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INFLUENCE OF *IN SITU* TEMPERATURE ON THE SENSITIZATION OF QUARTZ: A SIMULATION STUDY

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Abstract: The influence of ambient geological and burial temperatures, prevailing in nature, on the charge population of the defect centers and, eventually, the sensitivity of the luminescence emission of quartz was simulated using empirical model. Various permutation and combination of these temperatures were incorporated so as to observe, both, the collective and independent impact of these two temperatures on the charge kinetics. The results of seem to demonstrate the role of the ambient temperature in the sensitization of quartz mineral.

Keywords: sensitization, quartz, *in situ* temperature, TL, OSL.

1. INTRODUCTION

The optically stimulated luminescence (OSL) of natural quartz, though useful in a variety of applications, has been extensively used in dating of sediments, deposited during the last 100 thousand years (Aitken, 1998). The weathered quartz grain in geological setting gets transported by some mode of natural transport and, eventually, settles down as sediment. The bleaching encountered by the grain during its transportation acts as a zeroing agent and the time period since this zeroing episode could range from few years to tens of thousands of years.

One of the assumptions perceived for the reliability of the methodology using techniques based on the luminescence emission is that the sensitivity of the specimen, i.e. signal emitted per unit radiation dose, remains constant since antiquity. The luminescence sensitivity of quartz would remain unperturbed if (i) the population of luminescence centre, L, remains constant with time and (ii) the competition among various centers during charge build up and read out stages remains unperturbed. One more mechanism which could perturb it would be the charge transfer among various centers in nature. In fact, a sensitization phenomenon, called pre-dose sensitization, observed in case of luminescence emission of quartz has been explained in terms of a phenomenological model, based on this transfer of charge from one recombination centre to another (Zimmerman, 1971). The model was found to reproduce most of the features of the pre-dose phenomenon (Pagonis *et al*., 2003). This pre-dose effect has been extensively studied and applied in a variety of applications using 110°C TL peak (Bailiff, 1994; Kitis *et al*., 2006). Subsequently, this phenomenon was seen to prevail in the OSL signal also, having characteristics similar to that of the 110°C TL peak (Koul and Chougaonkar, 2007; Oniya *et al*., 2012). The main hypotheses governing the Zimmerman's model are (i) pre-dose (paleo-dose in the case of natural samples) populates the reservoir centre, R, like any other centre (ii) thermal activation transfers holes from R to L centers and (iii) the sensitization results due to increase in the availability of the activated luminescence centers, L. The thermal activation may initiate sensitization process as early as ~200°C, peaks at a typical maximum activation temperature, exhibits some plateau region and, eventually, de-

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crease. Though this model was found to be satisfactory, it had to be modified in order to take all the aspects of the pre-dose signal in to account. In this regard, based on the various studies, like thermal activation characteristics (TAC), isothermal sensitization and the nature of TAC for different pre-dose values, more than one R-centers, R_1 and R_2, have been proposed (Bailey, 2001; Adamiec, 2005). Most of the features of the pre-dose phenomenon have been simulated successfully using Bailey's model (Pagonis *et al.*, 2008).

The procedures developed for optically stimulated luminescence (OSL) emission measurement of quartz involve pre-heating. This treatment has been found essential to evacuate charge from the shallow traps, especially trap corresponding to the 110°C TL peak, so that these traps do not interfere with the OSL trap, 325°C TL, during the measurement (Aitken and Smith, 1988). But, apart from removing charge from these thermally unstable traps the pre-heating has been found necessary to generate parity in the case of the sensitization of the natural and laboratory irradiated samples (Murray and Roberts, 1998). The reason for this disparity has been proposed to be due to *in situ* sensitization of the natural sample occurring during its lifetime while as this might not be true in the case of the laboratory irradiated sample (Wintle and Murray, 1999). In fact, this was one of the reasons for proposing an elevated value of the pre-heat temperature of 260°C in the SAR procedure as this treatment was found to ensure, to a greater extent, similar sensitization in case of all samples. It is important to mention here that this sensitization has been reported to be dependent on (i) the ambient temperature experienced by the sample during its lifetime and (ii) the age of the specimen (Wintle and Murray, 1999). A study was undertaken to understand the role of the reservoir hole centers, R- centers, in the sensitization of the OSL signal (Koul *et al.*, 2009). Based on the experimental results and kinetic considerations of these centers, it was suggested that these centers, especially the shallow one (R_1), seem to participate in the ambient sensitization of the quartz.

The simulation study presented in this paper was carried out to look into the influence of the *in situ* temperature experienced by the specimen over geological and burial time periods on the charge build up in these centers and, subsequently, on the luminescence sensitization. The various permutation and combination of geological and burial temperatures ambient temperatures which generally prevail in nature were considered in this work. The findings of this study did suggest an appreciable impact of ambient temperature on the charge kinetics among various centers and, thereby, the sensitivity of the quartz mineral.

2. SIMULATION PROCEDURE

The simulation in this paper was carried out using phenomenological general model of quartz developed on the basis of empirical data (Bailey, 2001). The model has been very effectively used in simulations involving various aspects of luminescence in quartz and has been found to reproduce most of the phenomenon observed in TL and OSL emissions of quartz (Pagonis *et al.*, 2007). It comprises of five electron and four hole trapping centers. The electron trapping centers consists of 110°C trap, 230°C trap, fast and medium OSL traps, and thermally disconnected trap. The hole traps consist of thermally unstable non-radiative recombination centers (R_1 and R_2), thermally stable radiative recombination centre (L) and thermally stable non-radiative recombination centre. It must be mentioned here that the model has been evolved considering only 380 nm emission band of quartz and it, also, allows re-combination at R- centers, unlike the earlier models (Zimmerman, 1971). The transport equations describing build up of charge with time in various centers in the electronic system of quartz are:

$$\frac{\mathrm{d}n_i}{\mathrm{dt}} = n_c\left(N_i - n_i\right)A_i - n_i\lambda_i(\mathrm{P},\mathrm{T}) - n_i s_i e^{\left(-E_i/\mathrm{K}_\beta T\right)} \qquad (2.1)$$
$$\mathrm{i} = (1,\ldots,5)$$

$$\frac{\mathrm{d}n_j}{\mathrm{dt}} = n_v\left(N_j - n_j\right)A_j - n_j s_j e^{\left(-E_j/\mathrm{K}_\beta T\right)} - n_c n_j B_j \qquad (2.2)$$
$$\mathrm{j} = (6,\ldots,9)$$

$$\frac{\mathrm{d}n_c}{\mathrm{dt}} = R - \sum_{\mathrm{i=1}}^{\mathrm{q}}\left(\frac{\mathrm{d}n_i}{\mathrm{dt}}\right) - \sum_{\mathrm{j=q+1}}^{\mathrm{q+r}}\left(n_c n_j B_j\right) \qquad (2.3)$$

$$\frac{\mathrm{d}n_v}{\mathrm{dt}} = R - \sum_{\mathrm{j=q+1}}^{\mathrm{q+r}}\left(\frac{\mathrm{d}n_j}{\mathrm{dt}}\right) \qquad (2.4)$$

$$\mathrm{L} = \mathrm{n_c}\ \mathrm{n_8}\ \mathrm{B_8}\ \eta(\mathrm{T}) \qquad (2.5)$$

The **Eqs. 2.1** and **2.2** represent the variation in the charge population with time in case of electronic and the hole trapping centers respectively. Similarly **Eqs. 2.3** and **2.4** represent the change in the charge population with time in the conduction and valence band respectively. The luminescence signal occurring due to recombination at the luminescence centre, L, is described by **Eq. 2.5**. The various parameters described in the above equations are; N_i, the concentration of electron trap (cm^{-3}); n_i, the concentration of trapped electrons (cm^{-3}); s_i, the frequency factor (s^{-1}); E_i, the electron trap depth below the conduction band (eV); N_j the concentration of hole traps (cm^{-3}); n_j, the concentration of trapped holes (cm^{-3}); E_j, the hole depth above the valance band (eV); K_β, the Boltzmann's constant (eV K^{-1}); T, the absolute temperature (K); A_i, the conduction band to electron trap transition probability $(s^{-1})^3$; A_j, the valence band to hole trap transition probability $(s^{-1})^3$; B_j, the conduction band to hole trap transition probability $(s^{-1})^3$; λ_i, the optical detrapping rate (s^{-1}); t, the time (s); η, the luminescence efficiency factor; β, the rate of change in temperature (K s^{-1}) and R, the ionization (pair production) rate (s^{-1}).

The optimum values assigned to these parameters for different centers of the model are listed in Bailey (2001).

The **Eqs. 2.1** to **2.5** describing the variation of charge with time in the quartz lattice were solved numerically with MATHEMATICA using Adam's method**.** The computer code was formulated to simulate the charge concentrations prevailing in different hole centers, R_1, R_2 and L during the specimen's geological and burial time spans. The simulation procedure here consisted of (i) unpopulating all the traps, crystallization, (ii) irradiation during geological time period of 0.1 million yr, (iii) bleaching episode of 2 hrs before the burial and (iv) irradiation during burial time of 50 kyr (0.1 million yr in some cases). The simulation was performed by subjecting the sample to R value which corresponded to a radiation dose rate of 6.34×10^{-11} Gy s^{-1}, close to the natural one, during its geological and burial time spans. It is impossible to simulate the actual history of a natural quartz grain and the sequence of events experienced by it (Bailey, 2004). Therefore, various parameters, related to the history of quartz grains, incorporated in the simulation procedure in this work represent a very simplistic picture. The environmental temperatures generally prevailing on the globe, –10 to 40°C in steps of 10°C, were incorporated as the ambient temperatures experienced by quartz grains in the simulation. All the permutations and combinations of the geological and burial ambient temperatures were considered, i.e. a sample with a geological temperature of –10°C has been simulated for all the burial temperature of –10, 0, 10, 20, 30 and 40°C and vice versa. The charge build up in all the centers and, subsequently, the sensitization of the 110°C TL signals were simulated with these ambient temperatures.

3. SIMULATION RESULTS

Simulation involved resulted in the estimation of charge build-up in various centres of quartz and, eventually, luminescence sensitization with various ambient temperatures. The details of the simulations involved in this work are described below.

Charge population of various centres

The quartz specimen, as expected, prior to burial was subjected to a bleaching episode. The bleaching consisted of the stimulation with the sunlight for two hours. As the geological quartz can settle down as sediment in an alien place, many permutations and combinations of the ambient temperatures which the specimen might experience during its stay in geological and sedimental settings do exist. For example, a sample from a temperate region might settle down after burial in a moderate or cool region. Accordingly, charge population has been simulated for all the three possibilities which specimen might experience during their lifetimes (i) identical geological and burial temperatures, (ii) identical geological and varying burial temperatures and (iii) varying geological and identical burial temperatures. This formalism, also, allows one to understand the role of the geological and burial temperatures on the charge kinetics of various centres in an independent way. The simulation details involved in case of charge population of various centres for different combination of geological and burial settings is explained as under:

Charge population of R_1- centre

Identical geological and burial temperatures

The charge build up in R_1- centre during a geological time period of 0.1 million years was simulated for different ambient temperatures, –10, 0, 10, 20, 30, 40°C. As mentioned above, the quartz specimen was subjected to a dose rate of 6.34×10^{-11} Gy s^{-1} during its lifetime, which includes the geological time duration also. The results, depicted in **Fig. 1**, show the variation in charge population of R_1- centre with various ambient temperatures. The charge growth curves corresponding to temperatures up to 10°C do not show much variation and, therefore, almost coincide with one another in **Fig. 1**.

The main features of the plot (i) the rate of populating the centre, (ii) the charge accumulated till the saturation level and (iii) the time taken to attain this charge saturation can be seen to increase with decrease in the ambient temperature, **Fig. 1**. Taking the simulation results of the extreme ambient temperatures of –10 and 40°C into consideration, the saturation charge population can be seen to be more than one order larger in case of –10°C. Again the time period involved in reaching this saturation value in R_1- centre takes more than two orders of time in case of –10°C than that of 40°C. So, this seems to indicate that

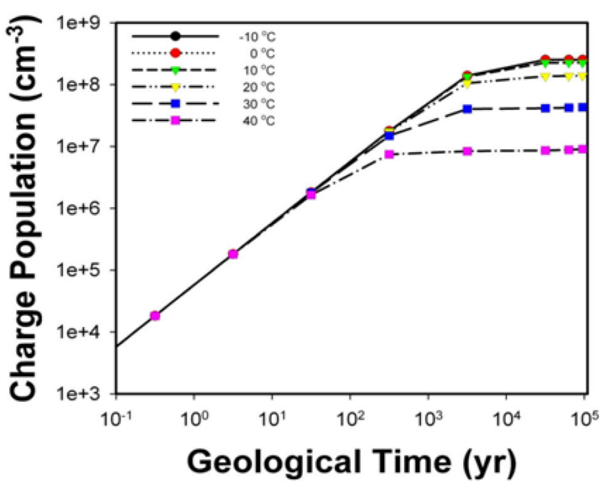

Fig. 1. *Charge population of R_1- centre of quartz sample simulated with various geological temperatures, –10, 0, 10, 20, 30, 40°C, for a time duration of 0.1 million yr. The specimen was administered a radiation dose rate of 6.34×10^{-11} Gy s^{-1}, typical natural dose rate, during this period.*

the charge accumulated in case of samples belonging to colder places will be larger and, also, the increase in this charge build up will continue for much longer time as compared to the warmer regions.

The charge build up in R_1- centre for various ambient temperatures during geological time period, simulated above, was further simulated with identical burial temperatures, i.e. a sample experiencing a geological ambient temperature of –10°C has been simulated for charge build up with the identical burial temperature of –10°C. All the temperatures employed in this study, –10, 0, 10, 20, 30, 40°C, were considered in this case. The variation in charge population in R_1- centre with burial time, 50 kyr, is represented by extreme temperatures 40 and –10°C in **Fig. 2**. These extreme temperatures were chosen here and elsewhere in this work for better presentation of the impact of the ambient temperatures on the charge population of various centers. The charge in R_1- centre was seen above to get saturated very early during its geological time period itself, **Fig. 1**. So, as, expected, the charge growth curves during burial time duration just followed the trend acquired during their geological settings, **Fig. 4**. The saturation charge levels acquired during geological time periods just continue without any variation during burial time periods, i.e. colder temperature, –10°C, resulting in larger charge population than that of the warmer temperature, 40°C.

Identical geological and varying burial temperatures

This case deals with situations in which samples experiencing identical geological temperature, say –10°C, settle down in different regions having burial temperatures of , –10, 0, 10, 20, 30, 40°C. The simulation for the charge build up with these burial temperatures was performed for a burial time of 50 kyr. The stimulated charge population of charge in R_1- centre in this situation is shown for two extreme geological temperatures (a) 40°C and (b) –10°C in **Fig. 3**. In other words, **Figs. 3a** and **3b** represent situations where samples in two identical geological setting having ambient temperatures of –10 and 40°C respectively are buried as sediments with various ambient temperatures of –10, 0, 10, 20, 30, 40°C.

The samples experiencing warmer geological temperature (40°C) once buried in colder regions showed rapid increase in the charge population of R_1- center, while as, it was quite contrary in the reverse case, *i.e.* samples experiencing colder geological temperature (–10°C) settling down in warmer regions, **Fig. 3**. The charge popula-

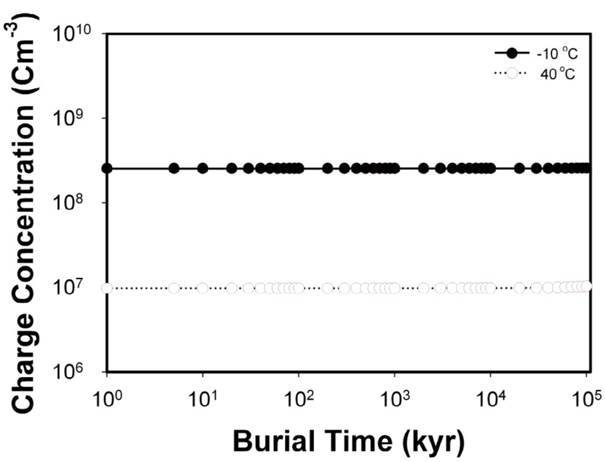

Fig. 2. *Charge population of R_1- centre simulated in case of samples having experienced identical geological and burial temperatures represented here by –10 and 40°C. A geological and burial time periods of 0.1 million yr were incorporated in the simulation respectively. The specimen have been administered a radiation dose rate of 6.34×10^{-11} Gy s^{-1} during their respective geological and burial time periods. This is true of the simulation represented by all the figures in this study.*

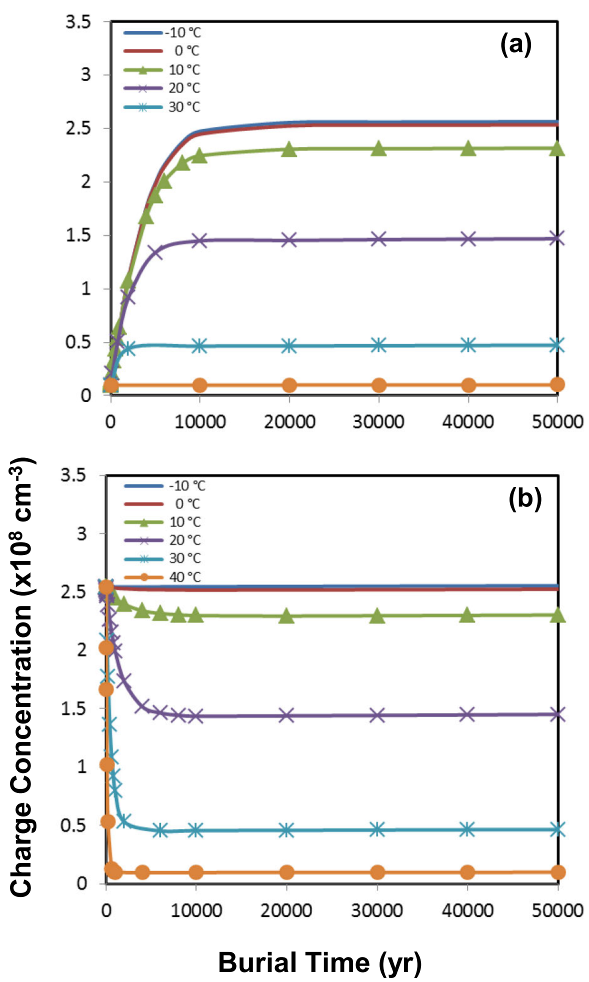

Fig. 3. *Charge population of R_1- centre simulated in case of samples having experienced identical geological temperatures represented here by (a) –10°C and (b) 40°C but buried in various settings with temperatures of –10, 0, 10, 20, 30, 40°C. A geological and burial time periods of 0.1 million yr and 50 kyr were incorporated in the simulation respectively.*

tion acquired during geological time period gets re-defined by the burial temperatures which the sample experiences. Eventually, the charge saturation or equilibrium value in this centre is decided by the burial temperature prevailing during a burial time period of ~ few thousand years, lower the ambient burial temperature higher the accumulated charge. Also, the burial time period required to reach the saturation or equilibrium charge concentration depends on the (i) the nature of transition from geological to burial setting and (ii) the temperature difference between the geological and burial temperature. The situation in which the warmer geological sample settles down at a cooler place larger the temperature difference in geological and burial temperatures larger is the time needed to reach the charge equilibrium value. On the other hand, in case of situation which is the other way around the results obtained were entirely opposite, larger the temperature difference in geological and burial temperatures lesser is the time needed to reach the charge equilibrium value. In short, R_1- centre in case of specimen buried in colder region can attain higher charge in comparison to the one from warmer region and, accordingly, the specimen in colder setting gets populated for a longer time in order to reach the saturation value.

Varying geological and identical burial temperatures

This is a situation in which the charge build-up in R_1-center was simulated for specimen which have been subjected to different geological temperatures but, thereafter, buried in regions having identical temperature. A typical case has been considered here in which the samples from two geological settings with extreme ambient temperatures, 40 and –10°C, get buried in regions with an identical ambient temperature of –10°C. In **Fig. 1**, depicted above, the charge population of R_1- center in case of sample from colder geological setting was found to be greater than the one from warmer one. The same is reflected by the initial data points of **Fig. 4** simulated in this case. These data points, essentially, determine the charge acquired by the centre with different geological temperatures before the burial time. But, after burial at an identical ambient temperature the charge build up of the sample derived from a warmer geological region, 40°C, accelerated and, subsequently, caught up with the one obtained in other case corresponding to a geological temperature of –10°C in a burial time of ~15 kyr. This result, again, demonstrated the importance of the burial temperature on the growth of charge in R_1- center. Whatever might be the geological temperature the sample has experienced, R_1-center attains the charge equilibrium value which is decided by the ambient temperature prevailing during a few thousand years of its burial span.

Charge population of R_2- centre

Identical geological and burial temperatures

The procedure adopted to simulate the charge build-up in R_2- centre was similar to that incorporated in case of R_1- centre. The charge population in R_2- centre for specimen encountering identical geological and burial temperatures is represented by the extreme temperatures of –10 and 40°C, in **Fig. 5**. It will be worthwhile to mention here that, unlike R_1- centre, the variation in the charge population of R_2- centre with various geological ambient temperatures was not found to be that significant. This is evident from the initial data points of the plots in **Fig. 5**, which represent the charge build up in the R_2- centre during a geological time span of 0.1 million yr for these two extreme temperatures of 40 and –10°C. These data point represent the charge population in the centre at the time of burial.

The charge population at the time of burial can be seen to be higher for a specimen subjected to a warmer geological temperature (40°C) than the colder one, –10°C, the initial data points in **Fig. 5**. This is just contrary to the situation encountered above in case of R_1- centre. But, at the same time one as can see from the slope of the charge growth curves that the rate of deposition of

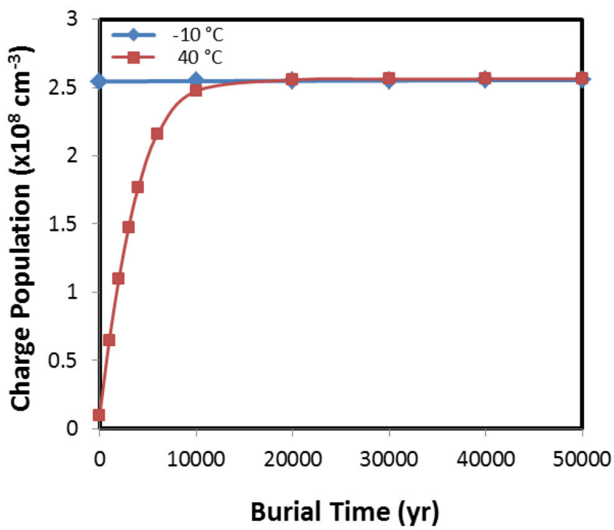

Fig. 4. *Charge population of R_1- centre simulated in case of samples having experienced various geological temperatures, represented by –10 and 40°C here, but buried in settings having identical temperature represented by –10°C in the plot. A geological and burial time periods of 0.1 million yr and 50 kyr were incorporated in the simulation respectively.*

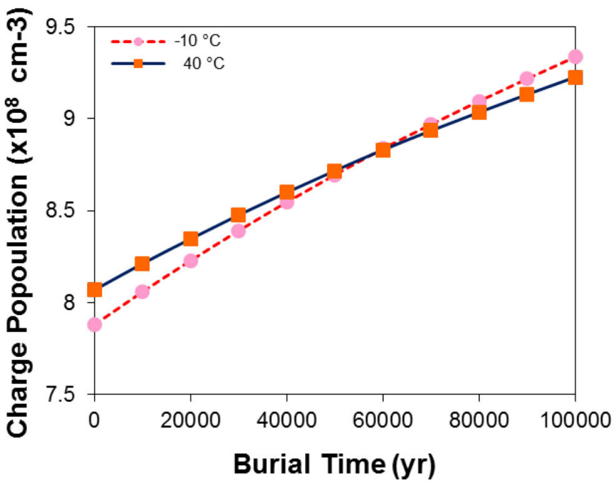

Fig. 5. *Charge population of R_2- centre simulated in case of samples having experienced identical geological and burial temperatures represented here by –10 and 40°C. A geological and burial time periods of 0.1 million yr and 50 kyr were incorporated in the simulation respectively.*

charge in R_2- centre is greater in colder region than the warmer one. Eventually, as a result of this the accumulated charge in case of colder regions takes over the warmer ones after a burial time of ~60 kyr and remains larger thereafter. In order to get a better feel of the trend in the charge growth curves a higher burial time of 0.1 million yr was considered here. Even with such a long burial span the variation in charge build-up of R_2 with burial temperature is very low as compared to the R_1- centre.

Identical geological and varying burial temperatures

In this case the quartz grains from identical geological setting were deemed to get deposited as sediments in regions which have different climatic conditions. The simulation is represented by two extreme cases (i) samples with geological temperature of 40°C settle down in regions with temperatures of –10 and 40°C (**Fig. 6a**) and (ii) samples w ith geological temperature of –10°C settle down in a regions with temperatures of –10 and 40°C (**Fig. 6b**). The extreme ambient temperatures, as mentioned above, were chosen for presentation to visualize the maximum influence of ambient temperatures on the charge kinetics.

In case of sample belonging to warm geological setting, 40°C, and getting buried in a cold setting, –10°C, the charge population of R_2- centre decelerates initially for a few thousand years, but, accelerates thereafter and takes over the charge growth curve corresponding to the higher burial temperature of 40°C after a burial time of ~40 kyr (**Fig. 6a**). In the reverse case, i.e. a sample from a cold geological region, –10°C, settling down in a warm region, 40°C, the charge build-up reacts in an opposite way. Initially, a fast growth was seen in the form of a spike for a very short duration of the burial time, but, subsequently the growth rate of charge was seen to be less than the one observed at lower burial temperature of –10°C. As observed above, the charge growth rate of R_2- centre in cold burial setting was, again, seen to eventually take over that of the specimen belonging to warm region after a burial time of ~40 kyr, **Fig. 6b**. So, similar to the previous case described above, the charge accumulation in R_2- centre is favored by warmer climatic conditions till a burial time of few tens of thousands years. But, thereafter, on account of the higher charge growth rate, the charge build up in case of specimen from colder regions assumed higher value.

Varying geological and identical burial temperatures

This case, essentially, looked in to the impact of burial temperature on the charge growth by subjecting sam-

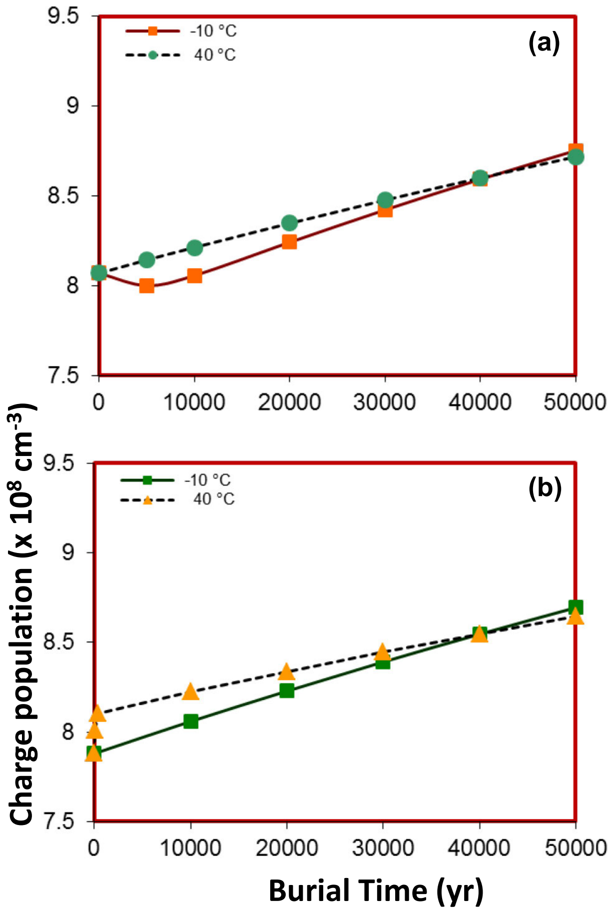

Fig. 6. *Charge population of R_2- centre simulated in case of samples having experienced identical geological but varying burial temperatures. The simulations are represented by two extreme cases (a) samples with geological temperature of 40°C settle down in regions with temperatures of –10 and 40°C and (b) samples with geological temperature of –10°C settle down in a regions with temperatures of –10 and 40°C. A geological and burial time periods of 0.1 million yr and 50 kyr were incorporated in the simulation respectively.*

ples with various geological temperatures to an identical sedimental temperature. The simulation here is represented by a situation in which the samples with geological temperature of 40 and –10°C are buried in identical environments with an ambient temperature of –10°C, as depicted in **Fig. 7**. As seen above in **Fig. 5**, the charge population in R_2- centre of the sample experiencing warmer geological temperature is larger as compared to that from the colder one. This, again, is reflected by the initial data points of the charge growth curves in this case, **Fig. 7**. These data points represent the charge concentration at the time of the deposition of quartz mineral. But, once the samples settle down in identical environmental conditions the charge concentration of the sample from warmer geological region decreases with burial time and, eventually, coincide with other charge growth curve, sample belonging to the colder geological setting, in a few thousand years of the burial time, **Fig. 7**. So, the disparity imparted by different geological temperatures on the charge accumulation gets diluted if thereafter the burial climatic conditions are identical, which was true in case of R_1- centre also.

Charge population of L- centre

Identical geological and burial temperatures

The charge build up in the L- centre was, again, simulated in a similar way as described in case of R_1 and R_2- centers, incorporating geological and burial ambient temperatures of –10, 0, 10, 20, 30, 40°C. The charge population of L-centre in case of sample experiencing identical geological and burial temperatures is represented by two extreme temperatures, –10 and 40°C, in **Fig. 8a**. The initial data points of the charge growth curves refer to the charge population accumulated after a geological time of 0.1 million years. As can be seen from the plots, the charge built up is greater in case of sample experiencing warmer geological temperature. After burial the divergence in the charge growth curves in this case can be seen to continue even till a burial time of 0.1 million yr, larger burial time was employed here to get a better feel of the charge growth patterns. So, the disparity in the charge population, generated by varying geological temperatures, grows further during the burial time period.

The simulation suggests the accumulative effect of the geological and burial in-situ temperatures on the charge concentration in L- centre, higher the ambient temperature greater the charge population which was not the case with other centers, R_1 and R_2. The charge in this centre, L, registered a constant disparity between the charge growth curves, while as, in case of other centres the charge population curves were seen to converge during their burial time period and the sample from colder region, eventually, taking over the one from the warm region, as shown in **Figs. 2** and **5** respectively. The characteristics of the centre, stability and charge occupancy level, looks to be responsible for this feature of charge build up in case of this centre.

Identical geological and varying burial temperatures

The simulation results of a the charge build-up in L-centre for the samples experiencing identical geological and varying burial temperatures are presented in **Fig. 8b** for a typical case, geological temperature of -10°C and burial temperatures of –10 and 40°C. The slope of the charge growth curve increases immediately after the burial in case of a sample encountering warmer burial temperature, thereby, resulting in a higher charge population than the sample buried at a lower ambient temperature. There is continuous divergence in the charge growth curves with burial time, which means the disparity in the charge build-up in L- centre enhances with burial time in case of specimen experiencing two different burial temperatures. This, essentially, means that the charge population of this centre would attain greater value in case of a sediment from warm region compared to the one from colder region, even though they get derived from identical geological settings. Such behavior of continuous enhancement in the disparity in the charge growth resulting due to different burial temperatures only was not, again, observed in case of other charge centers as shown in **Figs. 3** and **6** for R_1 and R_2- centres respectively.

Varying geological and identical burial temperatures

The charge growth rates of L- centre for samples with varying geological but identical burial temperatures is represented by a situation where samples corresponding to two geological temperatures of 40 and –10°C settle

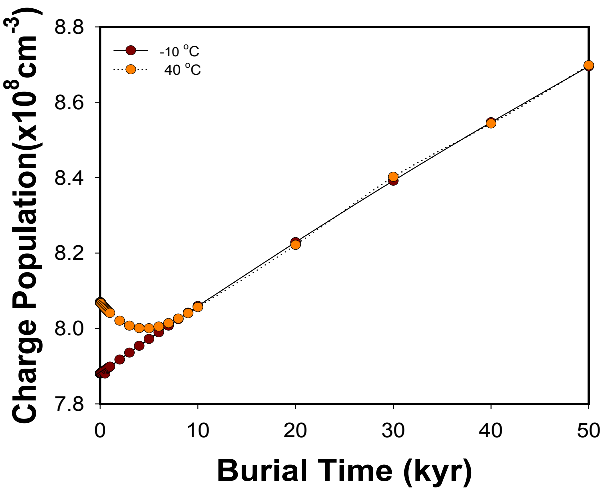

Fig. 7. *Charge population of R_2- centre simulated in case of samples having experienced various geological temperatures, represented by –10 and 40°C here, but, buried in settings having identical temperatures represented by –10°C in the plot. A geological and burial time periods of 0.1 million yr and 50 kyr were incorporated in the simulation respectively.*

down in region with identical ambient temperature of –10°C, as shown in **Fig. 8c**. The initial data points of the plots in the figure correspond to the charge build up in 0.1 million years at two different geological temperatures

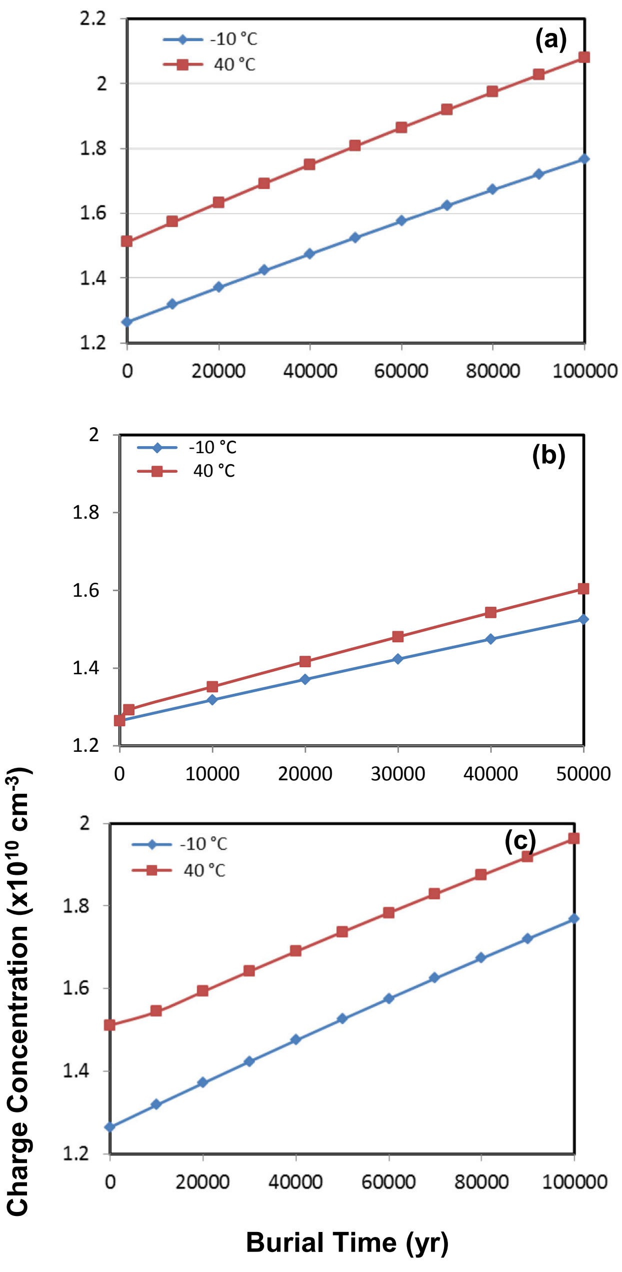

Fig. 8. *Charge population of L- centre simulated in case of samples having experienced (a) identical geological and burial temperatures represented here by –10 and 40°C, (b) identical geological temperature represented by –10°C and varying burial temperature represented by –10 and 40°C in the plot and (c) varying geological temperature represented by –10 and 40°C and identical burial temperature represented by –10°C here. A geological and burial time periods of 0.1 million yr were incorporated in the simulation in case of (a) and (c), while as, these periods were 0.1 million yr and 50 kyr respectively in case of (b).*

of 40 and –10°C. The settling down of these samples in region with identical ambient temperature, –10°C, does not significantly reduce the disparity in the charge accumulation during geological time period, though the two charge growth curves seem to converge very slowly. This feature leads to an important result that the impact of geological temperature on the charge build up does not get removed significantly irrespective of samples experiencing identical burial temperature, even up to a burial time period of 0.1 million yr, employed in this simulation. But, the same has not been true in case of R_1 and R_2-centers where the influence of geological temperature on charge population was significantly diluted and, eventually, eliminated within a few thousand years of the burial time, as shown in **Figs. 4** and **7** respectively.

Sensitization

The population of the charge in various centers, R_1, R_2, and L, simulated for various permutations and combinations of geological and burial ambient temperatures were, eventually, incorporated in transport equations to simulate the luminescence sensitization of the quartz specimen. To measure the sensitization of luminescence signal, the sample was administered a test dose of 0.5 Gy at a dose rate of 0.072 Gy s^{-1} and heated up to 160°C at a heating rate of 5°C s^{-1} to recorded the 110°C TL glow peak. The sensitization of the 110°C TL peak was, again, simulated for three typical cases, as mentioned above, (a) identical geological and burial temperatures, (b) identical geological and varying burial temperatures and (c) varying geological and identical burial temperatures. The details of the simulations carried out in this study are described below.

Identical geological and burial temperatures

As described above, this case refers to situations where quartz grains have experienced identical geological and burial temperatures. Simulations carried for all the temperatures considered here, –10, 0, 10, 20, 30, 40°C, are represented by the 110°C TL glow peaks stimulated for three temperatures, –10, 20, 40°C, as shown in **Fig. 9a**. A geological and burial time periods of 0.1 million years and 50 kyr, respectively, were utilized in the simulation. The impact of the ambient temperature on the luminescence intensity can be seen to be quite appreciable, enhancing with the ambient temperature. The disparity in the intensity of the glow curves in this case was observed to be largest as compared to the other cases described below. It, in fact, might be expected, as the accumulative effect of temperature difference during, both, geological and burial temperature on the growth of charge population would affect the sensitization much more than the situations with other permutation and combination of geological and burial temperatures.

To get a better feeling of how sensitization responds to in-situ temperatures the summary of results is depicted in **Fig. 10**. Also, the case of quartz grains inside ice cores was considered here by including low ambient geological and burial temperature of –40, –30 and –20°C in addition to other temperatures employed in this work. The **Fig. 10a** shows the variation of sensitization in case of samples encountering identical geological and burial temperatures of –40 to 40°C, in steps of 10°C for geological and burial time duration of 0.1 million years each. The sensitization remains, almost, constant till a temperature of 0°C and thereafter enhances monotonously with different slopes, the middle region, 10 to 30°C being the steepest one. This suggested that the sensitization is more sensitive to the temperatures in this range. A close look at the **Fig. 10a** indicates a very small increase in the simulated sensitivity as the ambient temperature decreases from –30 to –40°C, the lowest temperature considered in this study. This is quite interesting and needs to be explained. The **Fig. 10b** depicts the pattern of sensitization with time at two ambient temperatures –10 and 40°C. The magnitude and rate of increase in sensitization, both, can be seen to be larger in samples encountering warmer in situ temperatures.

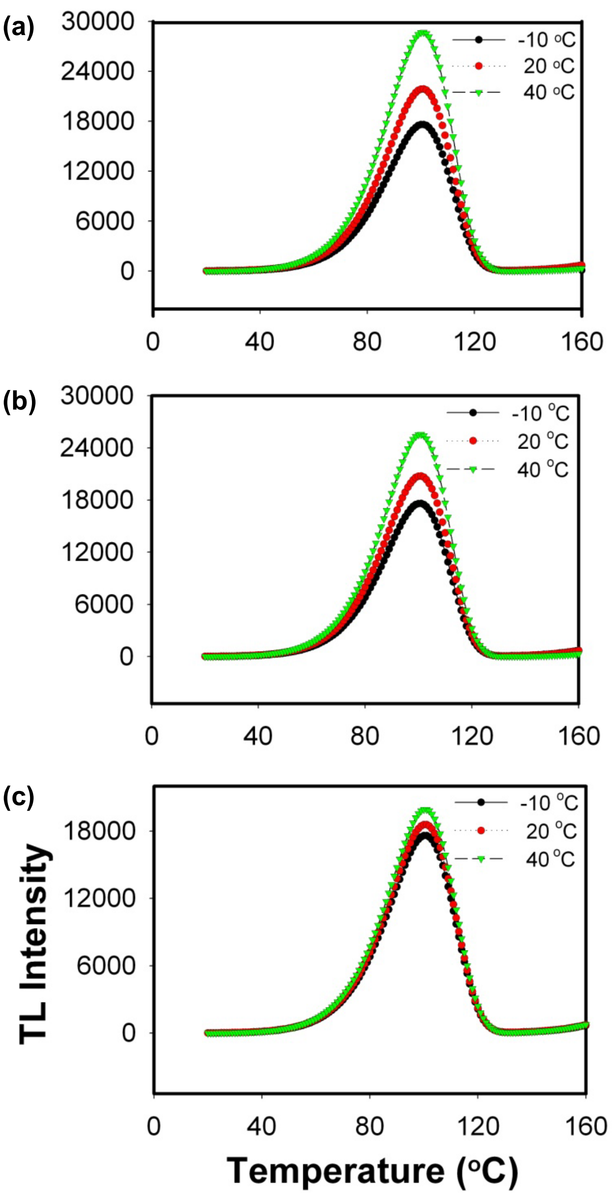

Fig. 9. *Luminescence sensitization simulated in case of samples having experienced (a) identical geological and burial temperatures represented here by –10, 20 and 40°C, (b) identical geological temperature represented by –10°C and varying burial temperature represented by –10, 20 and 40°C in the plot and (c) varying geological temperatures represented by –10, 20 and 40°C and identical burial temperature represented by –10°C here. A geological and burial time periods of 0.1 million yr and 50 kyr were incorporated in the simulation respectively. To measure the sensitization of luminescence signal, the sample was administered a test dose of 0.5 Gy at a dose rate of 0.072 Gy* s^{-1} *and the 110°C TL glow peak was recorded by heating it up to 160°C at a heating rate of 5°C* s^{-1}.

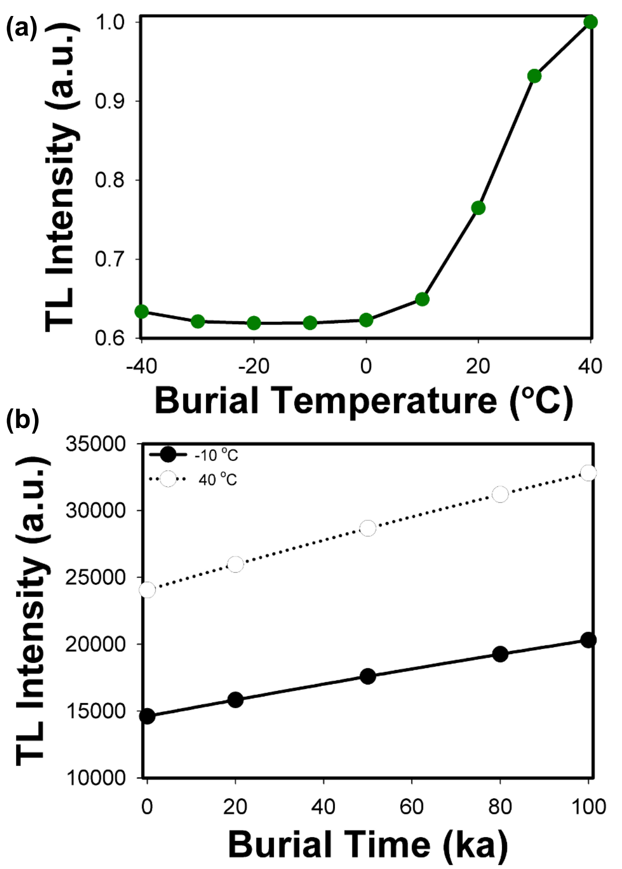

Fig. 10. *(a) Sensitization of quartz samples simulated with the in-situ temperatures of –40 to 40°C and (b) sensitization with time at two ambient temperatures –10 and 40°C. The in-situ temperatures represent the geological and burial temperatures experienced by the sample for a time periods of 0.1 million yr. The specimen were administered a radiation dose rate of 6.34×10*$^{-11}$ *Gy* s^{-1} *to the specimen during the geological and burial time period. The sensitization was measured in a similar way as described in case of Fig. 9.*

The activation energy, E, and the nature of the simulated 110°C TL peak were evaluated. As this peak is a well defined and well separated, the value of E was found out using initial rise method. The linear fit of $\ln(I)$ and $1/T$, where I defines the TL intensity at a temperature T, lead to E value of 0.96 eV. The fit was seen to be very accurate, yielding R value of 0.999. The evaluated E value matched with the input value of 0.97, employed in the simulation. Also, geometrical factor μ_g defined in **Eq. 3.1** was evaluated to know about the charge kinetics prevailing in the luminescence process. This value was found to be equal to 0.42, a clear case of first-order kinetics (Chen, 1969). So, the evaluated order of kinetics also matches with input kinetics presumed in the simulation of the 110°C TL peak.

$$\mu_g = \delta/\omega \tag{3.1}$$

where $\delta = T_2 - T_m$ and $\omega = T_2 - T_1$. The temperatures T_1, T_m and T_2 represent temperatures corresponding to the half value of the maximum intensity on the rising part of the glow curve, maximum intensity and half value of the maximum intensity on the falling part of the glow curve.

Identical geological and varying burial temperatures

The simulation in case of specimen subjected to identical geological and varying burial temperatures, essentially, looks into the role of burial temperatures on the sensitization in an independent way. All possible permutations and combinations of geological and burial temperatures were incorporated in the simulation. The results obtained are represented by a case where samples belonging to a geological temperature of –10°C have been buried at temperatures of –10, 20, 40°C, as depicted in **Fig. 9b**. A geological and burial time periods of 0.1 million years and 50 kyr, respectively, were considered here. The behavior of the glow peaks, clearly, shows the appreciable influence of burial temperature on the sensitization of the TL signal, higher the burial temperature greater the sensitization. But at the same time, the variation in sensitization does not look as significant as in the case described above, *i.e.* identical geological and burial temperatures situation. The reason, obviously, looks to be that the samples here have been subjected to the identical geological setting and, therefore, they would have acquired identical charge population till the burial time, which was not so in the above mentioned case.

Varying geological and identical burial temperatures

This combination of geological and burial temperatures would, essentially, assess the after effect of the geological temperatures on the sensitivity even after 50 kyr of burial of a specimen. The simulation in this case was carried out for specimen derived from various geological settings, but, buried in regions with identical ambient temperatures. The results are depicted in **Fig. 9c** for a typical case in which samples experiencing varying geological temperatures of –10, 20, 40°C settle down as sediments in regions having identical ambient temperature of –10°C.

Looking at the intensities of glow curves in **Fig. 9c** the sensitization can be seen to be different even though the specimen have been buried at identical temperatures for 50 kyr. The sensitization can be seen to be larger for specimen experiencing higher geological temperature prior to their burial. In other words, the impact of geological temperature on sensitization does not seem to get diluted completely even if the samples get buried in an identical setting for 50 kyr. However, the variation in the intensities of the glow peaks observed here is not as appreciable as in case of the other two situations described above, **Fig. 9a** and **9b**. The reason for this looks to be the dilution in the impact of different geological temperatures on the charge population by subsequent identical burial temperature. Considering these findings, though the role of geological temperature cannot be, altogether, neglected, the impact of burial temperature on the luminescence sensitivity looks to be more prominent than the geological temperature. These findings, as expected, are in agreement with that of the L- centre under these geological and sedimental conditions (**Fig. 8c**).

4. DISCUSSION AND CONCLUSION

The sensitization mechanism in quartz has been proposed to be due to transfer of charge from reservoir centre, R, to luminescence centre, L during thermal heating (Zimmerman, 1971). However, certain features of this sensitization, like thermal activation curves, isothermal sensitization and progressive sensitization made it essential to incorporate more than one centre. Accordingly, two reservoir centers, R_1 and R_2 have been incorporated in the models of quartz (Bailey, 2001). These centers have been categorized as shallow and deeper centers with activation energies of 1.43 and 1.75 eV respectively. The concentration of the available charge traps (N_i), which decides the charge saturation level of a trap, is nearly two orders of magnitude higher in R_2 as compared to R_1-centre in the Bailey's model (2001). The luminescence centre, L, is the most stable centre with the thermal activation energy of as high as 5 eV and its charge occupancy level is the highest among the three centers, one order more than that of R_2- centre**.**

The charge balance of various centers in nature is decided by (i) the charge filling occurring due to the natural irradiation and (ii) thermal eviction decided by the ambient temperature experienced by the specimen. In addition to these the charge transfer among various centres might also influence the charge distribution among them, as has been the case with quartz. In this natural mineral the charge released from one reservoir centre has been postulated to get transferred to either another reservoir centre or the luminescence centre, of course the probability for the two processes being quite different (Bailey, 2001). On the basis of kinetic considerations the shallow reservoir centre, R_1, being comparatively unstable has been found to be more susceptible to charge leakages even at lower ambient environmental temperature (Koul *et al.*, 2009). As expected, leakages from the deep reservoir centre, R_2, would be to a lesser degree than the shallow centre. Considering the Arrhenius equation, the probability of thermal charge eviction from these centers will enhance with increase in the ambient temperature. Given the stability of the L- centre, the thermal leakage from this centre will be negligible at the ambient environmental temperatures, considered in this work.

As expected, R_1- centre has been found to be most sensitive to the geological and burial temperatures in this study. The variation in the geological temperature was seen to affect the accumulated charge in this centre to a great extent, the charge population being higher in case of lower ambient temperature. The magnitude of difference in the charge build up with the two extreme temperatures, –10 and 40°C employed here, was found to be almost of one order**,** **Fig. 1**. Also the time period required to reach the charge equilibrium, saturation, has been seen to be influenced by the ambient temperature, lower the temperature more the time this centre gets to reach the saturation value. Since the charge occupancy level of this centre is postulated to very low, it was observed to reach saturation in, only, a few thousand years of geological time span.

The charge build-up in R_1- centre during the burial time period just followed its trend during the geological time period, colder the burial region large the charge accumulation. The impact of geological temperature on the charge build up in this centre is appreciably diluted by the subsequent burial temperature. It takes ~15 kyr of the burial time to completely remove the geological temperature effects and establish the charge equilibrium of this centre which is entirely decided by the burial temperature. This is clear from **Fig. 4** in which samples from two geological settings settle down in an identical environmental condition acquire same charge level after ~15 kyr. Both stability and charge occupancy being low in case of R_1- centre it seems to play a major role in the charge transfer and, therefore, sensitization mechanism of the specimen. This looks to be in accordance with the earlier work which also suggested the central role of this centre in the luminescence sensitization process (Koul *et al.*, 2009). Adamiec (2005) while studying the role of various reservoir centers in the sensitization process noticed in the thermal activation curve (TAC) that the sensitization initiated at different temperatures for fired and unfired geological samples, 200 and 300°C, respectively. But, the sensitization at the lower end of the TAC was seen to get restored in the case of natural geological specimen, also, once it was administered a radiation dose. This observation seems to imply an appreciable thermal erosion of charge from shallow reservoir centre R_1 at ambient temperature in quartz specimen.

The deep reservoir centre, R_2, though seen to be less sensitive to ambient temperature demonstrated an interesting variation in its charge population with different ambient temperatures. The geological temperature was not found to affect the charge build up in case of this centre as much as has been the case with R_1- centre and, also, the trend observed was entirely different, warmer temperatures favoring the charge build up. The influence of the geological temperature on charge growth was, again, seen to get removed in burial time duration of a few thousand years, **Fig. 7**. In contrast to R_1- centre the simulated charge population in case of R_2- centre was seen to be larger in case of sample experiencing warmer burial temperatures till a burial time of ~40 kyr, though the samples buried at colder temperature demonstrated higher growth rate, **Figs. 5** and **6**. On account of this steeper slope the charge growth curve corresponding to colder temperature (-10°C) was found to take over the one corresponding to the warmer burial temperature (40°C) at this epoch of burial time of ~40 kyr and continued to be larger, thereafter, till a burial time of 0.1 million yr, considered here in the simulation.

The behavior of charge kinetics of R_2- centre with ambient temperature suggested appreciable charge transfer from the shallow reservoir centre, R_1, to this centre and it was seen to enhance with the increase in the ambient temperature. This charge transfer seems to be appreciable enough to compensate for the thermal charge eviction even at ambient temperature of as high as 40°C and, thereby, enabling larger charge population than the one stimulated with a lower ambient temperature, –10°C, till a burial time of ~40 kyr, **Figs. 5** and **6**. But, considering the stability of this trap, thereafter, the charge eviction at such high ambient temperature looks to become too significant to be compensated by the charge transfer mechanism. Also, on the basis of kinetic considerations the charge eviction from R_2- centre will be comparatively lower at low ambient temperature even after 40 kyr of burial time. These two factors seem to result in the charge growth being overtaken by the sample in colder setting at this stage of burial time. Also the steeper charge growth at low ambient temperature observed in the plots seems to be due to this lower thermal eviction at such environmental temperatures, **Figs. 5**, **6** and **7**.

The luminescence centre, L, being a very deep trap was found to be, almost, insensitive to charge leakage even at high natural environmental temperatures, considered here. This can be understood from the fact that the population of this centre has been consistently favored at higher environmental temperatures, with all the permutation and combinations of geological and burial temperatures, which was not true of other centers, **Fig. 8**. It, essentially, means that the charge transfer from reservoir centers to this centre enhances with increasing environmental temperatures, but at the same time, negligible erosion of charge takes place from this centre at such temperatures. As a result, the divergence in the charge growth of the specimens with varying burial temperatures continued till a burial time of 0.1 million yr, considered here in the simulation, **Figs. 8a** and **8b**. Also, subjecting the specimen from various geological temperatures to identical burial temperatures was found to dilute to certain extent but not remove the impact of geological temperatures on the charge build up in L- centre for the time periods considered here, which was not true in case of other centres, **Fig. 8c**. These findings suggest that, unlike R_1 and R_2 centers, the charge population in this centre seems to be determined by, both, geological and burial temperatures the sample has experienced.

The luminescence sensitization, as expected, behaved in a way similar to the charge variation in L-centre with different ambient temperatures. The sensitization was seen to be favored in situations where sample had been in warmer geological or burial settings or both in tandem, **Fig. 9**. But, it was found to be most prominent in case of the latter due to cumulative effect of the two temperatures, geological and burial, **Fig. 9a**. Samples with similar geological setting buried in regions with varying temperatures, also, demonstrated significant disparity in the sensitization, higher temperatures yielding larger sensitizations, **Fig. 9b**. On the other hand, sediments from various geological settings once buried in identical environmental conditions were seen to have lowest variation in their sensitization, **Fig. 9c**. Obviously, like in case of L- centre, the burial time period here looks to dilute the disparity in the sensitization introduced by the varying geological temperatures. Considering all these results though burial condition seems to have a prominent role in the sensitization process, the geological condition, at the same time, does also have a bearing on the luminescence sensitization of quartz mineral. Looking at the plot of sensitization with various ambient temperatures, –40 to 40°C, the sensitization was seen to be most sensitive to the environmental temperature 10 to 30°C, **Fig. 10a**. This looks, primarily, due to the role of shallow reservoir centre (R_1) in the charge transfer mechanism, as this centre has been found be very sensitive to the environmental temperatures, though the contribution from deeper reservoir centre (R_2) cannot be ignored (Koul *et al.*, 2009). The samples in warmer environmental settings attain much larger sensitization with time as shown in **Fig. 10b**.

Any regenerative procedure for dose measurement, like SAR, must ensure parity in the sensitization of the natural and artificially irradiated specimen. Murray and Wintle (2000) during the development of SAR protocol observed the pre-heat induced sensitization to be much larger in the case of a laboratory irradiated sample as compared with the natural one. In a related study Murray and Wintle (1999) found the sensitization induced in case of OSL signal during pre-heat treatment to be due to increase in the charge population of the luminescence centre, L. These findings implied that the sensitization of natural sample seems to be larger than the laboratory irradiated one. This was suggested, as found in the present work, to be due to the sensitization process taking place during its storage at ambient temperature. As mentioned earlier, the *in situ* sensitivity was reported to be dependent on the ambient temperature, samples from warmer regions yielding higher values. Also, their observation of progressive sensitization with regeneration dose and pre-heat implied the magnitude of sensitization to be dependent on the dose received by the sample till read out stage, *i.e.* pre-dose. The sensitization was observed to become significant for samples that are more than few thousand years old. This aspect was, in fact, confirmed by Banerjee (2001) in his studies related to the OSL test dose response with cycle of measurement and previous irradiation history. To take all these observations into account the SAR protocol was developed to generate parity between the sensitization encountered in natural and artificially irradiated samples.

Combining all these findings mentioned above point towards the mechanism of in-situ sensitization of quartz specimen prevailing in nature due to the transfer of charge from reservoir to luminescence centres. But, unlike in case of pre-dose phenomenon observed in laboratory, where the transfer from R to L centers happens very fast during the heat treatment, it might be a trickle effect in case of the *in situ* sensitization. The simulated results in this study suggested (i) significant influence of ambient temperature on charge population of various centres of quartz (ii) the participation of reservoir centers in the in-situ sensitization of quartz and (iii) the dependence of this sensitization on the ambient temperature prevailing during, both, geological and burial time periods of the specimen.

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