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Further investigations into the effect of charge imbalance on luminescence production

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ABSTRACT

Previous experiments and modelling suggest that quartz and feldspar grains receive a net negative charge when irradiated with electrons. Here we used silt-sized grains of quartz and feldspar to investigate the behaviour of luminescence at very high electron doses, when electrostatic effects become possible. Both quartz and feldspar show an increasing luminescence response up to 700 kGy, after which we observe a non-linear decrease in luminescence with dose which eventually stabilises, in contrast to modelling predictions using charge imbalance. The presence of an electric field on the grains is investigated as a possible explanation for the non-linear decrease, using several electron energies. Charge leakage and de-stabilisation of the electron trap at high doses is also discussed.

1. Introduction

Dielectrics are electrical insulators which, when exposed to an electric field, become polarised. They are widely used as electronic components, e.g. in optical storage, or as transistors, and, because of their ability to store charge, they are also of importance in dosimetry. Particularly in the space industry, electrical components may receive high cumulative exposures to ionising radiation during service. When a dielectric is exposed to ionising radiation, charges (electrons and holes) are separated and become available for trapping in metastable states. In dosimetric applications, the amount of trapped charge is then measured, using a variety of methods including Electron Paramagnetic Resonance (EPR) and luminescence.

When using dielectrics in dosimetry or as electronic components, it is crucial that the insulating properties of the material are unaffected by radiation exposure, otherwise there is a risk of damage to the component itself or to the system as a whole. Such damage can occur if the dielectric does not remain charge neutral as a result of its exposure to ionising radiation, but instead begins to build up a net charge. A net charge can result in flash-over events to other components, or even within the dielectric itself (as it becomes locally conductive); such events can result in structural damage [1].

There is considerable evidence in the literature of charge build up during irradiation of dielectrics with electrons, from the fields of scanning electron microscopy (SEM), Auger electron microscopy (AEM), electron probe microanalysis (EPMA), electron spectroscopy chemical analysis (ESCA), secondary ion mass spectrometry (SIMS) and other analytical methods depending on particle irradiation [2]. Gross [3] studied the build-up of charge on borosilicate glass following irradiation with 2 MeV electrons and observed a change in the colour of the glass, corresponding to the creation of colour centres, which extended to a depth of 0.4 cm into the glass, equal to the penetration depth of the incoming electrons. Furthermore, electrical breakdown could be initiated after irradiation by touching the sample with a pointed (metal) conductor; this was accompanied by a flash of light and the creation of a characteristic discharge pattern in a well-defined planar volume parallel to the irradiated surface centred on the point of contact. Gross [3] also observed that breakdown could be initiated several months after irradiation, suggesting that the excess charge was stable on that timescale, this is consistent with observations by Frederiksson and Denisson [4]. Nevertheless, excess charge could be removed by annealing to high temperatures. It was suggested that the stored negative charge gave rise to a compensation charge at the unirradiated sample surface. These observations were further expanded by Gross and Wright [5] who observed charge deposition curves in Plexiglass following irradiation with 3 MeV electrons. These experimental curves confirmed the existence of a charged layer in the dielectric, of thickness equal to the penetration depth of the incident electrons. It is even possible for the...
electrostatic potential of the implanted charge to increase during irradiation until the local field produced is sufficient to divert (or even stop) the incoming particles, producing a defocusing or bending of the beam by the sample [6,7].

In luminescence theory, net charge build-up on the dosimeter is not considered, instead a dosimeter is considered to be essentially charge-neutral and reusable, regardless of dose history (see Ref. [8]). This is especially true when using natural minerals such as quartz and feldspar in luminescence dosimetry; these are exposed to ionising radiation on timescales ranging up to the age of the earth (>10^9 years) at dose rates of a few Gy/ka. Since these minerals may undergo thermal or optical resetting at any time after formation, this can result in absorbed doses of up to several MGy. Although grains of natural quartz and feldspar routinely absorb much higher doses than those used by Gross [3] of ~4 kGy, electrical breakdown has not so far been observed in these materials. This suggests an inconsistency between laboratory experimental observations using a variety of dielectrics and that of luminescence dosimetry using natural minerals.

In other papers [9-11] modelling has been used to investigate whether sand-sized grains remain charge neutral during exposure to particle radiation in natural and laboratory settings, as invariably assumed in luminescence production models. The authors hypothesised two separate outcomes - either excess electrons or excess holes as a result of irradiation; the former was supported by Geant4 modelling of sand-sized quartz grains [9-11]. In both cases, the previously assumed symmetry between conduction and valence band filling is invalid and this is reflected in the trapped charge populations, and even in the presence of direct band-to-band transition.

Autzen et al. [10] and Baly et al. [11] used the output of Geant4 modelling [12] to modify luminescence production models (e.g. Refs. [8,13-18]) and so showed that when excess electrons are present, the hole population will begin to decrease as a result of these unpaired excess electrons, eventually leading to the complete annihilation of all holes in the system. They also showed that excess electrons would result in the luminescence production decreasing with dose; after some peak value was achieved, still higher doses resulted in decreasing luminescence output, until eventually luminescence production ceased altogether.

Autzen et al. [9] experimentally tested the effect of excess electrons on 40–63 μm diameter quartz grains using a Comet EBLab-200 electron beam and showed that after an initial increase with dose, the luminescence response began to decrease linearly. However, extinction of the luminescence response was not achieved by 5 MGy, although all samples showed an initial increase in luminescence with dose, two of the samples (quartz extracted from sensitised Chinese loess and from natural Chinese loess) showed a decrease in luminescence while the third (quartz extracted from Serbian loess) showed no change in luminescence between 1.9 and 5 MGy, see their Fig. 4a [9].

Despite the low resolution of the curves, it seems likely in all three cases that the luminescence did not decrease linearly to zero with dose, as predicted by Autzen et al. [9]; but rather that the luminescence asymptoted towards some finite value. Both Autzen et al. [9] and Autzen et al. [10] only considered the effect excess electrons could have on the trapped hole population; they did not consider other effects of net charge such as electrical breakdown, build-up of an electrical field, or increased conductivity. The generation of an electrical field in particular has important implications; it will decelerate incoming electrons with the result that both dose rate and charge deposition rate will become a function of the dose and charge history of the grain.

In this paper, we expand on the previous experiment with a higher dose resolution to investigate in more detail the nature of the decrease with dose of the luminescence signal and whether the signal asymptotes with dose. We test whether this behaviour is the result of an increasing electric field by using different electron beam energies to investigate the presence and stability of such a field; if the embedding of charge at low electron energy eventually leads to the complete repulsion of electrons, then increasing the energy should allow us to further deposit charge in the crystal or the charge could maybe be removed by heating or optical bleaching. Using feldspars, we test whether any reduction in luminescence results from a depletion of trapped holes or if the electron trap becomes unstable at high doses using Infrared Stimulated Luminescence (IRSL), which tracks recombination, and Infrared Photo-Luminescence (IRPL) [19-21], which tracks electron trap population only. Feldspars are particularly suited to investigations into the separate behaviour of trapped electron and trapped hole populations because of these 2 distinct signals: In addition, the athermal fading rate (of both signals, but particularly the IRSL [22], is a measure of distance between electron traps and recombination centres [23]. IRPL allows us to probe the trapped electron population of the IRSL trap and compare it with the IRSL response as a function of dose. If the IRSL signal behaves similarly to the quartz OSL we would expect to see an initial increase as the electron population builds up and then a decrease as the hole population is reduced and eventually stabilises. As the IRPL probes the trapped electron population without relying on recombination, we would expect this to increase until all electron traps are filled and remain at a constant value. Anomalous fading [22] is believed to be the result of quantum mechanical tunnelling from the ground or excited state of the electron trap to nearby holes [23]. As the trapped populations increase, the average distance between trapped electrons and holes should initially decrease, and we would expect to see an increase in fading rate until all traps are filled. Thereafter, if the hole population is then decreased as a result of combination with excess electrons, we would expect a reduction in fading rate as the electron-hole distance would once again increase.

2. Experimental design

Here we describe experiments intended to expand on previous studies [9] and used to test the hypotheses outlined above.

2.1. Instrumentation

Irradiations and measurements were carried out using:

(i) Riso TL/OSL DA-20 readers each fitted with a calibrated 90Sr/90Y beta source (E = 523 keV) of activity ~1.5 GBq. Grains were mounted as a mono-layer on 0.1 mm thick stainless-steel discs using silicone oil prior to any experimental treatment (including electron beam irradiation). The readers were equipped with 7.5 mm Hoya glass U-340 filters for quartz OSL measurements, 2 mm Schott BG-39 and 3 mm Schott BG-3 for feldspar IRSL measurements, Thorlab RG850 longpass filters and an Edmund Optics 880 nm bandpass filter for 880 nm feldspar IRPL measurements, and 2 Edmund Optics 925 longpass filters and Edmund Optics 950 bandpass filter for 950 nm feldspar IRPL measurements.

(ii) A Comet EBLab-200 electron beam. Electrons are emitted from a hot wire and accelerated through titanium and aluminium windows to give a mono-energetic 100–200 keV beam delivering dose rates at the sample position of 2.5–50 kGy s^{-1}. The stainless-steel discs containing the grains were placed on a tray which moved through the electron beam under a constant air flow to minimise temperature increase.

(iii) A Shimadzu UV-2700 UV-VIS spectrophotometer with a spectral range of 200–900 nm

2.2. Sample preparation

The sample (H28112, see Ref. [24]) was sieved to 40–63 μm before being treated with hydrochloric acid (10%) and hydrogen peroxide (30%) before a brief etch with 10% hydrofluoric acid to remove residual clay grains and clean grain surfaces. Quartz- and feldspar-rich extracts
were separated using aqueous heavy liquid (LST Fastloat) (feldspar \(< 2.56 \text{ g cm}^{-3} \) and 2.62 g cm\(^{-3}\) < quartz) and the quartz-rich extract was etched with 40% HF to remove any remaining feldspar. Finally, the extracts were sieved again to \(>40 \mu\text{m}\) to ensure a controlled grain size fraction.

The quartz sample was then sensitised by heating to 700 °C for 1 h, and giving a 2 kGy gamma dose using \(^{60}\text{Co}\) source. Finally, the quartz was heated to 450 °C for 1 h (Hansen et al., 2015). The natural feldspar sample was simply heated to 550 °C for 1 h (Hansen et al., 2018).

Quartz slices (1 mm thick, 9 mm diameter) were obtained from a cobble of quartz arenite (Eriboll formation, Scotland) and sensitised in a similar manner to the quartz sample to test any change in absorption due to electron beam irradiation (see Figure S4 in Supplementary Material).

2.3. Measurement procedures and signal integration

Quartz and feldspar extracts were measured in different ways and these measurement sequences are described in detail in the coming subsections. Our definition of sensitivity, common to all signals used in these experiments, is the ratio of the average response of an aliquot to a test dose after electron beam treatment to the average response to the same dose before electron beam treatment, i.e.

\[
\text{Sensitivity} = \frac{\sum_{i=1}^{n} T_{\text{IR}}(i)}{\sum_{i=1}^{n} T_{\text{IR}}(i) - T_{\text{prior}}(i)}
\]

(1)

where \(T\) denotes the luminescence response to the test dose and \(i\) is the measurement number as indicated in Table 1 for quartz and IRPL\(_{450}\), IR\(_{50}\), or pIRIR in Table 5 for feldspar.

Known exposures delivering \(~5, ~10, ~50, ~or ~100\) kGy were given in short (ca. 2 s) passes in the Comet EBLab-200 electron beam. The irradiations were repeated on a 10 min cycle to allow both samples and instrument to cool.

2.3.1. Quartz

For all quartz aliquots we used two separate signals; the fast component [25] and the net OSL, summed over 40 s of illumination. The intensity of the fast component was determined using the initial 0.4 s as the signal and the next 0.4 s as the background. For the summed OSL, we subtracted an average of the last 6 s from the entire OSL decay curve before summing all counts.

The stability of the response of the sensitised quartz to the test dose was confirmed, as described by Autzen et al. [9]; Supplementary Material). All aliquots were measured using the protocol shown in Table 1 prior to and after electron beam treatment.

The luminescence response to a dose of 0 Gy (T5) was included to ensure that the OSL signal was fully reset before starting the electron beam irradiations.

2.3.1.1. Measuring response to 200 and 100 keV electron beam. For measuring the response to irradiation with 200 keV electrons (cf [9]), the aliquots were split in 19 groups, each of 12 aliquots. Each group was given a different net exposure to the beam. For the 100 keV irradiations this number was increased to 25 groups, with one irradiation (300 kGy) repeated at the end of the experiment, but over a period of 72 h, instead of the usual 1.5 h, by increasing the pause between individual 100 kGy irradiations from 10 min to 24 h. This was intended to test whether the 10 min pause was sufficient to complete any charge recombination and conduction band emptying, even if all electron traps were full.

2.3.1.2. Measurements of the electron beam doses were performed using the protocol shown in Table 2. After the response to the electron beam dose had been measured, the protocol given in Table 1 was used again, to measure the response to the test dose after electron beam irradiation.

The absorbance spectrum of six solid quartz slices was measured using the spectrophotometer before and after electron beam irradiation with 100 keV electrons, to test any potential change in opacity due to the large doses.

2.3.1.3. Investigations into the presence (and stability) of electric field. A second experiment to investigate the presence and stability of any potential electric field arising from these large irradiations was also carried out using three separate sets of quartz aliquots.

To test for the presence of an electric field, 84 aliquots were measured as described in Table 1, before being given 4 MGy with 100 keV electrons. These aliquots were then split into 7 groups of 12 aliquots, with one group acting as control. Each of the remaining 6 groups was then given, in turn, 500 kGy with 100, 120, 140, 160, 180, or 200 keV electrons. The aliquots were then measured using the protocol described in Tables 2 and 1.

To test whether any potential electric field could be reduced by bleaching the sample and potentially allowing some electrons to leave the crystal, a further 72 aliquots were measured according to Table 1 before being given a 4 MGy dose with 100 keV electrons. The aliquots were then treated using the protocol described in Table 3.

A further 48 aliquots were given 4 MGy with 100 keV electrons before being stored in the dark for up to 5 weeks with measurements (8 aliquots per measurement) being performed once a week to test signal stability using Tables 2 and 1.

Finally, to test the thermal stability of any electric field, 228 aliquots were measured using the protocol described in Table 1 before being given a 4 MGy dose using 100 keV electrons. The samples were then treated using the protocol described in Table 4.

2.3.2. Feldspar

Prior to the electron beam treatment, the response to a dose was measured repeatedly (20 cycles) on a single aliquot to ensure the stability of the response. We observed no change in the sensitivity corrected signal with cycle (Figure S3 in Supplementary Material) and assumed this behaviour applied to all 228 aliquots. The response to a dose before electron beam treatment was then measured using the sequence outlined in Table 5.

Following electron beam irradiations, the aliquots were first measured using the protocol outlined in Table 6, before the response to the test dose was measured again, using the protocol in Table 5.

We used the IRPL remaining after a pIRIR\(_{290}\) measurement as an estimate of background [26] and used the high temperature optical
3.1. 200 keV irradiation of quartz

The quartz 200 keV electron beam irradiations are discussed first, and compared with previously published results [9].

The fast component signal following electron beam irradiation (observation L in Table 2) is shown in Fig. 1a; it decreases monotonically with given dose. This is surprising; the smallest dose increment is 50 kGy, and the fast component is known to saturate at much lower doses than 1 kGy (e.g. 100–200 Gy, [27]). The sensitivity of the fast component decreases in a similar manner (see Fig. 1b); in both cases the rate of decrease becomes much lower at higher doses.

The summed OSL signal from quartz (Fig. 2a) shows a similar behaviour to that shown in Fig. 4a [9]; note they did not present fast component behaviour). Both the luminescence intensity and the sensitivity decrease rapidly at first, but at high doses only slowly, if at all. This is inconsistent with the hypothesis of Autzen et al. [9] that the luminescence response and sensitivity would continue to decrease linearly until luminescence production ceased.

Autzen et al. [10] have formalised the qualitative predictions of Autzen et al. [9] using a combination of radiation transport modelling with the luminescence model of Bailey [8,15,16] and Pagonis et al. [17]. As expected, this quantitative modelling confirms the earlier qualitative predictions, i.e. the hole population is expected to decrease linearly with dose once all electron traps are saturated. Despite this, the predicted decrease in OSL response as a function of dose is non-linear (Fig. 9 in Autzen et al. [10]); at high doses they predict that the OSL will show an increasing rate of decrease with dose, rather than the decreasing rate found shown here (Figs. 1 and 2).

One possible explanation for this disagreement with model predictions could arise from the electrostatic effects of the build-up of a trapped excess charge; with increasing dose, this would lead to an increasing electric field around the target grains. Such a field would decelerate the incoming electron beam (and so reduce the actual dose rate below that expected), until eventually the field was sufficient to prevent the electrons entering the target, reducing the dose rate to zero.

We have calculated the surface potential on small spheres (50 μm diameter; see Figure S2 in Supplementary Material) as theimbalance with dose in a 50 μm diameter spherical grain of 200 kV (i.e. sufficient to completely stop incoming electrons). In practice the dose rate will asymptote to zero as the surface potential increases while excess charge will increase as the electron energy decreases as long as dose is delivered.

If the accelerating potential is reduced, the rate of increase of charge imbalance with dose in a 50 μm diameter spherical grain is further increased (see Figure S2b in Supplementary Material). For instance, if we reduce the accelerating potential to 100 kV, the surface potential should equal the accelerating potential at a dose of only ~550 kGy (rather than at ~4.4 MGy for a 200 keV beam).

3.2. 100 keV irradiation of quartz

From the above, reducing the electron energy is expected to result in a constant luminescence intensity being reached at lower dose. To test this prediction, irradiations were repeated using 100 keV electrons. The smallest dose was reduced to 5 kGy (instead of 50 kGy) in order to investigate the initial behaviour of the luminescence at low dose.

The fast component OSL, shown in Fig. 3a, initially increases for doses up to ~40 kGy, and begins to decrease slowly after about 400 kGy. The sensitivity of the fast component signal and the luminescence sensitivity both appear to become independent of apparent dose. This is in contrast to the 200 keV experiment, where the evidence for independence of dose at high apparent dose is weaker (Fig. 1).

Giving the repeated 300 kGy dose over 72 h (unfilled circle) rather than 1.5 h as in the first irradiation (filled circle), results in both a significantly higher luminescence response (~44%) and a higher

### Table 3

| Step | Procedure | Observation |
|------|-----------|-------------|
| 1    | OSL at 20 °C for 100 s | – |
| 2    | 10 ks pause | – |
| 3    | OSL at 20 °C for 100 s | – |
| 4    | 500 kGy with 100/120/140/160/180/200 keV electron beam treatment | – |
| 5    | Follow Tables 2 and 1. | – |

### Table 4

| Step | Procedure | Observation |
|------|-----------|-------------|
| 1    | Preheat to 180–500 °C, 10 s | – |
| 2    | OSL at 20 °C for 100 s | – |
| 3    | 10 ks pause | – |
| 4    | OSL at 20 °C for 100 s | – |
| 5    | 10 kGy with 100 keV electron beam treatment | – |
| 6    | Follow Tables 2 and 1. | – |

### Table 5

| Step | Prior/After electron beam measurement | Observation |
|------|---------------------------------------|-------------|
| 1    | Preheat to 320 °C, 10 s | – |
| 2    | IRPL (880/955 nm) at 20 °C | – |
| 3    | IRSL at 50 °C, 100 s | – |
| 4    | IRPL (880/955 nm) at 20 °C | – |
| 5    | IRSL at 290 °C, 250 s | – |
| 6    | IRPL (880/955 nm) at 20 °C | – |
| 7    | Blue bleach at 700 °C for 100 s | – |
| 8    | IRPL (880/955 nm) at 20 °C | – |
| 9    | Repeat from 1. once | – |

bleach to reduce the IRPL to a minimum before the next cycle. The temperature for the optical bleach was determined prior to the start of experiments by measuring the reduction in IRPL as a function of temperature (data not shown).

For the IR50 signal, a background, based on the light sum in the last 8 s of stimulation, was subtracted from the light sum from the initial 2 s of stimulation. For the pIRIR50, we used the signal from the initial 5 s, less a background based on the light sum from the last 20 s of stimulation. For all IRPL measurements we took the average of the on-time count rate and used the average count rate remaining after the pIRIR50 as the background signal.

3. Results and discussion

3.1. 200 keV irradiation of quartz

The quartz 200 keV electron beam irradiations are discussed first,
sensitivity for the fast component, although the effect on sensitivity may be smaller (~22%). For the 200 keV irradiations, the fast component response dropped by almost 80% from 50 kGy to 5 MGy, while for the same apparent dose range the fast component OSL from the 100 keV irradiations only drops ~30%. The smaller decrease in luminescence when irradiating with lower electron energy is consistent with the hypothesis of the build up of a surface potential of grain surfaces due to excess charge; because the beam is delivered with a lower energy, the accelerating potential would be reached with a smaller number of excess charges, and so at a higher hole population. In addition, the absorbed dose in Figs. 1–4 is calculated from the dose rate and irradiation time – given the discussion above, this must now be regarded as an apparent dose, rather than a true dose. This also implies that the two dose axes calculated for the two beam energies (100 and 200 keV) are no longer...
The luminescence response could be affected by excess charge that remained after optical stimulation and stable on a timescale of days. This difference in sensitivity behaviour compared to initial luminescence response was less pronounced in the summed luminescence signal and the summed relative sensitivity asymptote to a stable value above 3.5 MGy. The response at 50 kGy is similar to that at 5 MGy (the latter is ~37% lower than the peak intensity at 400 kGy). In contrast, the summed OSL following 200 keV irradiations (Fig. 2a) decreases ~40% from 50 kGy to 5 MGy (and the latter is 57% of the peak intensity at 400 kGy). For the 100 keV irradiations, the summed luminescence response to 300 kGy is 41% larger when the dose was administered over 72 h (Fig. 4a, unfilled circle) rather than 1.5 h (filled circle). However, the repeat sensitivity measurement is the same as for the short irradiation time. The luminescence response could be affected by excess charge that is stable on the timescale of a few hours whereas the sensitivity would only be affected by excess charge remaining after optical stimulation and stable on a timescale of days. This difference in sensitivity behaviour compared to initial luminescence response was less pronounced in the 200 keV experiment, perhaps because the charge was deposited more uniformly in the target grains. This leads us to suggest that the difference is due to charge deposition/location rather than charge recombination.

This set of experiments has served as an expansion of our previous work [9] as we use the same sample and electron beam energy. Importantly, the higher dose resolution now allows us to be confident that the total OSL output does not decrease linearly, as previously hypothesised but appears to asymptote to some finite value at large apparent dose. This is inconsistent with both the qualitative hypothesis of Autzen et al. [9]; that the OSL should linearly decrease to zero with dose, and with the quantitative luminescence modelling predictions of Autzen et al.’s [10]. Fig. 9. There the fast component OSL signal is also predicted to decrease with dose until luminescence is no longer generated (although in this case the decrease is non-linear).

As discussed above, one explanation for this deviation from modelling is electrostatic repulsion of the incoming beam by the build-up of excess negative charge in the grain. This would tend to prevent further deposition of energy (and charge), because incoming electrons would enter the grain with less energy, if indeed they were able to enter the grain at all. In this case the dose axis is no longer an indication of actual absorbed dose but rather expected dose for a neutral target. From the modelling predictions shown in Supplementary Material (Figures S2b and S2d), we would expect a lower incident electron energy to significantly increase the charge imbalance for a given dose. As a result, the asymptote in OSL response to a finite value at high doses would be observed at a lower dose (and a higher OSL signal); the lower energy incident electrons would require less net charge on the grain to repel them and so the decrease in OSL would not be as marked as that of the 200 keV experiment. This is also what is observed here in our experiments with a 100 keV beam (Figs. 3 and 4).

We next attempt to confirm the existence of the build up of excess charge during irradiation, and consider its stability.

3.3. Investigations into the presence (and stability) of an electric field

In the previous sections, we hypothesised that the luminescence response and sensitivity deviate from modelling predictions at higher doses due to the presence of an electric field resulting from the build-up of charge on the grains. If this charge increases sufficiently, the surface potential will eventually equal the accelerating potential and prevent further absorption of energy or charge. If this is the case, irradiating with the lowest energy available (100 keV for our Comet Electron Beam system) until the luminescence response and sensitivity reach their stable state (>3.5 MGy for 100 keV, Figs. 3 and 4) and then continuing the irradiation with increasing electron energies should result in a further reduction of the luminescence response and sensitivity. This reduction is expected because the increased electron energy should be sufficient to overcome the electric field on the grains and so continue charge and energy deposition.

Fig. 5 shows the results of an experiment designed to test this hypothesis, for both the fast component luminescence response (Fig. 5a and b) and for the summed luminescence signal (Fig. 5c and d). First, a 4 MGy dose was delivered at 100 keV, and subsequently a further 500 kGy was delivered at a range of electron beam energies between 100 and 200 keV. All data in Fig. 5a and c are normalised to the response immediately following the apparent 4 MGy dose delivered at 100 keV, to better show any reduction in the luminescence response to a further irradiation. For both the fast component and summed luminescence response, we do not observe a decrease in luminescence response when the energy is kept at 100 keV, rather the response increases by ~20%, and this increase remains across all electron energies up to 200 keV (red circles in Fig. 5). This is surprising - we might have expected from Figs. 2a and 3a that the luminescence response of both the fast component and summed luminescence would remain constant between 4 MGy and 4.5 MGy. However, this observation is consistent with the behaviour of the repeat point in both Figs. 3a and 4a, where we also observed a higher luminescence response when the dose was given over a longer period of time. The 500 kGy irradiations could not be carried out immediately following the 4 MGy but were given 18–24 h later.

The sensitivity was less affected by the delay between irradiations in the earlier experiments (Figs. 3b and 4b) and so we would then expect the sensitivities in Fig. 5b and d to be more consistent with our expectations. We do observe a slight decrease in sensitivity, even when the energy is unchanged from the prior saturating irradiation at 100 keV,
and we then observe a small continuing decrease in sensitivity as the energy is increased (red circles). This may be due to renewed charge deposition, although when considered together with Fig. 5a and c, it is also possible that this reduction is simply a reflection of the possible slight decrease in sensitivity observed in Figs. 1b and 2b, at doses above 3.5 MGy.

The sensitivity data of Fig. 5b and c have not been renormalized to the 4 MGy sensitivity; sensitivities are already expressed relative to the response to a test dose before the treatment of the sample. In the case of the fast component, the sensitivity remains below 1 for all electron energies, indicating that the electron beam irradiations have reduced the response to a test dose. However, the summed luminescence sensitivity remains above 1, showing that more light in total is produced after the electron beam treatment. This may be the result of residual charge storage in traps which are not sufficiently emptied by the protocol in Table 2. This is examined next, by optically bleaching some aliquots between the 4 MGy dose at 100 keV and the subsequent 500 kGy doses at various energies, to test whether an optical bleach would be sufficient to reduce or remove any surface potential. The effect of annealing at various temperatures after the 4 MGy dose administered at 100 keV are shown in Fig. 6 as the response to a 10 kGy dose given with a 100 keV beam. The fast component response (Fig. 6a, black squares) does not appear to change significantly with anneal temperature. Given that the fast component in quartz is known to saturate at much lower doses than those used here (e.g. 100–200 Gy [27], and that the sample was initially heated to 700 °C prior to any later treatment, we would have expected a change with annealing temperature in the presence of a thermally unstable electric field on the grains, i.e. these results are inconsistent with our hypothesis.

The summed luminescence response (Fig. 6a, red circles) does show a decrease with increasing anneal temperature, at least up to about 400 °C, consistent with our hypothesis of a thermally unstable electric field. However, at lower temperatures, deep traps that do not directly contribute to the fast component, would not have been completely emptied by heating. Thus they would retain some fraction of the charge deposited by the prior 4 MGy dose, and the progressive loss of this charge would be superimposed on the response to the 10 kGy dose given after annealing. Thus, only at higher temperatures, when the 4 MGy dose has been completely erased, would the response to the 10 kGy dose dominate. At these higher temperatures, the response to the 10 kGy dose given after annealing does not decrease with temperature.

The sensitivity for both the fast component and summed luminescence (Fig. 6b) decreases with increasing anneal temperature. Although the fast component sensitivity (left axis) always remains below 1, the sensitivity of the summed luminescence (right axis) only approaches 1 -
the sensitivity before electron beam and anneal treatment - at high anneal temperatures. The thermal stability of the fast component appears to have been somewhat reduced (Fig. 7c) by irradiating to 4 MGy (red circles) compared with the unirradiated material (black squares). We would expect to see a fast component that begins to decrease rapidly above 260 °C [27]; this is indeed what is seen for the sample before electron beam irradiation (black squares). After electron beam irradiation, however, both the fast component (red circles) and the OSL sum (blue triangles) decrease continuously from 150 °C, although the slope increases around 250 °C. There is also significant OSL remaining above 325 °C, in contrast to the signal from the unirradiated material. It does appear that, following electron beam irradiation, either the fast component is contaminated by another source of charge, or the stability of the fast component has decreased. This may be because of: i) the

Fig. 6. Sensitivity to a 10 kGy dose given at 100 keV following the 4 MGy dose (100 keV) and a subsequent anneal for 10 s at the temperatures shown. a) Normalised fast component (black squares) and summed OSL (red circles), b) Fast component sensitivity (black squares, left axis) and summed OSL sensitivity (red circles, right axis). Sensitivities calculated using Equation 1, and c) Multi-aliquot pulse anneal curve (sample H28112 after sensitisation): fast component without electron beam irradiation (black squares), fast component after 4 MGy electron beam irradiation (red circles), and summed OSL after 4 MGy electron beam irradiation (blue triangles).

Fig. 7. Aliquots were first given a 4 MGy dose at 100 keV, and then stored for various times before measurement. a) Normalised fast component (black squares) and summed OSL (red circles), b) Fast component sensitivity (black squares, left axis) and summed OSL sensitivity (red circles, right axis).
presence of an electric field within the crystal which reduces the effective trap depth or ii) tunnelling as a result of increased charge density within the crystal. We should also note that the stability of the summed OSL signal is similar to that of the fast component after electron beam irradiation, although the fast component only makes up about 3% of the OSL sum after electron beam irradiation, but almost 33% before electron beam irradiations. This could indicate that either all traps become less thermally stable or that the medium and slow components in this sample originate from the same electron trap as the fast component and that their slower decay is determined by the behaviour of recombination sites.

The stability of any charge imbalance effects has also been investigated by simply storing aliquots at room temperature after giving 4 MGy using the 100 keV beam. This storage results in a decrease in both the fast component signal and the summed luminescence (Fig. 7a, data normalised to the measurement made immediately following the 4 MGy irradiation).

The fast component signal resulting from the 4 MGy dose drops by almost 33% over the course of 5 weeks of storage, while the summed luminescence drops almost 50% over the same time span. This is broadly consistent with the expected thermal decay of the 220 °C TL trap (life time: ~33 days [28]), however, since we did not observe a great reduction in OSL annealing past 220 °C in the unirradiated material (Fig. 7c, black squares) we would not expect the 220 °C TL trap to contribute significantly to the fast component and as such it is more likely that the fast component trap has been made more unstable. The fast component sensitivity and summed OSL sensitivity (Fig. 7b) do not decrease significantly with time which would further indicate that a shallow TL trap is unlikely to be the cause of the decreased OSL as it would have to use up a significant number of holes.

All of these experiments suggest that the deviation from a linear decrease with dose of the luminescence response in Figs. 1a, 2a and 3a, and 4a and the stabilisation at high doses may not be the result of electrostatic repulsion, but rather some other mechanism so far not considered.

Nevertheless, if the change in luminescence response was the result of a reduction in holes and the presence of an electric field (preventing further dosing) we would expect the electron trap populations to follow a saturating exponential, reaching a maximum, stable value at the peak of the luminescence response curves, and thereafter be unaffected by further dosing. This hypothesis can be tested using a combination of IRSL and IRPL in feldspar.

3.4. Feldspar

The behaviour of the IRSL (both IR50 and a pIRIR290, see Table 1) is examined first, to compare with that of the quartz OSL in Figs. 1a and 2a for the 200 keV irradiations. The data are presented in Fig. 8, and both signals show a similar behaviour to that of the summed luminescence from quartz in Fig. 2a, although neither drop below their initial value even at the highest doses. The increase in signal is comparable to that in Fig. 2a, although the peak here is much sharper and the signals decrease more rapidly with increasing dose than was observed for the OSL signal. Above 1 MGy there is no further change in the luminescence response and it is indistinguishable from the response to a 50 kGy dose. While the sensitivities (Fig. 8b and c, respectively) mirror the initial behaviour of the IR50 and pIRIR290 signals, above 1 MGy the sensitivities again increase. The sensitivity immediately after the shortest electron beam irradiation (50 kGy) is reduced compared to that measured before irradiation (by ~50%) and we observe a steady increase in both

Fig. 8. a) IR50 response as a function of irradiation with 200 keV electrons, b) IR50 sensitivity calculated using Eq. 1, c) pIRIR290 response as a function of irradiation with 200 keV electrons, and d) pIRIR290 sensitivity calculated using Equation (1).
sensitivity and luminescence response until the peak around 200 kGy. At this point the sensitivity is 95% of the sensitivity prior to irradiations, and both sensitivity and luminescence response then begin to decrease until 1 MGy.

These observations are consistent with the observations made earlier using the quartz OSL. But in this case, the fading rate can be used to test whether the reduction in luminescence is due to a reduction in the trapped hole population, as predicted by the model of Huntley [23]. Measurements of fading were undertaken, using the protocol described in Table 5, on aliquots with three different dose histories: (i) natural, i.e. bleached and undosed material, and on aliquots which had absorbed (ii) 50 kGy, and (iii) 5 MGy, after the 50 kGy and 5 MGy doses had been measured. All were measured using a 50 Gy dose and test dose, and all (6 aliquots per group) were stored for periods of up to five days. For IR50, fading rates of 6.4 ± 0.6%/decade, 6.5 ± 0.9%/decade, and 6.4 ± 0.9%/decade (all n = 6) were obtained for the natural, 50 kGy and 5 MGy dose groups respectively. The corresponding values for pIRIR200 were 1.29 ± 0.12%/decade, 1.54 ± 0.03%/decade, and 1.69 ± 0.31%/decade (all n = 6). Thus, the predicted change in fading rate with prior dose is not observed in these experiments.

There are two possible explanations for this unexpected result. (i) It is possible that the test dose introduces sufficient holes to support a constant fading rate, but this seems unlikely for such a small dose, if holes and electrons are trapped independently of each other, i.e. are not spatially correlated. We also observe a change in the IRSL sensitivity to a test dose after electron beam irradiation which would not be expected if the system has no memory of the previous treatments. However, if every electron/hole pair are in fact trapped close to each other, then the fading rate would tend to be independent of dose; given that thermal electrons (e.g. a few eV - those that are about to be trapped) have a range of only ~3 nm (Fig. 5 in Ref. [29]), this possibility cannot be dismissed. (ii) The second explanation is that the reduction and stabilisation of the

![Fig. 9. a) IRPL (880 nm emission) response as a function of irradiation dose with 200 keV, b) sensitivity of the IRPL (880 nm emission) calculated using Equation 1, c) IRPL (955 nm emission) response as a function of irradiation dose with 200 keV, d) sensitivity of the IRPL (955 nm emission) calculated using Equation 1, and e) fraction of IRPL (955 nm emission) lost by IR50 measurement in Fig. 9c.](image-url)
luminescence is not due to a reduction in hole population as first hypothesised, but rather due to another mechanism, possibly a reduction in the trapped electron population.

The stability of the electron population as a function of dose can be investigated in this experiment by considering the IRPL observations at 880 nm and 955 nm (Table 5) shown in Fig. 9a and b, respectively. These do not follow the saturating exponential shape predicted by modelling, but rather a pattern similar to that of the IRSL signals.

As previously discussed, we would not have expected these data to show any decrease with dose. IRPL probes the trapped electron population and this is expected to increase until all traps are filled; it should then remain constant with further increase in dose. It is possible that the reduction is due to anomalous fading, however we have shown that there is no dose dependence on the fading rate and IRPL is believed to be less susceptible to fading (see Supplementary Material from Ref. [21]. The fraction of IRPL which is lost by an IR50 measurement appears to be independent of dose (Fig. 9a); this implies that the fading rate must be constant during the electron beam irradiations irrespective of dose and therefore the decrease in IRSL and IRPL cannot be due to fading. This is supported by the observation that the fading rate, measured using a test dose response after the electron beam irradiations, is also independent of prior dose. While the 880 nm emission (Fig. 9a) could be assumed to be reasonably constant with dose, the 955 nm emission shows a much clearer resemblance to the IR50 and pIRR200 as well as the results from quartz (Fig. 2a). Assuming that both emissions are probing the same trap [20], this suggests that the reduction in luminescence response with dose, at least for feldspars, is more likely to be due to a reduction in the trapped electron population rather than the trapped hole population. This could be the result of charge leakage either during irradiation or between irradiations, leading to the reduction of the trapped electron population.

4. Modelling charge leakage during irradiation and stimulation

Charge leakage from insulators during irradiation [30] and storage [4] is a known phenomenon from other fields. Due to the presence of charge in the conduction band during both irradiation and stimulation of the quartz or feldspar grains, it is likely that the materials lose some of their insulating properties and instead act more like conductors. To investigate the possible effects of such a process, we used the luminescence production model of Bailey [8,15,16] with the modifications introduced by Pagonis et al. [17,18] (see Ref. [10], and introduced a loss term in the equation describing the change in conduction band population; the loss rate is set equal to some fraction of the current conduction band population. The deSolve package [31] in R was then used to solve the system of coupled partial differential equations simultaneously for each time step. We simulated the irradiation of quartz from formation, i.e. zero dose, and up to 50 kGy with a 2% excess of electrons and the luminescence response for a range of doses, the results are shown in Fig. 10a and b for the fast component and summed luminescence respectively.

The modelled fast component and summed luminescence show a broadly similar behaviour to that of the observed luminescence for both quartz and feldspars as a function of dose, although the shape of the decrease is slightly different. For the summed OSL, the presence of excess electrons (red line, Fig. 10b) leads to an increased luminescence signal, which may result from having more electrons available for recombination. It is, however, now possible to reach a constant and finite luminescence signal at high dose, something which was previously not observed when modelling with only excess electrons (Autzen et al., submitted). In addition, we were unable to reproduce the results of Fig. 10 if excess electrons were not included (see black lines in Fig. 10); this suggests that excess electrons are essential for the decrease in the luminescence signal, but that their effect at high cumulative dose is eventually balanced by charge leakage. The literature evidence for charge leakage during and after irradiation is ambiguous - Thompson [32] was unable to measure any Thermally Stimulated Conductivity (TSC) greater than the inherent ionic conductivity of quartz, but Gross [3] noted that the conductivity of crystalline quartz is higher during and following irradiation [33]. Further investigations into the conductivity of quartz and feldspar grains during irradiation and stimulation would give insights into charge transport within grains and would possibly also help to determine the ultimate fate of the excess charge predicted by modelling. It should be noted that a non-monotonic OSL has been shown in Al2O3:S by Yukihara et al. [34] and supported by modelling in Pagonis et al. [35] and Chen et al. [36] and reference therein, occurring a much lower doses (<5 kGy). These models do not include charge leakage but instead a competition between radiative and non-radiative recombination centres. Such competition is also included in the model by Bailey [8,15,16]; but we were unable to reproduce our experimental results without including charge imbalance and charge leakage.

5. Conclusion

In this paper, we have expanded on the previous work by Autzen et al. [9] and observed that the luminescence response of quartz at MGy doses using a low energy electron beam does not decrease linearly as expected from modelling of hole concentrations [10,11]. Rather a quasi-stable luminescence response is reached for doses above 3.5 MGy, inconsistent with model predictions of excess electrons. Using IRPL we hypothesise that the behaviour of the luminescence of both quartz and feldspars observed in the electron beam experiments are the result of

Fig. 10. OSL as a function of dose using the energy deposition and luminescence production model of Autzen et al. (submitted) with excess electrons (red line) and without excess electrons (black line), modified to include charge leakage. a) Fast component, b) OSL sum.
charge leakage during irradiation, which is tentatively supported by a modified version of the luminescence production model. This would indicate that natural materials such as quartz and feldspar may have some conducting properties, either during irradiation or as a result of a charge storage or net charge build-up, both of which would have implications for luminescence theory. Further investigations need to be made into how luminescence observations compare with those of breakdown in dielectric as a result of irradiation with charged particles.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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Author statement

M. Autzen conceived the present idea with input from A. Murray, M. Jain and J.-P. Buylaert. The planning, experiments, simulations, and data analysis were performed by M. Autzen. The manuscript was written by M. Autzen with feedback from A. Murray, M. Jain and J.-P. Buylaert. J.-P. Buylaert supervised the project.

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