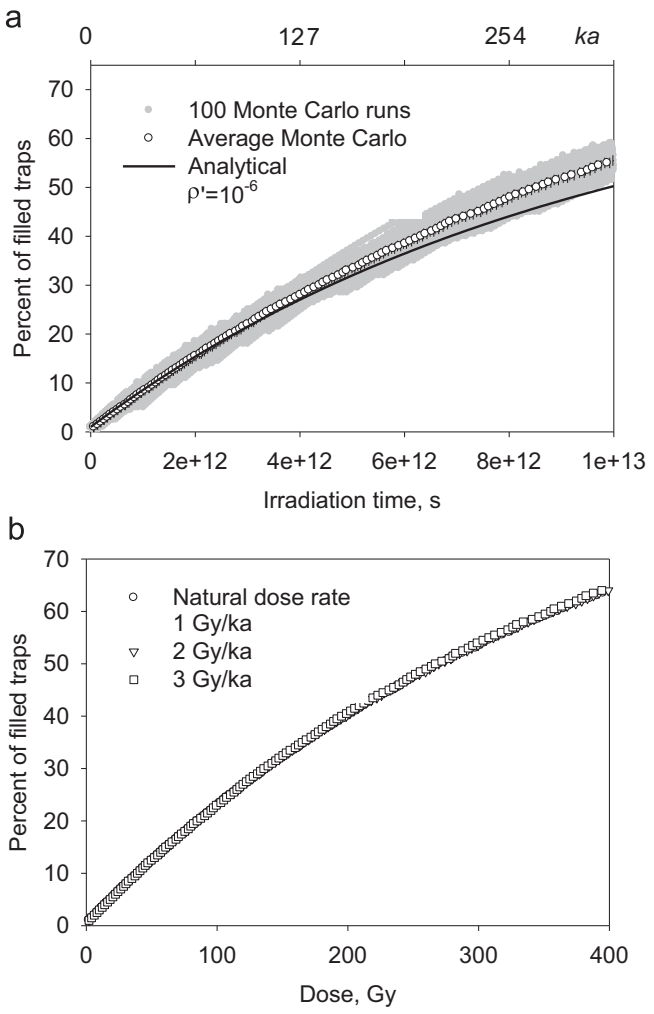

Fig. 5. (a) Simulation of sample irradiation in nature, using typical parameters for feldspars given in the text. The shaded area represents the results of 500 Monte Carlo runs. Note the additional time scale at the top of the graph, showing the irradiation time in ka. The solid line is the analytical equation discussed in the text. (b) The simulated dose response at three different natural irradiation rates of 1,2,3 Gy/ka. The x-axis has been converted into the actual dose in Gy, and no dose rate effects are observed in these simulations.

The solid line in Fig. 5a represents the following analytical equation derived by Pagonis and Kitis [27] for the luminescence L_n as a function the natural dose D_n, based on the model by Li and Li [5]:

$$L_n(D_n) = \left[1 - \exp\left[-\frac{D_n}{D_0}\right]\right] M \exp\left[-\rho' \ln\left[\frac{D_0 s}{D_R}\right]^3\right] \quad (10)$$

where D_n is the irradiation dose (Gy), M is the total number of traps, and s (s^{-1}) is, as previously, the tunneling frequency.

Fig. 5a shows good agreement between the Monte Carlo simulations and the analytical Eq. (10), except at very long irradiation times where the Monte Carlo simulation overestimates the analytical expression. From the time scales of Fig. 5a, it is seen that the disagreement between the Monte Carlo method and the analytical expression corresponds to irradiation times larger than ~200,000 years for the example given here. This disagreement at longer irradiation times can possibly be attributed to the discrete/stochastic nature of the Monte Carlo simulations, as opposed to the continuous functions assumed in the analytical Eq. (10). Another possible reason for the disagreement is the use of non-stochastic Eq. (9) for estimating the time interval between irradiation events. A third possible explanation for the observed differences is the redistribution of electron-hole distances taking place during the Monte Carlo simulations. Specifically, at long geological times there are fewer electron-hole pairs left in the Monte Carlo simulation, and the distribution of distances deviates from the symmetric distribution in Eq. (6). This was also reported in Ref. [7]. On the contrary, the derivation of the analytical Eq. (10) assumes that there is no redistribution of the distances. It is not clear which of these three possible explanations is the cause of the observed differences, and this will be the subject of a separate study.

Fig. 5b shows the results of repeating the simulation in Fig. 5a with three different natural irradiation rates of 1,2,3 Gy/Ka. The x-axis in Fig. 5b has been converted into the actual dose in Gy for all three sets of simulations. The three simulations are identical, indicating that there is no dose rate effect in the simulated data. This may have been expected from a physical point of view, since the natural irradiation process is very slow; however, this may not be the case in the laboratory, or for different sets of parameters in the model.

Fig. 6 shows the results of repeating the natural irradiation simulations in Fig. 5 for samples of different sizes, in the range d=250–1000 nm. As in the case of Fig. 4b, the differences in the simulations are very small for the different sample sizes, and no changes are observed for sizes d > 750 nm.

2.3. Monte Carlo simulations of hopping processes in feldspars

In many important luminescent and dosimetric materials, the transport of charge takes place by the well-known mechanism of hopping conduction, which is based on the presence of localized states. Generally speaking, charges are considered to be localized, but occasionally they may "hop" to another localized state. Two well-known types of this hopping conduction mechanism are the *nearest neighbor hopping* and the *variable range hopping* (VRH) (see for example Refs. [28–31]. In the formalism developed by Mott [31] the probability P (s^{-1}) for the hopping process is described by the Mott equation:

$$P = s_{hopping} \exp\left[-2\alpha r_h - \frac{W_h}{k_B T}\right] \quad (11)$$

where W_h is the hopping energy (eV), r_h is the hopping length (m), α is the barrier penetration factor as in Eq. (1), and $s_{hopping}$ is the attempt to escape frequency characterizing the *hopping* process. The importance and the numerical value of the tunneling frequency $s_{hopping}$ is considered in the DISCUSSION section of this paper. In cases of strong localization and/or low concentration of

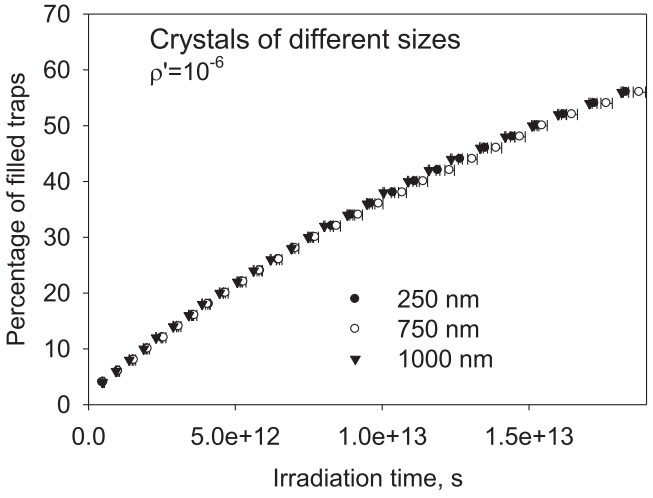

Fig. 6. Simulations of natural sample irradiations for different samples, represented by cubes of side d=250–1000 nm.

localized states, then the first term on the right hand site of Eq. (11) is dominant, and the conduction mechanism is called *nearest neighbor hopping*. However, in other materials the second term in Eq. (11) contributes significantly to the hopping probability, and hops to sites that are further away in space but closer in energy might be preferable. This is the VRH process, a concept introduced by Mott in 1968 [31]. It is noted that usually the term "hopping" in the literature refers to transport of carriers via several closely placed energy levels or sites [29,30]. However in this paper the term 'hopping' is limited to a single "hop", since we only consider nearest neighbor interactions.

In this subsection we investigate the possibility of using the Monte Carlo model to simulate hopping processes, based on Eq. (11). Furthermore, we present a first quantitative attempt to compare the results of the Monte Carlo model with the experimental data of Morthekai et al. [28]. These authors studied time-resolved infrared stimulated luminescence (TR-IRSL) signals in feldspars at elevated temperatures. They analyzed the relaxation signals measured after the excitation of the sample with infrared had ceased, and proposed that these signals originate from band tail states in these materials. One of the main findings of their detailed study is that for at least three of their samples and for certain temperature ranges, the process is most likely a variable range hopping mechanism. Their analysis was based on Eq. (11), and yielded the following values of the parameters for their sample FL1: attempt-to-tunnel frequency $s_{hopping}=2\times10^{7}\ s^{-1}$, $\alpha=1.5\times10^{9}\ m^{-1}$, $W_h=0.046$ eV for signals recorded at 50 °C, and $W_h=0.020$ eV for signals measured at a higher stimulation temperature of 225 °C. The low value of $s_{hopping}$ is in the same range of estimations given by Pagonis et al. [32]. One expects that as the stimulation temperature rises, the contribution of the band tail states to the signal will also increase.

The simulation of the hopping process is exactly similar to the ones presented in Section 2.1, with the important difference that the hopping process is based on Eq. (11). The simulation evaluates the time development of the total number of charge carriers $n(t)$; the experimentally observed relaxation signal is proportional to the time derivative dn/dt, which is evaluated numerically from the function $n(t)$.

Fig. 7a shows the results of the Monte Carlo simulation with the following slightly modified set of parameters from the experimental values given in [28]: $s_{hopping}=9\times10^{7}\ s^{-1}$, $\alpha=1.8\times10^{9}\ m^{-1}$, $W_h=0.040$ eV, $d=100$ nm, $n_{DONORS}=60$ and $n_{ACCEPTORS}=4890$. These are compared with the experimental data of Morthekai et al. [28], for a high stimulation temperature 225 °C. Good agreement is seen for this high stimulation temperature. Fig. 7b shows a similar calculation and comparison with the experimental data of Morthekai et al. [28], for a lower stimulation temperature of 50 °C and with the experimental value of $W_h=0.020$ eV. The Monte Carlo simulation overestimates the luminescence signal at times $t>20$ μs for this set of data. The disagreement is rather close to the accuracy/precision of the experimental data, however it may also be indicative of the decreased importance of the band tail states at the lower stimulation temperature. It is concluded that the Mott hopping model based on Eq. (11) gives reasonable quantitative agreement with experimental data measured during the relaxation period of TR-IRSL experiments, especially at higher stimulation temperatures.

Clearly more work is needed to test the agreement between this simple hopping model and experiment, using additional experimental data measured at different stimulation temperatures, different irradiation doses and with different LED wavelengths. A further test of the model will be whether it can reproduce correctly the variation of the intensity and overall areas underneath the time-resolved signals with the stimulation temperature.

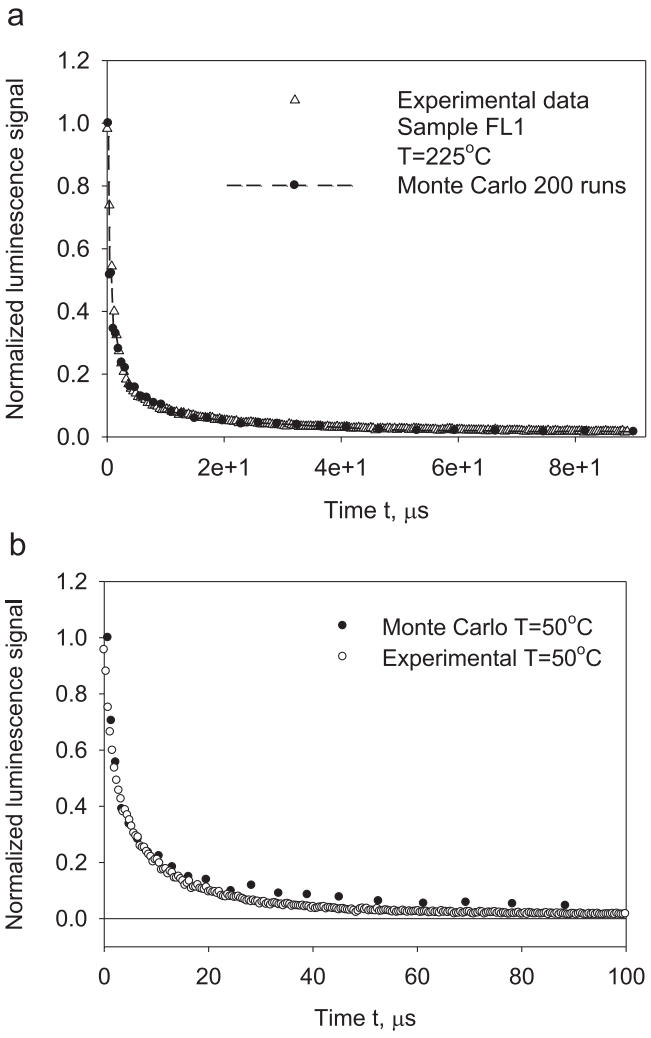

Fig. 7. (a) Monte Carlo simulation based on the Mott probability Eq. (11), with the parameters given in the text. The simulation is compared with the experimental data in [28], for a high stimulation temperature of 225 °C. (b) The Monte Carlo simulation is compared with experimental data in [28], measured at a lower stimulation temperature of 50 °C. The Monte Carlo results overestimate the observed experimental luminescence signal at times $t>20$ μs.

3. Discussion and conclusions

In this paper we verified the approximate analytical equation which can describe the loss of charge due to anomalous fading in feldspars, for time scales ranging from microseconds to thousands of years. In addition, the analytical expression for the natural dose response of feldspars in nature was verified for different dose rates. The Monte Carlo results were found to be independent of the crystal size, an important consideration when one considers the properties of nanodosimetric materials. A new version of the model was presented based on the Mott hopping Eq. (11), and was compared with experimental data at different stimulation temperatures.

The Monte Carlo approach in this paper was shown to yield very similar or comparable results with the approximate analytical equations. In our opinion the strength of the Monte Carlo method is that it provides a more direct insight into both the irradiation and luminescence mechanism over geological times. By varying the parameters in the Monte Carlo model (e.g. crystal size, irradiation rate, charge density), the user obtains a better understanding of the system on a microscopic scale, and how these parameters affect the macroscopic behavior of the system. On the

other hand, the analytical equations for irradiation and charge loss are easy to use on a practical level, since one can use them to fit experimentally observed luminescence signals on a macroscopic scale. Both the Monte Carlo approach and the analytical equations can also be used for samples which underwent previous optical and thermal treatments; in such pretreated samples one is dealing with truncated nearest neighbor distributions of distances, instead of the full distributions used in this paper (Eq. (6) in this paper and Ref. [33]).

A rather obvious next step in Monte Carlo work in feldspars is to extend the model in this paper to include localized transitions taking place via the excited states, and delocalized transitions which involve the conduction band. The results from such an extended model which would include both localized and delocalized transitions, could be compared for example with available experimental data on time-resolved experiments using infrared, blue and green LEDs.

The experimental work of Poolton et al. [8] and Jain and Ankjaergaard [11]) suggested that electron migration in the band-tail states of their feldspar samples occurs by a hopping mechanism. One of their important conclusion was that the excited state of the electron trap at 1.46 eV is probably embedded in the band-tail states, and that the IRSL process as a combination of two processes: tunneling of trapped electrons from either the excited state and/or from the band-tail states, into the excited state of the hole trapping center. This center eventually gets de-excited producing the luminescence signal. The stimulation temperature most likely plays a critical role in determining which of the two recombination avenues is dominant. The experimental study by Morthekai et al. [28] further contributed to the understanding of the physical processes producing the time resolved luminescence signals, and confirmed that charge transport in the band-tail states is of the variable range hopping type, at least for some of the samples and for certain ranges of stimulation temperatures. Their data analysis was able to extract the Mott parameters i.e., the variation of the average hopping length and the average hopping energy with the stimulation temperature. Of particular importance in any hopping model is the value of the attempt to escape frequency $s_{hopping}$ which appears in Eq. (11), which was found by Morthekai et al. [28] to be in the range $s_{hopping} = 10^6 - 10^7\ s^{-1}$ for all their samples. This is in the same numerical range of frequency given by Pagonis et al. [32] from their analysis of time-resolved signals in a variety of feldspars.

The simulations presented here are for nanosized crystals, with the exception of some larger crystals with sides of the order of thousands of nm. The elementary box does not contain periodic boundary conditions (PBC): due to the random distribution of charges, it is expected that inclusion of PBC will not change the results of the simulation. The situation would be of course very different if the charges were placed for example on specific periodic crystal sites, in which case one should study the fate of individual electrons in the whole crystal, during both irradiation and recombination processes. The inclusion of PBC would be indeed very useful in diffusion studies across the whole volume, which are beyond the scope of this paper but could be the subject of future work.

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