A coupled PL/OSL system to understand the dynamics of the metastable states

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Highlights:
Infrared photoluminescence (IRPL), a new method of trapped charge dating based on the non-destructive probe of trapped electrons.

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Highlights:
A novel luminescence-based physical system to track the concentration of trapped electrons and holes after any perturbation.

Abstract
Metastable states form by charge (electron and hole) capture in defects in a solid. These play an important role in dosimetry, information storage, and many medical and industrial applications of photonics. Despite many decades of research, charge transfer across metastable states and its role in luminescence production is poorly understood. This is mainly because the measurement of luminescence from metastable states involves several processes such as detrapping, transport, competition, and electron-hole (henceforth e-h) recombination.

Here we present a novel, coupled OSL-PL (optically stimulated luminescence – photoluminescence) system in a natural alumina-silicate feldspar which comprises >50% of the Earth’s crust, to understand the dynamics of the metastable states. Infrared PL (IRPL) in feldspar is capable of directly probing the trapped electrons. Whereas, OSL measures e-h recombination. Combining these two pieces of information, we develop here new analytical methods, and based on these elucidate for the first time the thermal dependence, diffusion, thermo-optical bleaching, and radiation-induced growth of electron and holes in feldspar. These results support a strong presence of localized recombination mechanisms in feldspar. These new methods and insights provide unique information for developing robust mathematical models that are crucial to the next generation applications of luminescence dosimetry in Earth and environmental sciences. We expect that this work will inspire a search of a similar coupled OSL-PL systems in other solid-state
dosimeters and enrich our understanding of luminescence phenomena involving the metastable states.
1. Introduction

Metastable states in solids play an important role in dosimetry (Bøtter-Jensen, 2003) and have exciting potential applications in bio-imaging, radiobiology and information storage (Chakrabarti et al., 1989; Meijerink et al., 1991). These metastable states are created by the creation of free charge in a solid by exposure to ionizing radiation (electrons and holes), followed by charge capture within distinct defects or defect clusters. This process is commonly referred to as trapping. The thermal lifetime of a metastable state (i.e. trapped electron or hole) may range from microseconds to millions of years depending on the depth of the potential wells formed by electron or hole capture and the ambient temperature. Eventual detrapping by photon/phonon interactions with the traps may lead to radiative recombination of the opposite charge carriers. The resultant luminescence, for example, can be used to estimate prior absorbed dose (J/Kg) from ionizing radiation (dosimetry), measure the burial age of sediment or rock (geochronology), map location of the emitting particles (imaging), etc. Depending on whether light or heat is used for detrapping (readout), the process is called optically stimulated luminescence (OSL), thermoluminescence (TL) or prompt phosphorescence, if it results in luminescence emission. Similarly, prompt e-h recombination at a luminescence center, during exposure to ionizing radiation can be measured as radio-luminescence (RL) (Trautmann et al., 1999; Erfurt et al., 2000).

Different metastable states are used in different applications. In SiO₂, for example, trapped electrons at about 2.8 eV below the conduction band edge are commonly used in OSL dating applications (Huntley et al., 1996). In persistent phosphors, on the other hand, traps with intermediate depths are required to obtain detrapping at room temperature (Van den et al., 2013).

Despite many decades of research aimed at understanding luminescence generation from metastable states, there remain significant gaps in our knowledge. There exist a plenitude of phenomenological and mathematical models to describe the same signal, even within the same material. Largely, this ambiguity arises from the fact that measurement of luminescence signal (OSL or TL) typically involves a convolution of three processes: charge release (detrapping), charge transport (localized or delocalized), and e-h recombination. Therefore, it becomes challenging to ascribe luminescence kinetics to any particular process; often there are multiple solutions impeding an exact understanding of the physical process. This challenge can be overcome if one were able to observe independently the dynamics of the trapped electron (or hole) population and thus by comparison with OSL or TL decouple these different processes.

Independent measurement of trapped electrons can be made through electron paramagnetic resonance (EPR), but this technique applies only to unpaired electrons, and it is often ambiguous to relate ESR signals to the traps that participate in OSL or TL. One can also probe metastable states by optically induced intra-defect transitions (excitation → radiative relaxation) using radio-photoluminescence (RPL); the prefix radio is used to indicate that the probed states are created by ionizing radiation, to distinguish it from the ordinary photoluminescence (PL). Until recently, the RPL method has only been available in hole trapping states, in materials such as Mg or Ag doped glasses, and C, Mg doped Al₂O₃. In these materials, there is no direct link between OSL and RPL making the technique inappropriate for providing a holistic picture of detrapping and charge transport.
For investigating the physics of charge transport across the metastable states, it is desirable to be able to observe RPL from trapped electrons using their excited state below the conduction band edge, and then de-trap the same electrons by higher energy excitation to produce OSL. Such a coupled OSL-RPL system can offer a better understanding of the OSL kinetics, by providing an opportunity to directly examine the changes in trapped electron population (through RPL). Furthermore, in terms of applications, such a physical system can be measured non-destructively by resonant excitation PL, providing a high sensitivity dosimetry system, and can be easily reset with light (similar to OSL and unlike the hole based RPL systems). Thus, a combined OSL-RPL system based on the excitation of trapped electrons offers great advantages both for improving our understanding as well as for practical applications. One example of such a system is the Sm\textsuperscript{2+} defect in YPO\textsubscript{4}: Sm, Ce. This shows both RPL and OSL behavior (Poolton et al., 2010, 2012 Prasad et al., 2017a; Dorenbos et al., 2003, 2011). Prasad et al. (2017) used this system to obtain insights into excited state tunneling induced recombination (Sm\textsuperscript{2+} \rightarrow Ce\textsuperscript{4+}) in YPO\textsubscript{4}. The PL from Sm\textsuperscript{2+}, unfortunately, quenches at around 180 K, severely restricting the physical investigations and applications.

More recently our group has shown the RPL mechanism in the electron trap in feldspar (Prasad et al., 2017; Kumar et al., 2018), an aluminosilicate that comprises > 50% of the Earth’s crust. Metastable states in feldspar are widely used in luminescence dating and retrospective dosimetry (Huntley et al., 1985; Hütt et al., 1988; Thomsen et al., 2008; Buylaert et al., 2012). The RPL signal in feldspar, termed as infrared photoluminescence (IRPL), derives from radiative relaxation of the excited state of the main dosimetric trap (principal trap) with a lifetime of about 30 µs at room temperature (Prasad et al., 2017). Based on low temperature spectroscopic measurements, Prasad et al. (2017) concluded that both the IRPL and the OSL obtained using near-infrared (NIR) excitation (i.e. infrared stimulated luminescence, IRSL) arise from the principal trap. A simplified IRPL-IRSL mechanism in feldspar is shown in Figure 1a,b; here electron detrapping followed by e-h recombination via the band tail states leads to IRSL (Poolton et al., 2002, 2009; Jain and Ankjærgaard, 2011). Whereas, electron retrapping/relaxation leads to IRPL. The excitation spectrum and the Stokes shifted IRPL emission spectrum are shown in Figure 1c. Each defect emits IRPL at the rate of thousands of photons per second (depending on the excitation rate). This provides an unprecedented sensitivity for 2D and 3D mapping (Sellwood et al., 2019) of defect distribution and examining charge transfer.

IRPL has the potential for providing a direct assessment of thermal and optical stabilities, as well as the behavior of trapped electrons during different laboratory protocols. In this study we explore the potential of the coupled OSL-IRPL from the principal trap, to obtain a better understanding of charge transfer and recombination processes. While the results here apply specifically to feldspar like systems (with both localized and delocalized charge transport), they give general insights into the behavior of metastable states under an external stimulus.

2. Materials and methods
Samples used in this study consist of K-feldspar (7) and Na-Feldspar (1) extracts from sediment samples. These samples, 072255(K), 981009(K), 981010(K), 981013(K), 092202(K), 092204(N) and H22553(K) have been reported in Buylaert et al. (2012), while R47(K) has been reported in Prasad et al. (2017) and Kumar et al. (2018). Note that we have added here (K) or (N) to indicate the composition, potassium or sodium, respectively. We have deliberately chosen sediment samples, because in our experience these samples generally consist of mature minerals that have survived the physical and chemical weathering process, and because the results of our investigations here are relevant for sediment dating. X-ray fluorescence (XRF) measurements show that our samples are K or Na rich feldspar samples.

All measurements were performed using the photomultiplier (PMT) based IRPL attachment to the Risø TL/OSL reader. This attachment consists of an external laser light source at ~1.49 eV (830 nm). We measure both the dose-dependent Stokes-shifted emissions in feldspar at ~880 and ~955 nm in all the measurements (Kumar et al., 2018). Two different photo-multiplier tubes in combination with the emission band-pass interference filters transmitting 880/10 nm or 950/50 nm were used for detecting the IRPL emissions at ~1.41 eV (880 nm) and ~1.30 eV (955 nm), respectively (Kook et al., 2018). The power density of the laser at the sample position was measured to be ~3 mW.cm−2. The IRPL signals were measured in pulsed excitation mode (laser on-time 50 µs, and off-time 50 µs; detection during off-time 51-100 µs). Throughout the text, the IRPL (955 nm) and IRPL (880nm) emissions are denoted as IRPL955 and IRPL880, respectively. Kumar et al. (2018) demonstrated that these signals do not represent the two excited states of the same defect site. Here, the respective (unknown) principal traps that give rise to these signals are referred to as the 880 or 955 nm (emission) centers. Room temperature refers to the controlled laboratory temperature of 25 °C.

The OSL signals obtained using a NIR excitation (i.e. 850 nm), known as infrared stimulated luminescence (IRSL) were detected using the same PMT as the IRPL880 but using BG39 and BG3 filters. IR light-emitting diodes (LEDs; power density ~250 mW.cm−2 at the sample position) were used as the excitation light source. The switch over between different filters and detectors was achieved using the automated detection and stimulation head (DASH) (Lapp et al., 2015).

Both IRPL and IRSL data were analyzed using the Matlab and Microsoft Excel software. OriginPro 2018b is used for model fitting and for plotting the figures.

3. Current understanding of stimulated-luminescence generation in feldspar

Infrared stimulated luminescence (IRSL) is widely used in luminescence dating (Balescu and Lamothe, 1994; Buylaert et al., 2009; Li and Li, 2011; Thiel et al., 2011; Tsukamoto et al., 2017). This method, however, suffers from an athermal loss of signal (anomalous fading), a problem that has been addressed in the last decade using preferential sampling of a more stable signal. Discrimination between more and less stable signals can, for example, be achieved using a sequential measurement of IRSL at increasing sample temperatures; it is observed that the subsequent elevated temperature IRSL is more stable than the preceding low temperature measurement (Thomsen et al., 2008). Buylaert et al., 2012 tested an approach using post-IR50
IRSL$_{290}$ (pIR$_{50}$IRSL$_{290}$, subscripts refer to IR stimulation temperature at °C; Thiel et al., 2011) using known age samples, to determine if it is possible to eliminate the fading component. These authors found that pIR$_{50}$IRSL$_{290}$ gives an age that is consistent with the expected age, on an average, supporting that such an approach can be successful in isolating stable trapped electron population. Such data indicate the existence of localized recombination in feldspar (Jain and Ankjærgaard, 2011, Jain et al., 2012, 2015), explained as follows. Around room temperature, the recombination primarily occurs between close e-h neighbors either by excited-state tunneling or by limited diffusion within the band tail states. Such close neighbors are likely to recombine in nature due to tunneling, and therefore prone to fading (Huntley, 2007). There remains however a finite population of distant e-h neighbors that are not accessed by the first IRSL (IR$_{50}$) measurement since the probability of recombination is much lower than the probability of retrapping or relaxation (i.e., mean diffusion length $\ll$ the distance to the nearest hole). However, when the temperature is increased in the subsequent IRSL measurement it becomes possible for detrapped electrons to access distant holes and thereby recombine, thus giving rise to the regeneration of IRSL (i.e. pIRTIRSL$_{T}$) signal; since this signal is based on distant pairs it is by definition less prone to athermal fading in nature.

Numerical models of feldspar suggest that intra-defect transition (excitation-relaxation) within the principle trap is the most dominant process during the resonant light excitation (Jain et al., 2012, 2015); however, this transition is overlooked in the typical anti-Stokes measurements performed in OSL. IRPL measures this transition. IRPL shows a dose response similar to that of OSL, but since it does not involve e-h recombination, the signal can be read out non-destructively (especially at cryogenic temperatures). Since IRPL can be measured even from traps remote from recombination centers (Prasad et al., 2017b), it must include a stable, steady-state component (i.e. one that does not suffer from anomalous fading).

While this model successfully explains our experimental observations, we do not have any information on how electrons-hole distances are actually distributed in the crystal. Furthermore, there is no direct proof that only a fraction of trapped electrons are measured during IRSL at a given temperature and the remaining electrons that do not participate in the IRSL are more stable. Within this model framework, the specific questions that we ask of a coupled PL-OSL system are:

1) What fraction of the occupied principal trap participates in the IRSL process?

2) How do trapped electrons and/or trapped holes deplete by thermal vibrations, and which of the two processes (electron or hole depletion) is responsible for the thermal stability of the IRSL signal?

3) What is the nature of the increase of trapped electron and hole concentrations due to exposure to ionizing radiation?

4) Does electron trapping cross-section vary as a function of the e-h distance?

5) How does thermal partitioning of detrapped electrons occur within the band tail states?

6) How does the probability of finding a recombination center changes with thermal diffusion of electrons in the band tail states?

These aspects are investigated in the following sections.
Here we try to experimentally determine how different sub-populations in the nearest-neighbor e-h distribution recombine in response to thermal or thermo-optical excitation. We do this by monitoring IRPL (trapped electron population) before and after IRSL (e-h recombination) at different temperatures. The experimental protocol is outlined in Table 2. Seven different samples with palaeodose ranging from about 100 to 300 Gy were measured. First three large aliquots of each sample were measured using their ‘natural’ signals (i.e., signal due to dose received in nature). Subsequently, the protocol in Table 2 was repeated on these aliquots, after delivering the same beta dose as the palaeodose to avoid any dose dependence. A high temperature IR bleach (step 7) was carried out at the end of the cycle to reset the signal.

Before we discuss the effect of IRSL on IRPL, it is interesting to examine the change in trapped electron population due to a preheat (step 2) and high temperature cleanout (step 7) for the laboratory dose cycle. For the 955 emission, the residual IRPL after a high temperature IR bleach (IRPLt - IRPLbg / IRPLt) ranged from about 3% to 14% in different samples, with a mean (%) ±1σ (absolute standard deviation) of 9±4 of the IRPLt. This residual level is similar to that obtained after several hours of exposure under solar simulator (data not shown) and therefore considered to represent the difficult-to-bleach trapped electron population. The residual signal was found to be reproducible from cycle to cycle (data not shown). The change in the IRPL signal due to preheat (IRPL0 - IRPLt / IRPL0) ranged from -14 to +5% with a mean of -2 ± 8%. This change arises from a combination of a) thermal depletion of the electrons in the principal trap, and b) recuperation due to electron capture in the principal trap during the decay of other shallow states. The minus sign indicates that there is a net increase in IRPL after preheat, i.e., recuperation is more dominant. For the 880 emission, the IRPLbg ranged from about 4% to 25% in different samples, with a mean of 16±8% of the IRPLt. The change in IRPL880 due to preheat (IRPL0 - IRPLt / IRPL0) ranged from -20 to +1% with a mean reduction of -7 ± 9%.

The comparison of these IRPL880 and IRPL955 data shows that there is a greater net capture of electrons in the 880 nm traps during preheat than in the 955 nm traps. Similarly, there is a greater proportion of difficult-to-empty electrons in the 880 nm traps compared to the 955 nm traps.

The depletion in the trapped electron population due to IR stimulation was calculated as follows:

$$\Delta IRPL (T)\% = \frac{IRPL_t - pIR_T IRPL_t}{IRPL_t - IRPL_{bg}} \times 100$$

(1)

$\Delta IRPL$ was measured both for the IRPL880 and IRPL955 signals. Figure 2a shows $\Delta IRPL$ graphically for the IRSL measurement at 50 °C for the laboratory irradiated aliquots. The IRSL signal reaches a near-constant level towards the end of the 95 s measurement. This level represents a stage where e-h recombination becomes inefficient at 50 °C due to reduced access to the nearby holes; the dominant mechanism is, therefore, excitation-relaxation (or retrapping) within the principal trap (Figure 1a). The difference in the IRPL signals before and after the IRSL (i.e., $\Delta IRPL$) should reflect the population of the principal traps that participated in the IRSL (e-h
recombination) process. This reasoning is tested in Figure 2b, which plots the relationship between \( \Delta \text{IRPL} \) and net IRSL counts from the 3 aliquots each of all seven samples. We see a positive correlation between the two, however, there is a slightly greater scatter in IRPL\(_{880}\) compared to IRPL\(_{955}\) signal. Interestingly, the three outliers in the IRPL\(_{880}\) are all from the same sample 092202. There seems to be a tendency for a slight sub-linear \( \Delta \text{IRPL} \) vs. IRSL behavior with an increase in the luminescence sensitivity; this indicates that the depletion ratios may vary from aliquot to aliquot depending on IRSL sensitivity. In general the majority of these data, despite very different geographical origins of the feldspar samples, support to a first-order approximation that \( \Delta \text{IRPL} \) is proportional to IRSL.

\( \Delta \text{IRPL} \) for the IR bleach at different temperatures are plotted in Figure 3 (note that the data for pIR\(_{250}\) IRPL are not plotted since IR stimulation temperature is significantly higher than the preheat temperature). The trends between laboratory and natural dose are similar; however, there is a tendency for slightly greater \( \Delta \text{IRPL} \) for the laboratory irradiated samples compared to the naturally irradiated samples. For IRPL\(_{955}\) one can conclude that about 40-50\% trapped electron population participates in IRSL (step 5) at 50\(^\circ\) C. There is a significantly large spread in \( \Delta \text{IRPL} \) from sample to sample for IR depletion at 50\(^\circ\) C than at the higher temperatures; this partly explains the scatter observed in Figure 2b. Further, sequential raising the IRSL temperature (step 5) to 100, 150 or 200\(^\circ\) C results in a depletion of trapped electrons to about 70, 85 and 95\% of the initial signal, respectively.

In contrast, for IRPL\(_{880}\) only about 20\% of the trapped electron population participates in IRSL (step 5) at 50\(^\circ\) C. Further sequential raising the IRSL temperature (step 5) to 100, 150 or 200\(^\circ\) C creates and depletion of trapped electrons to about 40, 65 and 80\%, respectively. A higher \( \Delta \text{IRPL}_{955}\) (50\%) than \( \Delta \text{IRPL}_{880}\) (20\%) is perhaps the reason for a higher correlation between IRSL and \( \Delta \text{IRPL} \) for the 955 emission than the 880 nm emission; these observations show that there is preferentially higher contribution of luminescence from the 955 traps over the 880 traps during the IRSL measurement.

We also measured \( \Delta \text{IRPL} \) following Table 2 but with a preheat of 320 \(^\circ\)C for 60 s, commonly used in feldspar pIR\(_{50}\)IRSL\(_{290}\) dating. The results are shown in Figure 4. The IRPL\(_{880}\) behaves in a similar way as in Figure 3. However, in case of IRPL\(_{955}\), some samples show only 20 and 40\% depletion at IR\(_{50}\) and pIR\(_{100}\) IRPL, respectively. This change probably represents a significant depletion of the unstable electron population in the IRPL\(_{955}\) center in some samples due to a higher preheat for the data in Figure 4 than in Figure 3.

With regards to dating, this implies that the stable electron population in the pIR-IRSL methods samples from 50-80\% (depending on the preheat) of the total population remaining after the preheat.

5. Thermally-induced depletion of trapped electron and hole populations

The response of OSL to heating is commonly investigated through so called ‘pulse annealing curves’, where the sample is heated to different temperatures between beta or gamma irradiation and the OSL measurement (Duller, 1991). Since OSL measurements involve both electrons and
holes, the OSL pulse anneal curve cannot distinguish between which of the general processes below (a-d) are responsible for the decrease in the signal. Here, $E_e$ is the trap depth of the principal trap, and $E_h$ is the trap depth of the recombination center involved in OSL or IRSL.

a) $E_e > E_h$ in a delocalized model (i.e. eviction of electrons into the conduction band or holes into the valence band). The pulse anneal curve will reflect the thermal depletion of the trapped holes.

b) $E_e < E_h$ in a delocalized model. The pulse anneal curve will reflect the thermal depletion of the trapped electrons. This is the common conventional interpretation of the OSL or IRSL thermal depletion data.

c) Simultaneous depletion of holes and electrons in a localized model (Jain et al., 2012). Here both $E_e$ and $E_h$ are significantly larger than the activation energy required to induce local e-h recombination. The pulse anneal curve will reflect the thermal activation energy for excited state tunneling or localized recombination.

d) Localized or delocalized model with competition from shallow traps. Here holes (or electrons) are used up due to thermal depletion of electrons (or holes) in a shallow trap, i.e. both $E_e$ and $E_h$ are greater than $E_{shallow\, trap}$. The pulse anneal curve will reflect the thermal depletion of charge in the shallow trap.

In a coupled PL-OSL system one can make some predictions of the behavior of the pulse anneal curves under these different scenarios. In a) and d), the IRPL curves will be more stable than the IRSL. In both b) and c) the IRPL and IRSL pulse anneal curve will overlap.

A combination of IRPL and IRSL can for the first time directly provide tracking of both electrons and holes in the system as follows:

$$IRPL(T) \propto n_e(T)$$  \hspace{1cm} (2)  

$$IRSL(T) \propto n_e(T).m_h(T)$$ \hspace{1cm} (3)  

$$\Rightarrow m_h \propto \frac{IRSL(T)}{IRPL(T)}$$ \hspace{1cm} (4)

Here $n$ represents the population of the occupied principal traps, and $m$ represents the trapped hole population in the crystal, that is available for IRSL or OSL.

However, one needs to be cautious, as in the context of the feldspar model (Jain and Ankjærgaard, 2011; Jain et al., 2015) we know that pure delocalized transitions do not exist at near room temperature IR stimulations. As discussed in the previous sections 3 and 4, the IRSL process has a strong recombination bottleneck; so only fraction of the electron population (20-50%) takes part in the IRSL production, e.g. at 50° C. Thus, Equation 4 is not fully justified since IRPL originates from the entire crystal, whereas IRSL only originates from a small sub-population that satisfy nearest neighbor condition for IRSL production. To tackle this problem, we also derive the thermal dependence of the IRPL lost due to the IRSL measurement, i.e. $\Delta IRPL(T)$ following equation 1. As discussed in the last section (Figure 2b), this signal should correspond to the population that
participates in the IRSL process. Thus, we define two new parameters $n'_e$ and $m'_h$; these are more relevant estimates of the behavior of trapped electrons and holes that are active in the IRSL process:

$$n'_e \propto \Delta IRPL (T)$$

$$m'_h (T) \propto \frac{IRSL (T)}{\Delta IRPL (T)}$$

The pulse anneal data were measured using the protocol outlined in Table 3 using three aliquots of sample 981010. The protocol followed here is based on a single aliquot regenerative (SAR) dose method where any possible sensitivity change during repeated measurements is corrected for by using the response to a test dose. We derived the following data as a function of anneal temperature using the protocol outlined in Table 3:

#1. IRSL (T) / IRSL (test dose): sensitivity corrected IRSL signal.

#2. IRPL (T) / IRPL (test dose): sensitivity corrected IRPL signal. This signal measures the changes in trapped electrons in the principal trap in the entire crystal ($n_e$) as a function of preheat temperature (Equation 2).

#3. pIR$_{50}$IRPL(T) / pIR$_{50}$IRPL(test dose): sensitivity corrected pIR$_{50}$IRPL, i.e. IRPL signal measured after an IRSL measurement at 50°C. This signal should measure the relatively stable principal trap population, i.e. distant e-h neighbors.

#4. $\Delta$IRPL (T) / $\Delta$IRPL (test dose): this represents the thermal dependence of electrons in the principal trap ($n'_e$; equation 5), which participate in the IRSL process.

#5. IRSL(T) / IRPL(T): this represents thermal dependence of trapped holes ($m_h$; equation 4) for a delocalised model [models a), b) or d)].

#6. IRSL (T) / $\Delta$IRPL(T): this represents thermal dependence of trapped holes ($m'_h$; equation 6) for the localised model [models c) or d)].

For both #1, #2 and #3), the test dose response was almost invariable as a function of the SAR cycle; nonetheless using sensitivity correction improved the reproducibility. Therefore, we decided to use the sensitivity corrected ratio.

These ratios (#1 to #6) are plotted in Figures 5a and 5c for IRPL$_{880}$ and in Figures 5b and 5d for IRPL$_{955}$. The data were measured on 3 aliquots of the sample 981010. The thermal stability of the different signals is similar for both the IRPL (880 and 955 nm) emissions. The IRSL data (#1) show a steep decrease from 50 to 100°C where it reaches a plateau between 100 and 220°C, followed by a monotonic decrease up to 450°C where it reaches a near-zero value. IRPL (#2) on the other hand is relatively stable from 50 to 400°C, followed by a monotonic decrease from 400 to 600°C. Even at 600°C, ~10% of the IRPL still remains. The pIR$_{50}$IRPL, i.e. the IRPL signal remaining after IR bleach (#3), is only slightly more stable than the IRPL (#1) for the 880 nm emission, while it is significantly more stable than the IRPL (#1) for the 955nm emission. This
difference is not surprising since as discussed in the previous section, the change (depletion) in IRPL by IR stimulation at 50° C is much smaller for the 880 nm emission than the 955 nm emission. An increase in the stability is supported by the feldspar model, which suggests that IRSL uses the nearest e-h neighbors, which are easy to recombine through the excited state of the electron trap (Jain et al., 2012, 2015).

The IRSL signal has already decreased by 75% (compared to its plateau value at 100° C) at 400° C when the IRPL signal only begins to deplete. The ratio IRSL (T) and IRPL (T) gives $m_h$ (#5). These data very closely follow the IRSL (T) depletion pattern for both the 880 and 955 emissions, suggesting that to a first-order approximation, the main cause of the decrease in IRSL is hole depletion.

However, a slight shift in the pIR50IRPL compared to IRPL suggests that electrons participating in the IRSL measurement (AIRPL) are only a part of the total electron population. Thus, $m'_h(T)$ (#6) is the more relevant representation of the hole population participating in the IRSL process. Interestingly, both $m_h$ (Figure 5a, b) and $m'_h$ (Figure 5c, d) both show strong overlap with the temperature dependence of IRSL. These data ($m'_h$) indicate that (i) the IRSL pulse anneal curve is governed by the depletion of trapped holes and not the trapped electrons, and (ii) the thermal dependence of trapped electrons is very similar whether or not they are close to the holes IRPL(T) $\approx \Delta$IRPL(T). Thus, of the 4 possible processes (a-d) discussed at the beginning of this section, we can rule out that either b) or c) is responsible for the thermal depletion behavior of the IRSL; this is because the electron population is more stable than the IRSL curve. To distinguish between a) and d) as the relevant process, we examined the relationship between the TL emitted in the region 280-600° C and the subsequent IRSL counts (Figure 6). These data show a negative correlation between IRSL and TL between 300 to 400° C, i.e. the region in which the IRSL signal depletes rapidly. It is to be noted that both the IRSL and TL are measured in the same emission window (blue emission). Since we already know that the principal trap (both IRPL and $\Delta$IRPL) is quite stable up to a temperature of 400° C, the reduction in the IRSL must be arising from depletion of holes consumed during the TL production. These data suggest that the high temperature TL peak must be arising from an electron trap different from the principal trap and the electrons from this trap compete with the holes that are used by the principal trap.

In conclusion, based on the novel PL-OSL system, we are able to infer for the first time that thermal dependence of the IRSL curve can be attributed to process d), i.e., depletion of holes because of competitive recombination. This is a markedly different interpretation of pulse anneal curves which are commonly believed to arise from the thermal erosion of the electrons in the principal trap (e.g., Li and Li, 2011; Murray et al., 2009), or from localized e-h recombination (Jain and Ankjærgaard, 2011). Furthermore, we establish unequivocally that TL and IRSL may not arise from the same electron trap but both the processes use the same hole traps. Thus commonly observed a decrease in the area of the high temperature TL peak due to IR exposure (Murray et al., 2009) must be due to a reduction in the hole population during IR light exposure.

6. Competition in electron transport pathways
During resonant excitation, such as during IRSL, electrons can undertake several different pathways from the excited state: a) tunneling recombination, b) relaxation to the ground state, and/or c) diffusion through the band tail states (temperature-dependent) followed by eventual recombination or retrapping (Jain and Ankjærgaard, 2011; Jain et al., 2012). Furthermore, during, relaxation there may exist a combination between radiative and non-radiative processes leading to the well-known thermal quenching of luminescence in defects by the Mott-Seitz mechanism (Pagonis et al., 2010). A coupled IRPL-OSL system can for the first time allows discrimination between these competitions involved in these different transport/transition pathways.

We examine the dependence of IRPL and IRSL on the measurement (stimulation) temperature from room temperature to 260° C. The measurement protocol is outlined in Table 4. Three aliquots of sample 981010 were first emptied of their natural signal by a high temperature IRSL cleanout. They were then given a laboratory dose of 220 Gy followed by preheating and measurement of IRPL signals at different temperatures. There is no detectable depletion of the signal due to the measurement itself, which makes it possible to do consecutive IRPL measurements at different temperatures without repeated beta irradiation. Several recycling points were introduced in the sequence in order to check that temperature trends are not affected by possible signal depletion during the repeated measurements. In a twin experiment, the same protocol was followed, however, an additional IRSL bleaching at 50° C for 100 s was inserted just before the IRPL measurements. The idea behind this modification was to selectively examine only those electrons \((n_e - n'_e)\) that are distant from hole centers and thus do not participate in the IRSL at 50° C (see section 1); by doing this we deliberately reduce the loss to the recombination centers.

In a similar manner, the stimulation temperature dependence of the IRSL signal was measured (Table 4). The measurement time of IRSL was restricted to 0.02 s per measurement in order to minimize any depletion during the measurement.

The data are plotted in Figure 7 as an Arrhenius plot (Log intensity vs. \(1/k_BT\), where \(k_B\) is the Boltzmann’s constant). The IRSL signal shows the well-known increase with measurement temperature, commonly referred to as thermal assistance. This increase observed mainly above 60° C, is understood to arise from the increased efficiency of transport in the band tail states at higher and higher temperatures (Poolton et al. 2009) leading to more efficient recombination (Jain and Ankjærgaard, 2011). In a simple model, we expect that the IRPL (T) data should mirror the IRSL (T) data since electrons lost to the recombination route through the band tail states must lead to a corresponding decrease in the IRPL signal. Such a trend in IRPL is, however, not observed (Figure 7a). Instead, the following observations can be made regarding the IRPL signal:

1) The decrease in IRPL\(_{955}\) with temperature is faster than IRPL\(_{880}\). This possibly indicates the fact that the IRPL\(_{955}\) center loses electrons more easily than the IRPL\(_{880}\) center, and is the main contributor to the IRSL; this inference is consistent with the data and interpretations based on Figure 2 and 3, where \(\Delta IRPL\) is larger for the 955 emission.

2) The pIR\(_{50}\)IRPL data (empty circles; Figure 7a), i.e. IRPL measured after the IRSL\(_{50}\) measurement, decrease much slower than the IRPL; this is consistent with the model that the decrease in IRPL is due to loss of electrons to the recombination route. Since a significant proportion of charge has already been removed by the IRSL\(_{50}\), the remaining
charge has less likelihood to find recombination centers and therefore likely ends up being re-trapped in the principal trap.

3) IRPL is not a mirror image of IRSL. The increase in IRSL with stimulation temperature is much more rapid than the decrease in IRPL (Figure 7 inset).

It is likely that the decrease in IRPL is a combination of charge loss to the recombination route and intra-defect quenching within the principal trap (Prasad et al., 2017). Intra-defect thermal quenching can be examined using time-resolved IRPL measurements. We repeated the measurements in Table 4 and collected IRPL data for both the 880 and 955 emissions in the time-resolved mode using time-correlated single-photon counting. Figure 8a shows these data for the same temperatures; unlike Prasad et al. (2017) our data is best fitted by a linear sum of two exponential decay functions. The two lifetimes are plotted as a function of measurement temperature in Figure 8b. The dominant lifetime of 20 µs is constant up to about 80° C and then decreases almost linearly to ~12.5 µs until 260° C. The lifetime of the less dominant component remains at ~4 µs up to 100° C and then decreases linearly to ~2.5 µs until 260° C. The net decrease in the lifetime is about 38% for both components. The tenfold drop in the IRPL intensity above 100° C is not consistent with the change in a lifetime, which only decrease by 38%. Instead, the lifetimes data indicate that we are, if at all, only at the beginning of an intra-defect thermal quenching process. This relatively weak dependence of lifetime on temperature probably suggests that the decrease in a lifetime at higher temperatures is not due to intra-defect quenching but due to loss of electrons from the excited state to the band tail states (this is equivalent to a non-radiative competition process). This is possible if electrons are not excited to the excited state but near it; thus, only a factor of electrons are in fact retrapped, and this changes with temperature.

A question then arises is why the decrease is IRPL is not mirrored by an increase in the IRSL signal. We interpret that the difference in the rate of change of IRPL and IRSL is due to a net increase in the number of holes available for recombination. As electrons become more mobile at higher and higher temperatures, there should be an increase in the probability of finding a trapped hole (because of the larger distance traversed by a detrapped electron). Thus, the probability of recombination per detrapped electron increases volumetrically with temperature (greater crystal volumes accessed at higher temperatures. If we divide the IRSL (product of electrons lost and the probability of finding a trapped hole) by the IRPL signal (probability of electron loss), the resultant ratio shows the availability of holes as a function of mean diffusion volume of a detrapped electron, which in turn is a function of the stimulation temperature. These data are plotted in Figure 7b; there is a non-exponential increase per unit energy; the mathematical form of this curve needs to be investigated but it is likely to be a convolution of the temperature-dependent loss of electrons from the excited state and the volume traversed by these detrapped electrons via the band tail states.

7. Electron and hole trapping by ionizing radiation

Finally, we examine how the population of electrons in the principal trap and the holes at the IRSL recombination centers grow by exposure to beta radiation. The measurement sequence for the dose response curves (DRC) for IRPL and IRSL is outlined in Table 5.
The DRCs were measured on three aliquots of sample 981010 whose average values are presented in Figure 9. Figure 9a shows the response of the sensitivity corrected IRPL signals and the IRSL signal. The dose response of the IRPL$_{880}$ is indistinguishable from that of the IRPL$_{955}$ signal. Both IRPL signals reach saturation in dose response slightly faster than the IRSL.

Figure 9b shows the dose response of the $\Delta$IRPL signals, which is also very similar to the response of the IRPL signal; note that IRPL data from Figure 9a is also plotted for comparison. Based on the reasoning in the previous section the dose response of the holes is derived by dividing the IRSL signal by the $\Delta$IRPL signals. These data indicate that there is about a 40% increase in the hole population from the smallest to the highest dose. The holes reach a saturation value much earlier ($\sim 0.5$ kGy) than the electron trap (IRPL or $\Delta$IRPL). Thus ‘hole trap dating’ as suggested in previous work (Li et al., 2013) is not feasible, probably because holes do not seem to be fully reset during a SAR cycle.

One question that arises is whether the dose response is similar for every principal trap, or if there is a systematic variation in the DRC as we approach more and more thermally stable components of the principal trap. To investigate this we examined the DRC of the IRPL$_{880}$ and IRPL$_{955}$ after different preheats ranging from 360° to 480° C. The same protocol was followed as outlined in Table 5, except for the change in thermal treatment after beta irradiation (TL to T° C; T = 360, 390, 420, 450 or 480). These data are plotted in Figures 5e and f for the IRPL$_{880}$ and IRPL$_{995}$, respectively. A linear sum of two exponential is fitted to these data. Figures 5a and b show the remaining electron population after each of these TL treatments. It is observed that there is a tendency for the DRCs to saturate earlier with dose as we access more and more thermally stable sub-populations within the principle trap. The biggest change occurs from no preheat to the preheat scenario (Figures 5e, f). This behavior is consistent with the response of pIR-IRSL signals, which show earlier saturation as a more stable signal is accessed (e.g., Anderson et al., 2012). In the framework of the feldspar nearest neighbor distribution model, these data suggest that it is more difficult to trap pairs with short distances (thermally unstable) than those with large distances. This is expected since trapping an e-h pair in a small volume is probabilistically a rarer event than trapping an electron and hole in a large volume.

4. **Summary and Discussion**

In order to develop the future applications of the OSL/IRSL technique to understand environmental processes such as erosion and transport (Gray et al., 2019), it is imperative that the luminescence kinetics under thermal or optical exposure is fully understood. Based on the coupled PL-OSL system in feldspar, we elucidate here the long-standing unknowns in the luminescence model of feldspar.

We propose a new quantity called $\Delta$IRPL, which reflects the principal traps that participate in the IRSL or OSL process. The very existence of $\Delta$IRPL and change in it after different pre-treatments support the feldspar luminescence model proposed by Jain and Ankjaergaard (2011). Our data indicate that IRSL may be preferentially derived from the principal trap emitting PL at 955 nm (IRPL$_{955}$ center) as against that emitting at 880 nm (IRPL$_{880}$ center). As demonstrated above
AIRPL is a powerful tool to examine individually the behavior of the electron and hole populations due to heating, laboratory irradiation, etc.

The measurements here give a new physical interpretation of the thermal stability of the IRSL signals. Conventional wisdom suggests that the decrease in the IRSL signal due to prior thermal treatment (preheat or thermal bleaching) results due to a decrease in the trapped electron population in the principal trap. We show instead that the electron population is stable up to 400° C (in this sample), a temperature by which about 60-75% of the IRSL is depleted. We show for the first time thermal response of the electrons ($n_e, n'_e$) and the holes participating in the IRSL process ($m_h, m'_h$) individually. Based on the relationship between different signals, we conclude that the thermally-induced decay of the IRSL signal occurs mainly because the IRSL active holes are used up by electrons derived from a different trap (i.e. not the principal trap) that produces the TL peak in the region 300-400° C. In other words, the main part of the IRSL decay curve represents the kinetics of this different electron trap. These unique first insights imply that the fundamental of the kinetic models (Jain et al., 2015; Guralnik et al. 2015b; Li and Li, 2013) need to be revisited in the light of these new data. To arrive at a universal picture, such data need to be measured on many different types of samples. This is especially important for producing robust models for thermochronometry (Guralnik et al., 2015; King et al., 2016; Brown et al., 2017).

The dose response data presented here show, for the first time, the growth of the electrons and holes separately. These data preclude the use of holes for dating as suggested by Li et al. (2013), since it is apparent that holes are not reset during a SAR protocol, and probably not in nature either. We propose a novel mechanism to explain the change in DRC of the trapped electrons a function of preheat temperature, which are reflected in both the IRPL and post IR IRSL data. According to this mechanism based on the nearest neighbor model (Jain and Ankjærgaard, 2011), it becomes increasingly difficult to capture electrons in the principal trap, below a certain threshold, as the e-h distance becomes smaller and smaller. In other words, the capture probability is a product of both the electron capture cross-section of a trap and the distance between that electron trap and its nearest hole. This is reflected as a higher $D_0$ for the less stable (i.e. nearer e-h) population. The difficulty in trapping in a small volume may arise from a combination of the following:

1) The probability of randomly trapping both an electron and a hole in a given volume element is a function of the pre-existing hole density. Based on Huntley (2007), this probability becomes smaller and smaller with a decrease in the nearest neighbor distance (see Figures 1a, 2a of Jain et al, 2012). The relative probability of creating a shorter-distance nearest-neighbor can be defined as:

$$p(r) = \frac{\int_0^r \exp\left(-\frac{4}{3}\pi \rho r^3\right)4\pi \rho r^2 dr}{\int_0^{r_{max}} \exp\left(-\frac{4}{3}\pi \rho r^3\right)4\pi \rho r^2 dr}$$

where $r$ is the distance between the nearest e-h neighbor and $\rho$ is the number density of holes.

2) As a free-electron approaches a principal trap at a few nm distance to a trapped hole, there is a finite probability that this electron instead of filling the electron trap may collide with
the hole trap and recombine with a hole. The electron and hole trapping has to then start again from scratch to create a nearby e-h pair.

The elegance of this model is that it does not invoke different principal traps to explain the variation in the dose response curves across different trapped electron populations. Instead, such a dependence comes naturally from our existing understanding of the existence of localized processes in feldspar. From the IRPL data, we have no suggestion that different sub-populations of the principal trap should have different physical characteristics, such as trap depth or electron capture cross-section. The apparent change in the electron capture probability for different subpopulations of the principal trap arises due to their proximity to the hole centers. This new understanding has important implications for developing a mathematical model of electron trapping which for example is relevant for thermochronometry.

The coupled OSL-PL system also throws light on the fate of the electrons in the band tail states after their release from the principal trap. We discuss that IRSL arises both from a) increased partitioning of electrons to the recombination route (vs the retrapping route) with an increase in measurement temperature above 80° C, and b) greater availability of holes because of an increase in the diffusion volume. This model assumes that electrons that do not recombine are trapped again into the principal trap, which needs to be tested in future studies.

Finally, a comparison between the 880 and 955nm IRPL emissions confirms that there are two different centers (sites) comprising the principal trap. These centers show a very similar radiation-induced growth behavior, as also observed by Kumar et al. (2018), and have indistinguishable relaxation lifetimes. However, they differ in their thermal stability, stimulation temperature dependence and ability to be bleached by IR photons (at different temperatures). These data suggest that it is likely that the principal trap consists of the same defect; however, the mean distance of this trap to the recombination sites is different for the IRPL$_{880}$ and IRPL$_{995}$ centers. Future studies involving high-resolution mapping of IRPL emitting volumes can throw light on possible dependence between micro-structure or compositional variations and their effect on the principal trap.

These physical insights obtained from direct observation of trapped electrons have significantly enriched the feldspar model. The next step is to obtain a universal picture by applying the new techniques developed here to different feldspar samples and develop robust mathematical models for developing areas such as thermochronometry and sediment transport, which currently work on ‘black box’ assumptions.

Conclusions

We develop here a coupled OSL-PL system and demonstrate its unique importance for understanding luminescence recombination pathways involving the metastable states in feldspar. We suggest for the first time new quantities measure changes in trapped electron and hole populations individually. The new insights obtained are:
1) Only a fraction of trapped electrons participate in IRSL.
2) The thermal stability of the IRSL is governed by hole depletion and not by electron depletion.
3) Electron trapping probability in the principal trap is both a function of electron capture cross-section (Coulomb attraction) and its distance to the nearest hole.
4) The volume-dependent probability of finding a hole is a major factor in the IRSL production.

These new insights are critical for the development of exact mathematical models of luminescence phenomena involving metastable states.
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Figure Captions

Figure 1. a) Band diagram showing the OSL (infra-red excitation) and the IRPL process from the principal trap. b) configurational coordinate diagram showing PL generation in the defect responsible for the principal trap. The corresponding excitation and Stokes-shifted emission spectra are shown in c).

Figure 2. a) An IRSL (bottom and left axis) signal and the corresponding change in the intensity of the IRPL signal (right axis) after different time intervals of the IRSL measurement (bottom axis). The net change in the IRPL at the beginning and the end of the IRSL measurement is used to calculate the ΔIRPL. b) correlation between ΔIRPL_880 (left) or ΔIRPL_955 (right) and the IRSL photons emitted during the depletion of the IRPL. Three aliquots were measured from each sample. Individual data points represent one aliquot.

Figure 3. Δ IRPL measured after IR exposures at different temperatures (denoted on the y-axis). IRPL after preheat (200 °C for 60 s) but before the IR50 exposure has been used as the baseline for the calculation. a) and b) show data for the natural dose for ΔIRPL_955 and ΔIRPL_880, respectively. c) and d) show data for the laboratory dose for ΔIRPL_955 and ΔIRPL_880, respectively. The size of the laboratory dose was kept to be the same as the natural dose for each sample. See Table 2 for details. Each data represents the average and standard deviation of 3 aliquots per sample.

Figure 4: ΔIRPL measured after IR exposures at different temperatures (denoted on the y-axis). IRPL after preheat (320 °C for 60 s) but before the IR50 exposure has been used as the baseline for the calculation. a) and b) show data for the laboratory dose for ΔIRPL_955 and ΔIRPL_880, respectively. The size of the laboratory dose was kept to be the same as the natural dose. The difference between Figure 3 (c, d) and Figure 4 is in the preheat temperature after the regeneration dose. Each data represents the average and standard deviation of 3 aliquots per sample.

Figure 5: Pulse-anneal curves (signal vs. preheat temperature) and the dose-response curves (signal vs. beta dose) measured for different signals using three aliquots of sample 981010. See Table 3 for details. a) Preheat dependence of the IRSL, IRPL, pIR50IRPL signals for the 880nm emission. The behavior of holes is calculated using equation 4. B) the same data as a) but for the IRPL signals at 955 nm emission. c) Preheat dependence of the IRSL (same data as in a) and b)), ΔIRPL, and behavior of holes calculated using Equation 6. d) Dose response curve of the IRPL signals remaining after different preheats for the 880 nm emission. e) Dose response curve of the IRPL signals remaining after different preheats for the 955 nm emission.

Figure 6. Correlation between integral TL intensity in the region 280° C to T° C, and the subsequent IRSL signal based on the pulse-anneal data (Table 3). The net TL signal corresponding to the IRSL was calculated from the TL curves (step 3) measured before each IRSL (step 5); this is the difference in TL counts (I) in the two integral regions (I_20-T° C minus I_20-
280° C. T is marked as the temperature against each data point. Inset shows the TL curve measured up to 600° C; the shaded area is the TL the peak used for TL - IRSL comparison.

Figure 7 a) Arrhenius plot of the IRPL, IRSL and pIR50IRPL signals for the different measurement temperatures. See Table 4 for the details. IRPL for both 880 nm and 955 nm emissions are shown. Each signal intensity has been normalized with its intensity at the room temperature. The inset shows the same data vs. the measurement temperature. b) Arrhenius plot of efficiency of finding a hole. The inset shows the same data on a linear temperature scale. Sample 981010 was used for these measurements. Each data point represents the mean and standard deviation from three aliquots of sample 981010.

Figure 8. a) Time-resolved IRPL880 curves for some selected measurement temperatures. Each curve is best fitted to a sum of two exponential decays. Sample 981010 was used for these measurements. b) IRPL lifetime as a function of measurement temperature. Each data point represents the mean and standard deviation from three aliquots of sample 981010.

Figure 9. a) Dose response curves of the sensitivity corrected IRPL880, IRPL955, and IRSL signals. See Table 5 for details. b) Dose response curves of the sensitivity corrected ∆IRPL880, ∆IRPL955 and IRPL880 (repeated from a) for comparison) signals. The dose dependence of holes using Equation 6 is also plotted for the 880 and 955 nm emissions. Each data point represents the mean and standard deviation from three aliquots of sample 981010.
Table 1: Feldspar samples investigated in this study. These samples are extracted from sediments from different geographical regions. (K) denotes K-feldspar and (N) denotes Na-feldspar.

| Sample code (K- or Na- Feldspar) | Site and Location       | Grain size (µm) | Known D_e (Gy) | Reference                                      |
|----------------------------------|-------------------------|-----------------|----------------|-----------------------------------------------|
| 981009 (K)                       | Gammelmark (Denmark)    | 150-250         | 279±11         | Murray and Funder (2003); Buylaert et al. (2012) |
| 981010 (K)                       |                         | 150-250         | 298±12         |                                               |
| 981013 (K)                       |                         | 90-250          | 274±12         |                                               |
| H22553 (K)                       | Sula (Russia)           | 180-250         | 209±11         | Murray et al. (2007); Buylaert et al. (2012)  |
| 072255 (K)                       | Carregueira (Portugal)  | 180-250         | 97±7           | Buylaert et al. (2012)                        |
| 092202 (K)                       | Indre-et-Loire (France) | 180-250         | 158±10         | Aubry et al. (2012); Buylaert et al. (2012)   |
| 092204 (Na)                      | Sinai peninsula (Egypt) | 180-250         | 97±3           | Buylaert et al. (2012)                        |
**Table 2.** Measurement of depletion in IRPL due to preheat and due to IRSL at different temperatures. ‘β’ denotes the heating rate. ‘p’ denotes the holding time (pause) after reaching the desired end-temperature before switching on the light.

| Step no | Measurement | Signal |
|---------|-------------|--------|
| 0       | Prepare naturally irradiated aliquots |        |
| 1a      | IRPL (880 nm) for 5 s | IRPL₀ (880) |
| 1b      | IRPL (955 nm) for 5 s | IRPL₀ (955) |
| 2       | Preheat (200° C) for 60s (β = 5°C.s⁻¹) |        |
| 3a      | IRPL (880 nm) for 5 s | IRPL₄ (880) |
| 3b      | IRPL (955 nm) for 5 s | IRPL₄ (955) |
| 4       | **IRSL at **T°C **for 95 s** (β = 5°C.s⁻¹; p = 5s) | **Bleaching using IR** |
| 5a      | IRPL (880 nm) for 5 s | pIR₁ IRPL (880) |
| 5b      | IRPL (955 nm) for 5 s | pIR₁ IRPL (955) |
| 6       | Repeat steps 3-5 for T=50, 100, 150, 200, 250 |        |
| 7       | IRSL at 290° C for 95 s (β = 5°C.s⁻¹; p = 5s) | **Cleanout** |
| 8a      | IRPL (880 nm) for 5 s | IRPL₈ (880) |
| 8b      | IRPL (955 nm) for 5 s | IRPL₈ (955) |
| 9       | Laboratory irradiation |        |
|         | Repeat steps 1-8 |        |
Table 3. Measurement of pulse-anneal curves. IRPLs ($\lambda$) refer to IRPL (880 nm) followed by IRPL (955 nm). ‘$\beta$’ denotes the heating rate. ‘p’ denotes the holding time (pause) after reaching the desired end-temperature before switching on the light.

| Step no | Measurement | Signal |
|---------|-------------|--------|
| 1       | Beta irradiation 110 Gy |        |
| 2       | IRPLs ($\lambda$) at 20°C for 10 s |        |
| 3       | TL to T° C ($\beta = 10^\circ C.s^{-1}$) |        |
| 4       | IRPLs ($\lambda$) at 20°C for 10 s | $IRPL_\lambda$ |
| 5       | IRSL at 30° C for 100 s ($\beta = 5^\circ C.s^{-1}$; p = 5 s) | $IRSL_T$ |
| 6       | IRPLs ($\lambda$) at 20°C for 10 s | $pIR-IRPL_\lambda$ |
| 7       | IRSL at 290° C for 100 s ($\beta = 5^\circ C.s^{-1}$; p = 5 s) | Cleanout |
| 8       | IRPLs ($\lambda$) at 20°C for 10 s | $IRPL_{bkg}$ |
| 9       | Test dose (td) of 110 Gy |        |
| 10      | IRPLs ($\lambda$) at 20°C for 10 s |        |
| 11      | TL to 250° C ($\beta = 10^\circ C.s^{-1}$) |        |
| 12-16   | repeat steps 4-8 | $IRPL_{td}$; $IRSL_{td}$; $pIR-IRPL_{td}$ |

Repeat the entire cycle (steps 1-16) for T= 50, 80, 100, 120, 140, 160, 180, 200, 220, 240, 260, 280, 300, 320, 340, 360, 380, 400, 420, 440, 460, 480, 500, 520, 540, 560, 580, 600, 100, 200, 300, or 100 °C.
Table 4. Dependence of IRPL and IRSL signals on the measurement temperature. IRPLs ($\lambda$) refer to IRPL (880 nm) followed by IRPL (955 nm). ‘$\beta$’ denotes the heating rate. ‘p’ denotes the holding time (pause) after reaching the desired end-temperature before switching on the light.

### For IRPL

| Step no. | Measurement | Signal |
|----------|-------------|--------|
| 1        | IRSL at 290°C for 95 s ($\beta = 5^\circ\text{C.s}^{-1}$; p = 5 s) | Cleanout |
| 2        | Beta irradiation 220 Gy |  |
| 3        | Preheat (300°C) for 60 s ($\beta = 5^\circ\text{C.s}^{-1}$) |  |
| 4        | No bleaching or IRSL bleaching at 50°C for 100 s |  |
| 5        | IRPLs ($\lambda$) at $T$° C for 10 s; ($\beta = 5^\circ\text{C.s}^{-1}$; pause =15 s) | IRPL$_T$ or pIR-IRPL$_T$ |
|          | Repeat steps 5 and 6 for $T = 20, 40, 60, 80, 20, 100, 120, 140, 160, 80, 180, 200, 240, 260, 80$ |  |
| 6        | IRSL at 290°C for 95 s ($\beta = 5^\circ\text{C.s}^{-1}$; p = 5 s) | Cleanout |
| 7        | IRPLs ($\lambda$) at 20°C for 5 s | IRPL-bkg |

### For IRSL

| Step no. | Measurement | Signal |
|----------|-------------|--------|
| 1        | IRSL at 290°C for 95 s ($\beta = 5^\circ\text{C.s}^{-1}$; p = 5 s) | Cleanout |
| 2        | Beta irradiation 220 Gy |  |
| 3        | Preheat (300°C) for 60 s ($\beta = 5^\circ\text{C.s}^{-1}$) |  |
| 4        | IRSL at $T$° C for 0.02 s; ($\beta = 5^\circ\text{C.s}^{-1}$; pause =15 s) |  |
|          | Repeat steps 4 for $T = 20, 40, 60, 80, 20, 100, 120, 140, 160, 80,180, 200, 220, 240, 80, 260, 280, 300, 80$ |  |
Table 5. Measurement of dose response curves. IRPLs ($\lambda$) refer to IRPL (880 nm) followed by IRPL (955nm). ‘$\beta$’ denotes the heating rate. ‘p’ denotes the holding time (pause) after reaching the desired end-temperature before switching on the light.

| Step no. | Measurement                                         | Signal               |
|----------|-----------------------------------------------------|----------------------|
| 1        | IRSL at 290°C for 95 s ($\beta = 5^\circ \text{C.s}^{-1}$; p = 5s ) | Cleanout             |
| 2        | Beta irradiation (regeneration dose)                |                      |
| 3        | Preheat (320°C) for 60 s ($\beta = 5^\circ \text{C.s}^{-1}$) |                      |
| 4        | IRPLs ($\lambda$) at 20°C for 10 s                  | L$_x$ IRPL           |
| 5        | IRSL bleaching at 50°C for 100s                     | L$_x$ IRSL           |
| 6        | IRPLs ($\lambda$) at 20°C for 10 s                  | L$_x$ pIR-IRPL       |
| 7        | IRSL at 290°C for 95 s ($\beta = 5^\circ \text{C.s}^{-1}$; p = 5s ) | Cleanout             |
| 8        | IRPLs ($\lambda$) at 20°C for 10 s                  | IRPL$_{bkg}$         |
| 9        | Test dose 220 Gy                                    |                      |
| 10       | Repeat steps 3-8 to monitor possible sensitivity changes | T$_x$ IRPL (880); T$_x$ IRSL; T$_x$ pIR-IRPL; IRPL$_{bkg}$ (880) |
Figure 1

(a) Band tail states

ΔE

~ 0.35 eV

~ 7.7 eV

(b) NIR

Stokes shift

~0.05 - 0.15 eV

IRPL

(c) 1033 954 886 827 775 729 nm

Em.

Exc.

Photon energy (eV)
Figure 3

(a) (b) (c) (d)
Figure 4
Figure 5: Pulse anneal curves
Figure 7: stimulation temperature

(a) Normalised Signal

(b) Normalised Signal

\[ \xi \approx \frac{\text{IRSL}}{\text{IRPL}_{880}} \]

\[ \xi \approx \frac{\text{IRSL}}{\text{IRPL}_{955}} \]
Figure 8: Lifetime data

(a) Lifetime data as a function of pulse off-time for different temperatures.

(b) Lifetime data as a function of temperature for different pulse off-times.
Figure 9: Growth curve