B_j ($cm^3\ s^{-1}$)	θ_{0i} (s^{-1})	E_i^{th}(eV)
i = 1	1.5e7	0.97	5e12	1e-8	–	0.75	0.1
i = 2	1e7	1.55	5e14	1e-8	–	0	0
i = 3	4e7	1.73	6.5e13	5e-9	–	6.0	0.1
i = 4	2.5e8	1.8	1.5e13	5e-10	–	4.5	0.13
i = 5	5e10	2.0	1e10	1e-10	–	0	0
j = 6	3e8	1.43	5e13	5e-7	5e-9	–	–
j = 7	1e10	1.75	5e14	1e-9	5e-10	–	–
j = 8	3e10	5.0	1e13	1e-10	1e-10	–	–
j = 9	1.2e12	5.0	1e13	1e-14	3e-10	–	–
i = 10	5e9	1.65	6.5e13	1e-11	–	0.01	0.2
i = 11	4e9	1.6	5e12	6e-12	–	0	0

A_j are the valence band to hole trap transition probability coefficients ($cm^3\ s^{-1}$), and B_j are the conduction band to hole center transition probability coefficients ($cm^3\ s^{-1}$). Other parameters used in these models include the photoionization cross-sections σ_i (cm^2), the photo-eviction constant θ_{0i} (s^{-1}) at T = ∞, and the thermal assistance energy E^{th} i(eV). The relevant systems of differential equations are given in Bailey (2001, 2004) and Pagonis et al. (2008b), and will not be repeated here.

3. Description of the program

The program KMS (Kinetic Model Simulations) was written using the R language and was based on original Mathematica code developed by one of the authors (VP). KMS is freely downloadable from the web depository https://github.com/pengjunUCAS/KMS. It contains three R scripts (i.e, "Bailey01_Model.R", "Bailey04_Model.R", and "Pagonis_Model.R") for simulating the kinetic models by Bailey (2001, 2004), and Pagonis et al. (2008b), respectively. Repository KMS also contains several separate R files which illustrate how to apply a Monte Carlo approach with these kinetic models. In these Monte Carlo examples, a "standard" quartz model is used as a starting point and a number of versions of the parameters are generated by randomly selecting concentration values within certain percent of the original values.

Model initialization and events including quartz crystallization, irradiation, illumination, and heating are simulated using a number of R functions, as described in Table 4. The sequence of events can be simulated in a command-window that enables a highly customizable environment. The set of differential equations governing an event is solved using function *ode()* from the R package deSolve (Soetaert et al., 2010).

The initial concentration of electron and hole must be supplied in order to simulate an event, and the resultant number of electron and hole populations is returned by the R function, once the simulation is terminated. The final values of center populations at the end of an event are used as the initial values for the next event.

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Table 4
A summary of R functions used for kinetic model simulations.

Function	Description
setInis()	Set all center populations equal to zero for quartz crystallization.
setPars()	Initialize the model using kinetic parameters listed in Table 1, Table 2, or Table 3.
irradiate(temp, tim, doseRate)	Irradiate at ***temp*** °C for ***tim*** s with a dose rate of ***doseRate*** Gy s^{-1}.
heatAt(temp, tim)	Heat at ***temp*** °C for ***tim*** s.
heatTo(temp1, temp2, hRate)	Heat from ***temp1*** °C to ***temp2*** °C with a heating rate of ***hRate*** °C s^{-1}.
stimOSL(temp, tim, pValue, nChannel)	OSL stimulation at ***temp*** °C for ***tim*** s with a photon stimulation flux of ***pValue*** s^{-1} cm^{-2}. The OSL signal is evaluated at the equally spaced number of channels ***nChannel***.
stimTL(lowTemp, upTemp, hRate, nChannel)	TL stimulation from ***lowTemp*** °C to ***upTemp*** °C with a heating rate of ***hRate*** °C s^{-1}, the number of equally spaced channels is ***nChannel***.

The R functions provided in program KMS save the center populations of electrons and holes internally as global variables in vector *inis*. That is, once an event is completed, all center populations in vector *inis* will be automatically updated correspondingly. In this manner, the user does not need to pass the initial center populations as arguments between functions when simulating a sequence of events. In this way events can be simulated elegantly using compact R commands, as the number of arguments to be typed is limited. The first step of a simulation is zeroing all center populations in vector *inis*, in order to simulate crystallization of the quartz sample using the R function *setInis()*.

The model must be initialized using the R function *setPars()* before simulating an event (or a sequence of events). The effect of this function is creating a vector of kinetic parameters stored in a global vector *pars*. A direct way to modify kinetic parameters is by changing the elements of vector *pars* manually inside the function. Parameters in vector *pars* can also be modified by using replacement functions. For example, the initial concentration of electrons trap for level 1 can be modified to be 1e8 by using the R command *pars["N1"]<-1e8*. Replacement functions of this kind are useful if the user wants to simulate a number of versions of kinetic parameters using a Monte Carlo approach, as performed in previous studies (Bailey, 2004; Bailey et al., 2005; Pagonis et al., 2011a,b,c).

Table 4 lists the functions *irradiate()*, *heatAt()*, *heatTo()*, *stimOSL()*, and *stimTL()*, which are used for simulating the experimental steps of a luminescence dating protocol. These steps are simulated using different values for the photon stimulation flux *pValue*, the electron/hole pair generation rate *rValue*, and the heating rate *hRate*. Specifically in function *irradiate()* one sets $pValue = hRate = 0$, $rValue > 0$, while in function *heatAt()* one sets $pValue = hRate = rValue = 0$. Similarly in function *heatTo()*, $pValue = rValue = 0$, $hRate \neq 0$ and in function *stimOSL()*, one sets $hRate = rValue = 0$, $pValue > 0$. Finally in function *stimTL()* the parameters are set at $pValue = rValue = 0$, $hRate > 0$.

The electron and hole populations at different simulation times are saved as columns of an invisible matrix, once the simulation of an experimental step is terminated. For example, during irradiation at 20 °C for 100 s with a laboratory dose rate of 0.1 Gy s^{-1}, the result can be saved to a matrix using the R command *res ← irradiate(temp = 20, tim = 100, doseRate = 0.1)*. The various elements in this matrix *res* can be retrieved using the R command *colnames(res)*. For instance, the first twelve elements in matrix *res* simulated from the kinetic model by Bailey (2001) are a vector of character *c("time", "n1", "n2", "n3", "n4", "n5", "n6", "n7", "n8", "n9", "nc", "nv")*. Vector *time* stands for the simulation time, *n1* to *n5* represent concentrations of electrons in the five electron traps, *n6* to *n9* denote concentrations of holes in the four hole centers, and *nc* and *nv* are concentrations of electrons in the conduction band and holes in the valence band, respectively. If R function *stimOSL()* or *stimTL()* is called, then two additional elements in matrix *res* will be *c("oslx", "osly")* or *c("tlx", "tly")*. In this case *oslx* and *osly* represent the measurement time and OSL intensity, respectively. Similarly, *tlx* and *tly* represent the heating temperature and TL intensity, respectively. Elements in matrix *res* can be accessed by filtering of the matrix. For example, values of *nc* and *nv* at different simulation times can be accessed by using the R command *res[,"nc"]* and *res[,"nv"]*, respectively. The user can also plot the change of *nc* against the simulation time graphically using the R command *plot(res[,c("time", "nc")])*.

4. Application examples

In this section we use several examples to illustrate how to simulate luminescence techniques for quartz samples flexibly, using functions provided by the R program KMS. The first example simulates the geological history of natural quartz samples (for both a sedimentary and a previously fired sample). The second example simulates the multiple aliquot additive-dose technique, and the last example is a simulation of the single aliquot regenerative-dose technique.

4.1. Simulation of the thermal and irradiation history of natural quartz samples

Simulating an appropriate geological history for the quartz crystal from the time of formation until laboratory measurement is an essential part of a comprehensive simulation study. Bailey (2004) used the following steps to simulate a natural sedimentary quartz sample: (1) Quartz crystallization by zeroing all center populations; (2) Irradiate for 50 Ma at 20 °C with an environmental dose rate of 1 Gy ka^{-1}; (3) Cycles of 10 ka irradiation at 20 °C with a dose rate of 1 Gy ka^{-1} plus 6000 s illumination at 20 °C; (4) Accumulation of the burial dose at 20 °C with a dose rate of 1 Gy ka^{-1}.

R code TEMPLATE1 simulates the sample history described by the steps above. The first two lines of commands load the R package deSolve and the R file "Bailey04_Model.R" into R. The user should make sure that the package has been installed and that the R file is available from the current working directory. The model is initialized and all center populations are zeroed using the command lines 3 and 4. In the 5th line the sample is irradiated for 50 Ma at 20 °C with a dose rate of 1 Gy ka^{-1}. Note that 50 Ma is equal to 50,000 ka and that a natural dose rate of 1 Gy ka^{-1} is roughly equal to 3.17e-11 Gy s^{-1}. After the excitation stage, a relaxation period in which the temperature of the sample is kept constant at 20 °C for 60 s is introduced, as indicated by the 6th line of command. This 60 s relaxation period allows the electrons and holes accumulated in the conduction and valence band (*nc* and *nv*) to be trapped into the available trap and recombination centers. During the relaxation period the concentrations of *nc* and *nv* will decay to negligible values.

The R code in the 7th line simulates a 6000 s illumination at

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20 °C with a photon stimulation flux (*pValue*) of 4.73e16 s^{-1} cm^{-2}. An important difference should be noted between the three models discussed in this paper: the kinetic models of Bailey (2001) and Pagonis et al. (2008b) use the photo-eviction constant θ_{0i} (s^{-1}) at T = ∞, while the kinetic model of Bailey (2004) uses the photo-ionization cross-sections σ_i (cm^2) instead. Consequently, in the kinetic model by Bailey (2004) the parameter *pValue* denotes absolute stimulation power (photon flux) instead of the normalized stimulation power used in Bailey (2001) and Pagonis et al. (2008b). An absolute stimulation power of 4.73e16 s^{-1} cm^{-2} is roughly equivalent to a 20 mW cm^{-2} illumination, with a wavelength of 470 nm. Readers are advised to consult Choi et al. (2006) for details of calculating absolute photon flux using values of stimulation power and wavelength. The R code in lines 8–13 use a *for()* loop, to simulate cycles of 10 ka irradiation at 20 °C with a dose rate of 1 Gy ka^{-1}, followed by a 6000 s illumination at 20 °C. Here the number of such cycles is set equal to 2. Line 14 in the R code simulates a burial dose of 20 Gy administered at 20 °C, with a natural dose rate of 1 Gy ka^{-1}.

```
### TEMPLATE1.
library(deSolve)                                                    #1
source("Bailey04_Model.R")                                          #2
setPars()                                                           #3
setInis()                                                           #4
irradiate(temp=20,tim=50000/3.17e-11,doseRate=3.17e-11)             #5
heatAt(temp=20,tim=60)                                              #6
stimOSL(temp=20,tim=6000,pValue=4.73e16,nChannel=6000)              #7
nCycle<-2                                                           #8
for (i in seq(nCycle)) {                                            #9
  irradiate(temp=20,tim=10/3.17e-11,doseRate=3.17e-11)              #10
  heatAt(temp=20,tim=60)                                            #11
  stimOSL(temp=20,tim=6000,pValue=4.73e16,nChannel=6000)            #12
} #end for.                                                         #13
irradiate(temp=20,tim=20/3.17e-11,doseRate=3.17e-11)                #14
heatAt(temp=20,tim=60)                                              #15
```

In the simulation performed by Pagonis et al. (2011b), the thermal and irradiation history of the previously fired quartz samples was simulated as follows: (1) Set all trap populations to zero; (2) Irradiate the sample with a geological dose of 1000 Gy, with a dose rate of 1 Gy s^{-1} at 20 °C; (3) Heat to 350 °C (geological time); (4) Illuminate for 100 s at 200 °C, to simulate repeated daylight exposures over long period of time; (5) Heat sample to 700 °C for 1 h, to simulate the high temperature firing of ceramics in antiquity; (6) Administer burial dose at 20 °C with an environmental dose rate of 1e-11 Gy s^{-1}. These steps for simulating the history of a sample which was fired in antiquity are simulated using R code TEMPLATE2.

The first four lines of commands in TEMPLATE2 are similar to those used in TEMPLATE1. The geological dose of 1000 Gy with a dose rate of 1 Gy s^{-1} at 20 °C is simulated using the R command in the 5th line. In command lines 7–8, the sample is heated from room temperature to 350 °C with a heating rate of 5 °C s^{-1}, followed by a cooling-down period from 350 °C to 200 °C with a cooling rate of −5 °C s^{-1}. The sample is illuminated for 100 s at 200 °C with a normalized stimulation power (photon flux) of *pValue* = 2, by using the 9th line of command. According to Bailey (2001), a normalized photon flux of *pValue* = 1 is equivalent to a 20 mW cm^{-2} illumination, with a wavelength of 514.5 nm. Thus a value of the parameter *pValue* between 0.01 and 10 is appropriate for the simulation of the power dependence between 0.2 and 200 mw cm^{-2}. The high temperature firing of ceramics in antiquity is simulated by heating sample to 700 °C for 3600 s using the R code given in lines 10–11. In the last several lines of commands, the sample is cooled to room temperature and administered a burial dose of 20 Gy at 20 °C with a natural dose rate of 1e-11 Gy s^{-1}. As the populations of electrons and holes are updated automatically in the global vector *inis*, the user can print the resulting values of trap populations into the screen using the R command *print(inis)* after a sequence of events are simulated. Trap populations saved in vector *inis* can be used as initial concentrations of electron and hole populations for further simulations (see below).

```
### TEMPLATE2.
library(deSolve)                                                    #1
source("Pagonis_Model.R")                                           #2
setPars()                                                           #3
setInis()                                                           #4
irradiate(temp=20,tim=1000,doseRate=1)                              #5
heatAt(temp=20,tim=60)                                              #6
heatTo(temp1=20,temp2=350,hRate=5)                                  #7
heatTo(temp1=350,temp2=200,hRate=-5)                                #8
stimOSL(temp=200,tim=100,pValue=2,nChannel=1000)                    #9
heatTo(temp1=200,temp2=700,hRate=5)                                 #10
heatAt(temp=700,tim=3600)                                           #11
heatTo(temp1=700,temp2=20,hRate=-5)                                 #12
irradiate(temp=20,tim=20/1e-11,doseRate=1e-11)                      #13
heatAt(temp=20,tim=60)                                              #14
```

4.2. Simulation of the multiple aliquot additive-dose technique for TL

The multiple aliquot additive-dose protocol (MAA) is the oldest method of TL dating. In this technique, different aliquots of the sample are given a sequence of known laboratory doses on top of their natural dose, and the TL glow curves are recorded for each aliquot. A plot of the TL signals against the additive doses yields the TL growth curve. The natural dose is obtained by extrapolation of the growth curve to zero TL intensity. Typical simulated steps of this protocol were given in Pagonis et al. (2011b) as follows: (1) Irradiate an aliquot of the natural sample in laboratory with dose D_i at a dose rate of 1 Gy s^{-1}; (2) Heat aliquot to 500 °C, to record maximum TL intensity for a glow peak; (3) Use a new aliquot and repeat steps 1–2 for a sequence of laboratory doses to reconstruct the growth curve.

Here we use TEMPLATE3 to simulate this protocol. In the 4th line of command, vector *reDose* is used for storing a number of different dose values. The first dose in vector *reDose* is taken to be 1e-13 Gy (practically zero), in order to simulate the natural-dose TL glow curve. The seven additive doses used for constructing the TL growth curve are $D_i = 0.3i$ $(i = 1,2, \ldots,7)$ (Gy). Vector *tlm* is used for storing maximum TL intensities of a glow peak for different additive doses (line 5). Matrix *tlx* and *tly* are used for storing the temperatures and

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TL intensities of the glow curves (line 6). Glow curves are simulated one after another using the *for()* loop. Values of center populations stored in vector *inis* (lines 8–10) were simulated using TEMPLATE2 with a burial dose of 2 Gy used in line 13. This means that the R code in the 8-10th lines of TEMPLATE3 can be replaced by commands in lines 4–14 of TEMPLATE2 (if the given burial dose in TEMPLATE2 is 2 Gy).

The code is used several times in the *for()* loop, to simulate a new aliquot for which a different additive dose is given. The additive doses are administered with a laboratory dose rate of 1 Gy s^{-1} using the R code in the 11th line. The aliquot is then heated from room temperature to 500 °C with a heating rate of 5 °C s^{-1}, and the glow curve is measured using 1000 equal-width channels (line 13). A cooling-down period with a cooling rate of −5 °C s^{-1} is introduced at the end of TL stimulation (line 14). Values of temperature and TL intensity for the ith glow curve are returned in the ith column of matrix *tlx* and *tly*, respectively (lines 15–16). The maximum intensity for the 230 °C TL peak is calculated by interpolating the simulated glow curve using the internal R function *approx()* (line 17). The maximum intensity for the peak at 330 or 370 °C can also be used to construct the growth curve by changing argument *xout* to be 330 or 370. The last three lines of commands are used for visualizing the simulated glow curves and growth curve graphically, as shown in Fig. 2.

```
### TEMPLATE3.
library(deSolve)                                                    #1
source("Pagonis_Model.R")                                           #2
setPars()                                                           #3
reDose<-c(1e-13,0.3,0.6,0.9,1.2,1.5,1.8,2.1)                        #4
tlm<-vector(length=8)                                               #5
tlx<-tly<-matrix(nrow=1000,ncol=8)                                  #6
for (i in seq(8))  {                                                #7
  inis<-c(n1=1.24e-1,n2=1.45e6,n3=3.37e6,n4=2.19e6,                 #8
    n5=1.22e8,n6=7.73e7,n7=1.46e7,n8=3.87e7,n9=1.76e4,              #9
    n10=8.81e5,n11=4.23e5,nc=2.39e-6,nv=7.85e-6)                    #10
  irradiate(temp=20,tim=reDose[i],doseRate=1)                       #11
  heatAt(temp=20,tim=60)                                            #12
  res<-stimTL(lowTemp=20,upTemp=500,hRate=5,nChannel=1000)          #13
  heatTo(temp1=500,temp2=20,hRate=-5)                               #14
  tlx[,i]<-res[,"tlx"]                                              #15
  tly[,i]<-res[,"tly"]                                              #16
  tlm[i]<-approx(x=res[,"tlx"],y=res[,"tly"],xout=230)$y            #17
} #end for.                                                         #18
par(mfrow=c(2,1))                                                   #19
matplot(tlx[-(1:270),],tly[-(1:270),],type="l")                     #20
plot(reDose,tlm,type="o")                                           #21
```

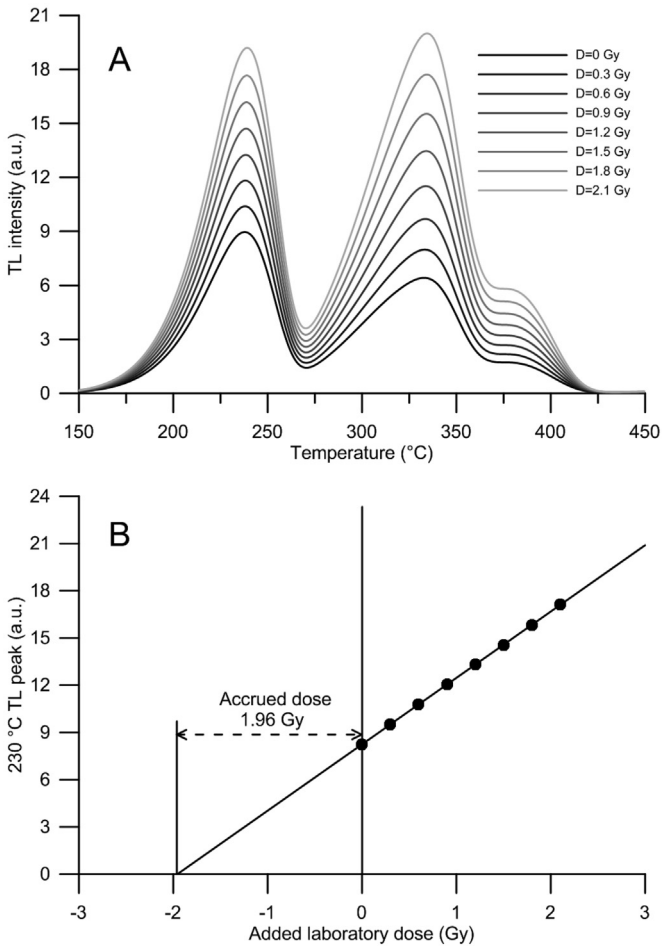

Fig. 2. (A) Simulated TL glow curves for various laboratory doses using the multiple aliquot additive-dose technique. (B) The growth curve constructed using the 230 °C TL peak.

4.3. Simulation of the single aliquot regenerative-dose protocol for OSL

The single aliquot regenerative-dose protocol (SAR) (Murray and Wintle, 2000) is widely applied for determining ED values of sedimentary or fired quartz samples, by using sensitivity-corrected TL/OSL signals. In the application of the SAR technique using OSL, the standardized natural OSL signal is projected onto the growth curve that is constructed using a series of sensitivity-corrected regenerative OSL signals (*L*/*T*), in order to determine the corresponding ED value. As outlined by Pagonis et al. (2011b), the measurement of a series of sensitivity-corrected regenerative OSL signals usually consists of the following steps: (1) The natural sample is given a laboratory dose D_i, known as the regenerative dose; (2) The sample is then heated to a preheat temperature, typically for 10 s at 260 °C, to empty the shallow thermally unstable traps; (3) Optical stimulation for 100 s using a blue LED source at 125 °C, to obtain the regenerative-dose OSL response (L_i); (4) The sample is again given a small laboratory dose, known as the test dose; (5) Heat the sample to a cut-heat temperature, typically for 10 s at 220 °C, to again remove electrons from shallow traps; (6) Additional optical stimulation for 100 s, to obtain the test-dose OSL response (T_i). Steps 1–6 are repeated for a sequence of regenerative doses, including at least one zero dose and at least one repeated dose.

The SAR protocol described above is simulated using R code TEMPLATE4. The simulation uses as initial values the electron and hole center populations of electrons simulated from Section 4.1 (not shown explicitly in TEMPLATE4). The first dose in vector *reDose* is taken to be 1e-13 Gy in order to measure the natural-dose OSL response (the same as TEMPLATE3). The six regenerative doses (i.e., 8, 16, 24, 32, 1e-13, and 8 Gy) are used to construct the growth curve, and are chosen in such a way that the resultant luminescence signals encompass the natural signal (note that the burial dose of the sample is 20 Gy, as simulated in Section 4.1). The second line of command allocates two vectors *LxTx* and *sLxTx* to store respectively

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the sensitivity-corrected regenerative OSL signals and their standard errors. The standardized OSL signals are simulated using the *for()* loop. The regenerative doses and test doses are administered using R commands in the 4th and 11th lines, respectively. The laboratory dose rate is 0.1 Gy s^{-1} and the test dose is 1 Gy. The preheat temperature is 10 s at 260 °C for the regenerative dose measurements (line 7), and the cut heat temperature is 10 s at 220 °C for the test dose measurements (line 14). The optical stimulation is carried out at 125 °C for 100 s using 1000 equal-width channels, and the simulated regenerative-dose and test-dose data are returned to matrix *Lxdat* and *Txdat* using commands in the 9th and 16th lines, respectively. The standardized OSL signal is calculated using the R code in the 18th line. The OSL signals from the first five channels are used to calculate the OSL response. The standardized OSL signal is assumed to have a constant relative uncertainty of 3% (line 19), in order to calculate its standard error. The ED value is calculated using function *calED()* from the R package numOSL (Peng et al., 2013) (lines 20–23).

Object *Curvedata* in line 21 is a three-column matrix used for storing the regenerative doses, the standardized regenerative OSL signals, and the standard errors of standardized regenerative OSL signals. *reDose[-1]* is a vector of six elements, starting with the second element in vector *reDose*. *Ltx* is a two-element vector used for storing the standardized natural OSL signal and its standard error. The R code TEMPLATE4 is appropriate for simulating the SAR protocol using the kinetic model by Bailey (2001) or Pagonis et al. (2008b), since a normalized photon flux of 2 (*pValue* = *2*) is used in the simulation. This means that if the user wants to simulate the SAR protocol using the kinetic model by Bailey (2004), then the argument *pValue* in function *stimOSL()* (lines 9 and 16) needs to be modified into absolute photon flux values.

```
### TEMPLATE4.
reDose<-c(1e-13,8,16,24,32,1e-13,8)                                  #1
LxTx<-sLxTx<-vector(length=7)                                        #2
for (i in seq(7)) {                                                  #3
  irradiate(temp=20,tim=reDose[i]/0.1,doseRate=0.1)                  #4
  heatAt(temp=20,tim=60)                                             #5
  heatTo(temp1=20,temp2=260,hRate=5)                                 #6
  heatAt(temp=260,tim=10)                                            #7
  heatTo(temp1=260,temp2=125,hRate=-5)                               #8
  Lxdat<-stimOSL(temp=125,tim=100,pValue=2,nChannel=1000)            #9
  heatTo(temp1=125,temp2=20,hRate=-5)                               #10
  irradiate(temp=20,tim=1/0.1,doseRate=0.1)                         #11
  heatAt(temp=20,tim=60)                                            #12
  heatTo(temp1=20,temp2=220,hRate=5)                                #13
  heatAt(temp=220,tim=10)                                           #14
  heatTo(temp1=220,temp2=125,hRate=-5)                              #15
  Txdat<-stimOSL(temp=125,tim=100,pValue=2,nChannel=1000)           #16
  heatTo(temp1=125,temp2=20,hRate=-5)                               #17
  LxTx[i]<-sum(Lxdat[1:5,"osly"])/sum(Txdat[1:5,"osly"])            #18
  sLxTx[i]<-0.03*LxTx[i] } #end for.                                #19
library(numOSL)                                                     #20
Curvedata<-cbind(reDose[-1],LxTx[-1],sLxTx[-1])                     #21
Ltx<-c(LxTx[1],sLxTx[1])                                            #22
calED(Curvedata,Ltx,model="exp")                                    #23
```

The SAR protocol can be simulated very efficiently using the R program KMS. It takes less than half a minute to run R code TEMPLATE4 for different kinetic models. The simulated growth curves and ED values according to two different models are shown in Fig. 3. The growth curves were fitted using a saturating exponential function and the ED values were determined by interpolating the growth curves. The standard error of ED was assessed using 1000 Monte Carlo iterations (Duller, 2007).

5. Conclusions

The program KMS developed in this study provides an easy, transparent, flexible, and adaptable environment for modeling quartz luminescence. The intended use of program KMS is to transparently, rapidly and systematically simulate kinetic models. The program can be understood easily, as the R programming language is relatively easy to learn. Many quartz modeling studies in the literature apply commercial software such as Mathematica and Matlab, and the details of these simulations are usually not explained sufficiently. The open source nature of program KMS enables researchers to "open the door" for quartz kinetic modeling. In this aspect, KMS can be used for educational purposes.

The illustrated application examples in this paper demonstrate that a combination of the small number of R functions provided by program KMS can be used to simulate complex luminescence protocols such as the MAA and SAR, by flexibly taking full advantage of the R environment. Indeed, a wide variety of simulations for quartz luminescence are performable by changing the sequence of events. Furthermore, users have full control of typical experimental

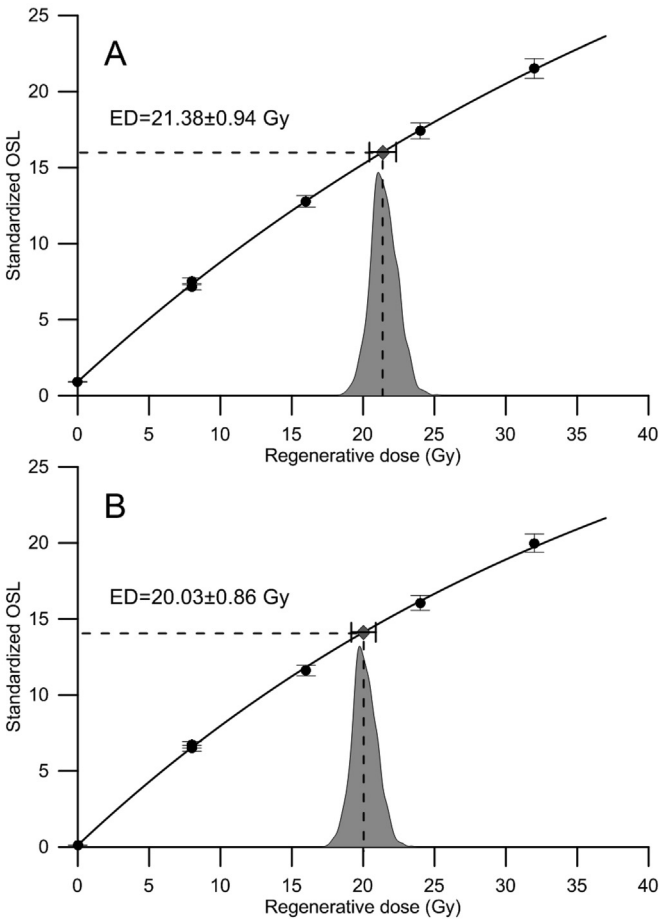

Fig. 3. Simulated growth curves and ED values using the kinetic models of (A) Bailey (2004) and (B) Pagonis et al. (2008b).

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parameters like temperature and heating rate, administered dose and dose rate, optical stimulation power and measurement time.

It is noted that these R programs can only be used for describing delocalized transitions in quartz, since both models described here involve the conduction and the valence band. These programs cannot be used for localized transitions and for tunneling recombinations. However, they already include explicitly thermal quenching effects in quartz. The software described here does not pretend to cover all published kinetic models, as there are several kinetic models of this kind which are available in the literature. However, the program can easily be modified to simulate other kinetic models, by a modification of the set of differential equations governing the model, and by changing the simulation conditions. Users are invited to use the program, or adapt the code for their own simulation studies.

References

Adamiec, G., 2005. Investigation of a numerical model of the pre-dose mechanism in quartz. Radiat. Meas. 39 (2), 175–189.

Adamiec, G., Bluszcz, A., Bailey, R.M., Garcia-Talavera, M., 2006. Finding model parameters: genetic algorithms and the numerical modelling of quartz luminescence. Radiat. Meas. 41 (7–8), 897–902.

Adamiec, G., Garcia-Talavera, M., Bailey, R.M., Iniguez de la Torre, P., 2004. Application of a genetic algorithm to finding parameter values for numerical stimulation of quartz luminescence. Geochronometria 23, 9–14.

Bailey, R.M., 2001. Towards a general kinetic model for optically and thermally stimulated luminescence of quartz. Radiat. Meas. 33 (1), 17–45.

Bailey, R.M., 2004. Paper I-simulation of dose absorption in quartz over geological timescales and its implications for the precisionand accuracy of optical dating. Radiat. Meas. 38 (3), 299–310.

Bailey, R.M., Armitage, S.J., Stokes, S., 2005. An investigation of pulsed-irradiation regeneration of quartz OSL and its implications for the precision and accuracy of optical dating (paper II). Radiat. Meas. 39 (4), 347–359.

Chen, R., Leung, P.L., 1999. Modeling the pre-dose effect in thermoluminescence. Radiat. Prot. Dosim. 84 (1–4), 43–46.

Chen, R., Pagonis, V., 2011. Thermally and Optically Stimulated Luminescence: a Simulation Approach. John Wiley and Sons.

Choi, J.H., Duller, G.A.T., Wintle, A.G., 2006. Analysis of quartz LM-OSL curves. Anc. TL 24 (1), 9–20.

Dietze, M., Kreutzer, S., Fuchs, M.C., Burow, C., Fischer, M., Schmidt, C., 2013. A practical guide to the R package luminescence. Anc. TL 31 (1), 11–18.

Duller, G.A.T., 2007. Assessing the error on equivalent dose estimates derived from single aliquot regenerative dose measurements. Anc. TL 25 (1), 15–24.

Fuchs, M.C., Kreutzer, S., Burow, C., Dietze, M., Fischer, M., Schmidt, C., Fuchs, M., 2014. Data processing in luminescence dating analysis: an exemplary workflow using the R package "luminescence". Quat. Int. 362, 1–6.

Kreutzer, S., Schmidt, C., Fuchs, M.C., Dietze, M., Fischer, M., Fuchs, M., 2012. Introducing an R package for luminescence dating analysis. Anc. TL 30 (1), 1–8. http://CRAN.R-project.org/package=Luminescence.

Murray, A.S., Wintle, A.G., 2000. Luminescence dating of quartz using an improved single-aliquot regenerative-dose protocol. Radiat. Meas. 32 (1), 57–73.

Pagonis, V., Adamiec, G., Athanassas, C., Chen, R., Baker, A., Larsen, M., Thompson, Z., 2011c. Simulations of thermally transferred OSL signals in quartz: accuracy and precision of the protocols for equivalent dose evaluation. Nucl. Instrum. Meth. Phys. Res. B 269 (12), 1431–1443.

Pagonis, V., Baker, A., Larsen, M., Thompson, Z., 2011a. Precision and accuracy of two luminescence dating techniques for retrospective dosimetry: SAR-OSL and SAR-ITL. Nucl. Instrum. Meth. Phys. Res. B 269 (7), 653–663.

Pagonis, V., Balsamo, E., Barnold, C., Duling, K., McCole, S., 2008a. Simulations of the predose technique for retrospective dosimetry and authenticity testing. Radiat. Meas. 43 (8), 1343–1353.

Pagonis, V., Carty, H., 2004. Simulation of the experimental pre-dose technique for retrospective dosimetry in quartz. Radiat. Prot. Dosim. 109 (3), 225–234.

Pagonis, V., Chen, R., Kitis, G., 2011b. On the intrinsic accuracy and precision of luminescence dating techniques for fired ceramics. J. Archaeol. Sci. 38 (7), 1591–1602.

Pagonis, V., Chen, R., Wintle, A.G., 2007a. Modelling thermal transfer in optically stimulated luminescence of quartz. J. Phys. D. Appl. Phys. 40 (4), 998–1006.

Pagonis, V., Kitis, G., Chen, R., 2003. Applicability of the Zimmerman predose model in the thermoluminescence of predosed and annealed synthetic quartz samples. Radiat. Meas. 37 (3), 267–274.

Pagonis, V., Wintle, A.G., Chen, R., 2007b. Simulations of the effect of pulse annealing on optically-stimulated luminescence of quartz. Radiat. Meas. 42 (10), 1587–1599.

Pagonis, V., Wintle, A.G., Chen, R., Wang, X.L., 2008b. A theoretical model for a new dating protocol for quartz based on thermally transferred OSL (TT-OSL). Radiat. Meas. 43 (2–6), 704–708.

Peng, J., 2015. Tgcd: Thermoluminescence Glow Curve Deconvolution. R Package Version 1.8. http://CRAN.R-project.org/package=tgcd.

Peng, J., Dong, Z.B., Han, F.Q., Long, H., Liu, X.J., 2013. R package numOSL: numeric routines for optically stimulated luminescence dating. Anc. TL 31 (2), 41–48. http://CRAN.R-project.org/package=numOSL.

R Core Team, 2015. R: a Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria. https://www.r-project.org.

Soetaert, K., Petzoldt, T., Setzer, R.W., 2010. Solving differential equations in R: package deSolve. J. Stat. Softw. 33 (9), 1–25. http://CRAN.R-project.org/package=deSolve.

Zimmerman, J., 1971. The radiation-induced increase of the 100 °C thermoluminescence sensitivity of fired quartz. J. Phys. C Sol. Stat. Phys. 4 (18), 3265–3276.

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