Ancient TL

Letters

Blue light stimulation and Linearly Modulated Optically Stimulated Luminescence

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We address here issues raised by Huntley (2006) on the use of Linearly Modulated OSL (LM-OSL, Bulur, 1996) and blue light stimulation in OSL measurements, namely 1) CW-OSL vs. LM-OSL, and the significance of 2) wavelength shift during LM-OSL, and 3) Raman scattering. We restrict our discussion mainly to quartz as both LM-OSL and blue light stimulation have been used widely for this dosimeter; nonetheless, feldspars are discussed when required.

1. CW-OSL and LM-OSL analysis

We agree with Huntley (2006) that CW-OSL contains the same physical information as LM-OSL. However, we argue that LM-OSL may be better suited for curve fitting analysis for extraction of trap parameters.

We first summarise evidence that the assumptions for the arithmetically transformed CW-OSL data to be consistent with true LM-OSL (Huntley, 2006) are indeed met for quartz; a transformation is achieved by scaling of both the luminescence and the time axis in the CW-OSL so as to obtain peak shaped data that are similar to LM-OSL (e.g. Bulur, 2000; Poolton et al., 2003). We then briefly discuss the problems inherent in the mathematical analysis of both CW-OSL and transformed CW-OSL data.

(i) Is there an apparent change in the measured photoionisation cross-section of quartz with the excitation light intensity ?

Such an effect cannot be determined conclusively from OSL measurement alone as the signal decay depends on both trapped charge eviction and its subsequent retrapping and/or recombination. However, for a first order system (one trap, one centre and negligible retrapping) a constancy of photoionisation cross-section will imply a linear change in OSL decay rate with the excitation light intensity. This relationship has been tested for blue light stimulation of quartz (Bulur et al., 2001). No dependence of photoionisation cross-section on excitation intensity was observed up to 50 mW.cm^{-2}.

The above can also be tested by comparing LM-OSL with a linearly transformed CW-OSL. Close correspondence between such curves has been observed for quartz (Jain et al., 2003, Poolton et al., 2003).

Alternatively, one can compare the decay rates obtained from CW-OSL and LM-OSL for the same maximum excitation intensity (Kuhns et al. 2000)., The data of Kuhns et al. (2000), obtained using green light emitting diodes (LEDs), apparently suggest that there may be a difference between cross-sections derived by applying first-order solutions to CW-OSL and LM-OSL data. Jain et al. (2007) point out that the difference observed by Kuhns et al. (2000) may have arisen from the presence of a peak-shaped isothermal TL (ITL) signal underlying both the CW-OSL and LM-OSL signals due to an insufficient preheat (162°C) followed by an elevated temperature measurement (127°C). This isothermal signal is observed as the LM-OSL curves not starting from zero for near zero stimulation light intensity, and an apparent fast component (in fact peak shaped ITL: see Jain et al., 2007) observed in the LM-OSL but not in the CW-OSL signal. Such a signal can be observed when holding the aliquot at the same temperature without shining light onto it.

It is worth noting that, unlike quartz, NaCl does not show a linear change in decay rate with blue light stimulation intensity (Bulur et al., 2001).

(ii) Evidence for non first-order kinetics in quartz OSL?

In addition to the evidence presented above, i.e. a good agreement between CW-OSL and LM-OSL (blue light stimulation at or above 125°C), the dose response of LM-OSL suggests that the fast, medium, and two slow components in quartz follow first-order kinetics (Singarayer, 2002). The decay rate (or peak position) of these components did not depend on the dose (i.e. trapped charge concentration), and, moreover, their dose response curve could be well described by a single saturating exponential. The fast

OSL component of quartz measured using IR stimulation, resulting in an orders of magnitude lower detrapping rate compared to that for blue light stimulation, also shows first order decay (Singarayer and Bailey, 2003; Jain et al., 2005).

The response after thermal annealing is observed to be more complex (i.e. non first-order) for the medium and slow components; but this may partly reflect thermal lag during sample heating.

One can thus suggest that there are insufficient grounds to invoke non first-order kinetics for the dominant components in quartz OSL as long as stimulation temperatures are sufficient to prevent known competition from the 110 °C TL traps (Murray and Wintle, 1997).

(iii) How does analysis of LM-OSL compare with that for CW-OSL ?

Since the main OSL components in quartz behave in a first-order manner, it can be inferred that the physical separation of the linearly superposed components in the LM-OSL and CW-OSL signals will be the same. This can be shown easily if one considers the change in trapped electrons per incident photon (instead of per unit time as is usually done). Thus, for first order:

$$-\frac{dn}{d\Phi} = \sigma.n \qquad \text{Eqn 1}$$

where n is the trapped electron concentration, Φ defines the number of excitation photons per unit area (fluence), and σ the photoionisation cross-section. The variation in n (from n_0 to n) with photon fluence Φ can then be described as:

$$n = n_0 \exp(-\sigma.\Phi)$$

If there are two components X and Y, then

$$\frac{n_X}{n_Y} = \frac{n_{X0}}{n_{Y0}} \exp\left[(\sigma_Y - \sigma_X)\Phi\right]$$

For a given OSL measurement, n_{X0}/n_{Y0} and $(\sigma_Y - \sigma_X)$ are constant; therefore, for a given photon fluence the ratio of the light output from any two components will be constant, no matter how that fluence was achieved in time (assuming that Eqn. 1 is true as argued earlier). In the time domain, however, different shapes of luminescence intensity can be

achieved by defining the time dependence of fluence, or more specifically the fluence-rate or flux $(= d\Phi/dt)$, i.e., $d\Phi/dt = f(t)$, but the actual overlap of the signals will not differ for a given fluence. For a better measurement of one component in the presence of another, the difference in cross-sections $(\sigma_Y - \sigma_X)$ needs to be increased; this can be achieved using different stimulation wavelengths and/or temperatures.

Thus, there is no extra physical information in an LM-OSL signal (or any other signal obtained by changing the photon flux through time) than in a CW-OSL signal and, as discussed above, a transformation of CW-OSL to provide an output with peaks should give the same visual information as LM-OSL.

One can also ask whether there is any fundamental advantage in analysis of LM-OSL as compared to the transformed CW-OSL.

Analysis of exponential decays is a mathematically ill-posed problem (see review by Istratov and Vyvenko, 1999). An experimentally determined OSL curve with superposition of first order components can be defined as:

$$f_{\exp}(t) = \sum_{i=1}^{n} A_i \exp(-b_i t) + B + \xi(t)$$

where A_i and b_i are the amplitude and decay constants of n discrete components in the transient (e.g. CW-OSL signal). B≥0 is a baseline offset and $\xi(t)$ is a noise component. A more general case can be defined using a spectral function g(b) for a continuous trap distribution; this can be reduced to a sum of n delta functions for discrete traps.

In the analysis of first-order OSL (e.g. quartz) the purpose of such multi-component analysis is to determine *A* and *b* as these quantities give information on the relative concentration and photoionisation cross-sections of each trap. However, there is a fundamental limit to the maximum resolution obtainable by such analysis. Two or more exponential decays can be derived from a transient (OSL decay curve) only if the ratio of their decay constants is greater than the resolution limit.

It remains to be investigated mathematically if analysis of LM-OSL is any less 'ill-posed' than the analysis of CW-OSL. However, it can be shown that analysis of LM-OSL should be better than that of the transformed CW-OSL. This is because the presence of error (noise) in the data further narrows the resolution limit. Noise $\xi(t)$ leads to a family of g(b)

out of which there is only one true solution (Istratov and Vyvenko, 1999). Thus, the resolution of any transformed CW-OSL data to peak shape will be poorer than LM-OSL because of error propagation inherent in the transformation.

Similarly, the actual derivation of trap parameters from the OSL data is generally achieved by non-linear least squares analysis (e.g. Levenberg - Marquardt algorithm). We believe that such analysis is more robust for multiple peaks (LM-OSL) than for multiple exponentials (CW-OSL) and, as stated in the previous paragraph, the fitting of LM-OSL will be superior to the fitting of transformed CW-OSL because of noise propagation in the latter. We, therefore, think that LM-OSL may perhaps be the most suitable method for signal analysis.

(iv) Time economy and the 'background' in LM-OSL and CW-OSL

CW-OSL gives a most time efficient measurement of the signal. However, for the same final fluence LM-OSL takes only twice as long as CW-OSL.

If no incident scattered light is detected, then the background in the CW-OSL and LM-OSL, will be almost constant with time, while it will increase linearly in the corresponding transformed CW-OSL. If there is some light breakthrough, then the background will increase linearly in the LM-OSL also. In either case the background can be measured and subtracted from the data; this is strongly recommended.

2. Does any wavelength shift during stimulation significantly affect the LM-OSL analysis?

Huntley (2006) mentions that 'excitation cross-section is exponentially dependent on the photon energy'. Presumably the author does not mean this literally as such a dependence is physically not possible. The cross-section for deep traps is likely to have a maximum as a function of photon energy (e.g. Lucovsky, 1965, Jaros, 1977). For some part of the photon energy range, the function may approximate to an exponential decrease or an exponential increase.

It is known that the LED spectrum changes slightly during use. However, this has not been documented before for the blue LEDs in the Risø reader. We present here the measured spectra for blue light stimulation as the intensity was ramped from 0 to 50 mW.cm^{-2} in 600 s. Instantaneous measurements were made every sixtieth second. It is seen that a) there is no change in the shape of the spectra, and b) the peak

wavelength decreases rapidly by about 3 nm in the first 10 mW.cm^{-2}, and then decreases more slowly by about 3 nm from 10 to 50 mW.cm^{-2} (Fig. 1) The total change in the peak wavelength is about 6 nm (Δ E = 0.03 eV).
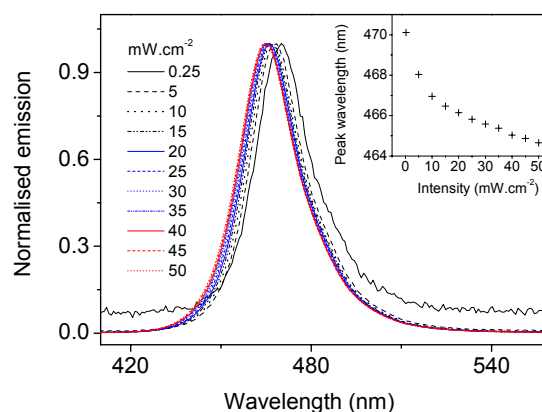

Figure 1: *Blue LED (NICHIA NSPB 500S) emission spectra measured during linear ramping from 0 to 50 mW.cm^{-2} in 600 s. The emission is achieved using four blue LED clusters in the Risø stimulation head, with each cluster consisting of seven LEDs and a 2.5 mm thick Schott GG-420 at the front. The spectra were recorded using a symmetrical crossed Czerny-Turner imaging spectrometer with a focal length of 101 mm, slit width of 25 microns, a ruled grating with a density of 300 lines/mm. The spectrometer, a QE65000 from Ocean Optics, is equipped with a Hamamatsu S7031-1006 FFT-CCD back-thinned detector.*

The fast and the medium OSL components are removed very quickly; under 600 s stimulation from the blue LEDs, they would be removed before the intensity reaches 10 mW.cm^{-2} (shift < 3 nm). For slower components a maximum shift of 6 nm can be expected during stimulation; the effective shift is more likely to be <3 nm because little stimulation of the components occurs below 10 mW.cm^{-2}. Such small shifts in excitation wavelength could cause < 5% variation in fast and medium component cross-sections (based on data in Singarayer, 2002). However the blue LED spectrum is rather broad (FWHM = 30 nm), and effects of shifts of the order of few nanometers are not likely to resolved in the experimentally obtained cross-sections.

We conclude that slight wavelength shift during LM-OSL using Risø reader configuration does not invalidate the analysis. A wavelength shift will also occur in CW-OSL as the diodes heat up during stimulation. In any case, it may be more appropriate

to use a spectral function of decay constants (see section 1) rather than discrete values in CW-OSL decay shape analysis, since the excitation spectrum is broad.

3. Is there a significant presence of Raman scattered photons in blue light stimulated luminescence ?

Raman scattering is an inelastic scattering process. The scattered photon can have either higher (anti-Stokes) or lower energy (Stokes) than the incident photon; this energy difference equates to the differences of the vibrational and rotational energy-levels of the molecule. In crystals, only specific photons are allowed by the lattice structure, so Raman scattering can only appear at certain frequencies.

Raman scattering is a rare event with a typical efficiency of 10^{-6} to 10^{-7} (Böer, 1990, page 413). At room temperature, Raman scattering in the anti-Stokes mode is generally much weaker than that in the Stokes mode. As a result, the main difficulty of Raman spectroscopy is separating the weak inelastic scattered light from the intense Rayleigh scattered light - even with laser stimulation one has to use holographic diffraction gratings and multiple dispersion stages or Raman notch filters to achieve an appropriate degree of rejection of laser light.

The issue for discussion here is whether there occurs a significant background in the anti-Stokes measurement from Raman scattering during blue light stimulation. Huntley (2006) states that 'for this reason I favour the use of green LEDs until someone proves that Raman scattering of blue photons by quartz is not significant'. No doubt there will be some Raman scattered photons from the dosimeter and the system components when stimulated not just with blue light but also with yellow, green, red etc., since Raman scattering, unlike fluorescence, can occur at any wavelength below the resonance wavelength (a special case is Resonant Raman Scattering). Moreover, the efficiency of this process is strongly dependent on the frequency of the excitation light; for example, blue light will cause more scattering than green or red light.

However, the important question is whether these scattered photons enter our UV detection window (Hoya U340) and is the intensity sufficient to be of any significance in our OSL measurements. We examine this question both theoretically and experimentally. The focus of this examination is blue light stimulation (470±30 nm and Schott GG-420 filter) in conjunction with UV detection using a Hoya

U340 filter (Bøtter-Jensen et al., 1999) as this is the most commonly used configuration for blue light stimulated luminescence from quartz and feldspar (for example, see any volume of the last three LED conference proceedings).

(i) Theoretical considerations

An important characteristic of Raman scattered light is that it is frequency-shifted i.e. with respect to the excitation frequency, but the magnitude of the shift is independent of the excitation frequency; the shift is constant in energy or frequency (or wave number). Therefore in wavelength units, the anti-Stokes photons move closer to the stimulation light with a decrease in the stimulation wavelength. For example, if we take an arbitrary Raman shift of 1200 cm^{-1}, then the anti-Stokes scattered photon will be at 489 nm for stimulation at 520 nm ($\Delta\lambda$= 31 nm), 445 nm at 470 nm ($\Delta\lambda$= 25nm), and 382 nm at 400 nm ($\Delta\lambda$= 18 nm). Thus, although, the intensity of the scattered light increases strongly, the wavelength of the scattered light moves closer and closer to that of the incident light for more energetic excitations. Therefore the problem of rejection of Raman scattered photons, if significant, may not be as bad as it may appear; various sharp edge-filters are available to achieve this.

Raman scattering from feldspars

Huntley et al. (1989, Figure 2) ascribe an anti-Stokes Raman origin to a broad, featureless, rising signal between 550 to 600 nm after laser stimulation at 632.8 nm (He-Ne laser, 10 $mW.cm^{-2}$) in their study of OSL emission spectra of feldspars. This signal did not show any decay between 100 and 400 s stimulation, and was, therefore, interpreted to arise from Raman scattering from feldspars. However, *the spectrum of this signal typically lacks any characteristic Raman peaks.* Other possible origins for this signal were overlooked in the paper. For example, the emission can arise from a very slowly decaying OSL signal (a measurement of thermally zeroed sample would have shown that), or scattered light from the system (a blank measurement would have clarified that), or quite simply an instrumental error (e.g. parasitic laser light). The argument for Raman scattering is not supported. Raman scattering vs. OSL origin can be checked from the temperature, time (relaxation) and/or wavelength dependence of the signal, as well as a comparison of Stokes and Anti-Stokes emissions.

Even if one were to assume that the origin of the broad rising signal with wavelength limit of 550 nm (for 632.8 nm excitation) is Raman scattering (Figure

2 of Huntley et al., 1989), the implications for blue light stimulation are not so severe. For example, based on this limit, the anti-Stokes Raman scattered photons will not occur at wavelengths smaller than 420 nm for excitation at 470 nm (excitation peak), and wavelengths smaller than 400 nm for excitation at 440 nm (higher energy side of the excitation spectrum; see figure 1).

Raman scattering from quartz

Several Raman spectra are available for SiO_2 in both amorphous (silica glass) and crystalline phases (alpha and beta quartz) for different temperatures and pressures. Raman spectra of both these materials show well defined peaks. For example, silica glass at 1 bar pressure is characterised by a relatively strong diffuse band at 440 cm^{-1} with two relatively sharp bands at 492 and 605 cm^{-1}. There are very weak features at 1060 and 1190 cm^{-1} (Hemley et al., 1986). In the case of crystalline α quartz, there are several strong peaks between 100 to 450 cm^{-1} and relatively weak peaks thereafter (Fries and Claus, 1973). Scott and Porto (1967) examined the Raman spectrum of quartz excited at 488 nm (80 mW). No mention of any continuum is made by these authors. Similarly, Chio et al. (2003) have examined the Raman spectra of alpha quartz grains of various sizes. The Stokes and anti-Stokes spectra between 400 and 600 cm^{-1} recorded with a source excitation of 488 nm at 25 and 150 mW do not show any sign of a continuum background on either side. (Fig. 1 and Figs. 9 & 10).

We have calculated the anti-Stokes Raman photon spectrum for blue LED stimulation (470±30 nm, 50 mW.cm^{-2}) using an efficiency of 10^{-7} and a Raman shift of 450 cm^{-1} (Fig. 2a). We chose this wave number as the limit of the relatively strong Raman peaks from α quartz (Fries and Claus, 1973). Fig. 2b shows that most of the Raman scattered photons will be swamped by the broad spectrum of the blue diodes, and that they do not pose any apparent problem for detection below 400 nm. The scattering because of other strong Raman modes below 450cm^{-1} in quartz will be intermediate between the two cases presented in Fig. 2. (This is only a crude demonstration to show that the effect is not significant - the actual Raman spectra will be somewhat skewed since the efficiency varies strongly with the frequency of the excitation photons. A further simplification was made by making a trivial (for this purpose) assumption there is no broadening of the emission line).

A variety of short-pass filters are available with OD > 6 in the blocking range (that is a reduction by >10^{6}); these can allow easy rejection of any Raman photons in the detection window.
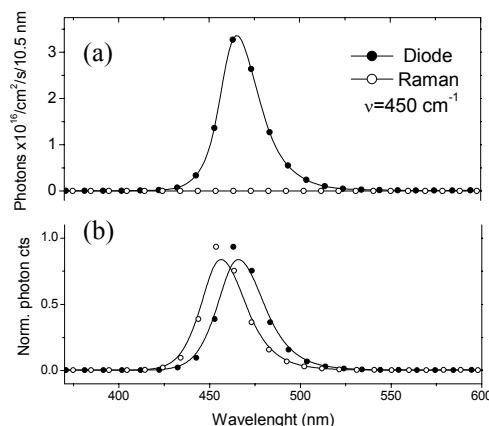

Figure 2: *a) Measured blue light photon spectrum (derived from figure 1) and the calculated Raman scattering spectrum (for assumed single emission line and an efficiency of 10^{-7} at each excitation wavelength) using a Raman shift of 450 cm^{-1} for quartz. The photon flux was calculated for an integral intensity of 50 mW.cm^{-2}. b) Data from a) plotted after normalisation by the peak counts.*

To take a different example, we refer to the quartz pulsed OSL measured by Denby et al. (2006) and Tsukamoto et al. (2007) using the same blue LEDs. The rise and fall time of the signal are adequately described by a single lifetime of about 40 µs; this number was in good agreement with the values published using green light (525 nm) stimulation (see Chithambo and Galloway, 2000). If Raman scattering were significant it would have affected the analysis of the rise time data (i.e. 'light on' signal) but not the 'light off' signal. This is because Raman scattering is almost instantaneous (e.g. picosecond or shorter time scales), while radiative OSL recombination occurs on microsecond time scales. Similarly, if Raman scattering emission was overlapping with the broad OSL emission then the problem may be more serious for blue light than for green light. Good agreement between the rise and fall time constants, and the similarity of lifetimes for the radiative relaxation using blue and green light suggests that Raman scattered photons in the detection window, if any, are not likely to be important.

Excitation of the quartz grains at 470 nm (excitation peak) and observation at 380 nm (emission peak) corresponds to an anti-Stokes shift of 5040 cm^{-1}. ***We do not expect any background due to Raman scattering at this wavelength***.

In summary, the above considerations are sufficient to discount any significant background due to Raman

scattering in the blue OSL from quartz or feldspars in the defined measurement configuration. Nonetheless, we test this by direct measurement from the substrate, and quartz and feldspar samples.

(ii) Experimental data using the blue LEDs in the Risø reader

We measured scattered light from blue light stimulation (LEDs at 470 ±30 nm, 50mW.cm^{-2}; + Schott GG-420 filter; see Bøtter-Jensen et al., 1999) in the Risø TL-DA15 reader using an empty stainless steel cup at various temperatures. Measurement was made using a photomultiplier tube placed over a 7.5 mm thick, broad band-pass filter Hoya U340. The measured count rate changed from ~100 s^{-1} to ~200 s^{-1} when the light was switched on at room temperature (Fig. 3a). This increase may be due to Rayleigh and/or Raman scattered photons from the reader and the disc into the detector. No detectable increase in the light intensity was observed by increasing the temperature of the discs from RT to 250°C (Fig. 3a). This implies that a) the contribution of light from the stainless steel cup alone is very small, or b) the detected light is not of Raman origin, or c) a stainless steel cup does not show Raman scattering (see e.g. Melgarejo et al., 2000).

Irrespective of the exact mechanism, one can conclude that background contribution from the reader and the sample substrate is insignificant compared to the OSL signal from quartz, and that it is independent of the measurement temperature.

We then tested for any scattered photons from quartz and feldspar grains from a sediment sample (972505). These grains were heated at 700°C for 1 hour to remove as much trapped charge as possible. Subsequently the grains were placed in stainless steel cups and OSL measured at different temperatures. The results for 125°C stimulation are shown in Fig. 3b. The count rate when the light is switched on is similar to that observed from the blank cup (Fig. 3a). No significant variation in the count rate was observed for stimulation temperatures between 50 and 200°C (data not shown) suggesting that the observed counts are not from Raman scattering. The OSL after 1 Gy dose and preheat to 260°C for 10 s from the same aliquots is shown in Fig. 3c together with the signal from unirradiated heated quartz (taken from Fig. 3b). The difference in the initial signal from the irradiated and the unirradiated heated aliquots is about three to four orders of magnitude.
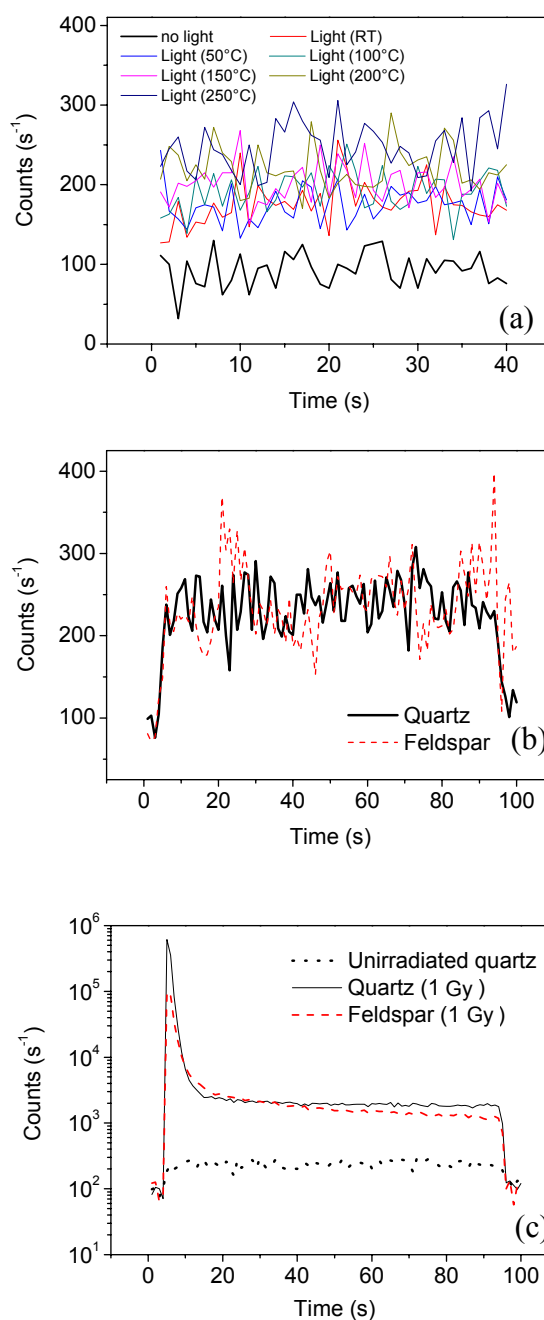

Figure 3: *a) Counts detected from a blank stainless steel cup at different temperatures (RT = room temperature) with or without blue light stimulation (470 ± 30 nm). b) Counts obtained from a quartz and a feldspar aliquot (sediment sample 972505) during blue light excitation. The grains were previously heated at 700°C for one hour to remove trapped charge. c) OSL response from the same aliquots after a 1 Gy dose and preheat for 10 s at 260°C. All measurements are made in the Risø TL-DA15 reader.*

We conclude that our experimental data shows excellent agreement with our theoretical reasoning that Raman scattering will not be significant for quartz and feldspar when using blue LEDs in the conventional Risø reader measurement configuration.

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Response to Jain and Lindvold

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Constant vs varying excitation intensity
As I pointed out, data taken with constant excitation can be transformed into data that would be obtained using excitation that increased linearly with time, provided certain conditions apply. One test that the conditions apply is a suitable comparison of data taken with both methods, and I gave a reference to an example of a test that failed. Jain and Lindvold refer to two examples where they state that correspondence was observed. In the first, Jain et al. (2003) state "The results showed a good match between the two for the samples reported here (data not shown)"; what we need to know is whether or not the matches were within experimental error; if not, the conditions referred to above were not satisfied. In the second example, that of Poolton et al. (2003), three samples were analyzed using a total of 14 fitting parameters, of which only seven are listed in Table 1. Comparisons of three of the parameters obtained using the two methods are in clear statistical disagreement; it may well be that the two largest disagreements (over 30 %) are the result of non-linearity of the PM tube as suggested, but that is not proven. For two other parameters one cannot say whether or not there is statistical agreement because of the way the figures are presented. No comparison is provided for the remaining parameters. Thus neither paper makes a suitable test for the thesis.

The example I gave of a clear disagreement was that of Kuhns et al. (2000). Jain and Lindvold suggest that this was the result of the authors unwittingly measuring thermoluminescence. I feel very uncomfortable with this suggestion; it implies the authors had not done the proper control tests, and without any evidence from the authors this is unwarranted.

Jain and Lindvold suggest that analysis of transformed data taken with constant excitation will lead to a poorer result than analysis of data taken with excitation that increases linearly with time, because of noise in the data. I do not understand this and would expect the reverse to be the case. The crucial part of the data is that near the start of excitation; for constant excitation the signal to noise ratio will normally be quite large, and decreasing with time. When the excitation linearly increases with time, initially the noise will dominate because the signal starts at zero and increases linearly with time; as time progresses the signal to noise ratio will eventually become comparable to that at constant excitation.

In short, Jain and Lindvold do not establish that the use of a linearly increasing excitation intensity is better than or even as good as the use of a constant excitation intensity. It would seem that a comprehensive study is needed to establish which method is best, or, perhaps, that the two methods do give different results.

Raman Scattering
There are two issues here, our interpretation of certain data as due to Raman scattering and whether or not this may be significant with the use of blue light-emitting diodes.

Jain and Lindvold dispute our interpretation of what we called the "Raman continuum", a spectrum for which the intensity decreases exponentially with energy away from the energy of the excitation photons. Their main argument is that our spectrum "lacks any characteristic Raman peaks". This is not a valid argument since no Raman lines are expected in the range shown in Huntley et al. (1989, Fig.5). Further, Jain and Lindvold appear not to understand that an experimental physicist's greatest fear is that he or she is not measuring what he or she thinks he or she is measuring, otherwise we would not have been also criticized for not having done a variety of tests listed. This criticism is thus also not valid. We were in the habit of doing many control experiments, including most or all of those suggested by Jain and Lindvold, to make sure that we knew what we were measuring; the results of these experiments were usually not reported in the publications. One of these, the energy dependence, Jain and Lindvold could have checked, as we did, from the data shown in Fig. 5; it is about right (the intensity should change a factor of about e per 0.025 eV at room temperature). The exponential continuum has been observed previously in feldspars, along with the Raman lines; see for example figures 536 and 537 in Deer, Howie and Zussman (2001) or Figs. 11.2a and 11.2b in Smith and Brown (1988), and these also show about the expected energy dependence.

One of our first control experiments was to measure spectra from 2.14 eV to 2.31 eV using a 1.96 eV laser (He-Ne) for plasticine and Apiezon-Q (a black versatile mouldable firm reusable sealing compound); both of these showed an exponential energy dependence which initially puzzled us. These data
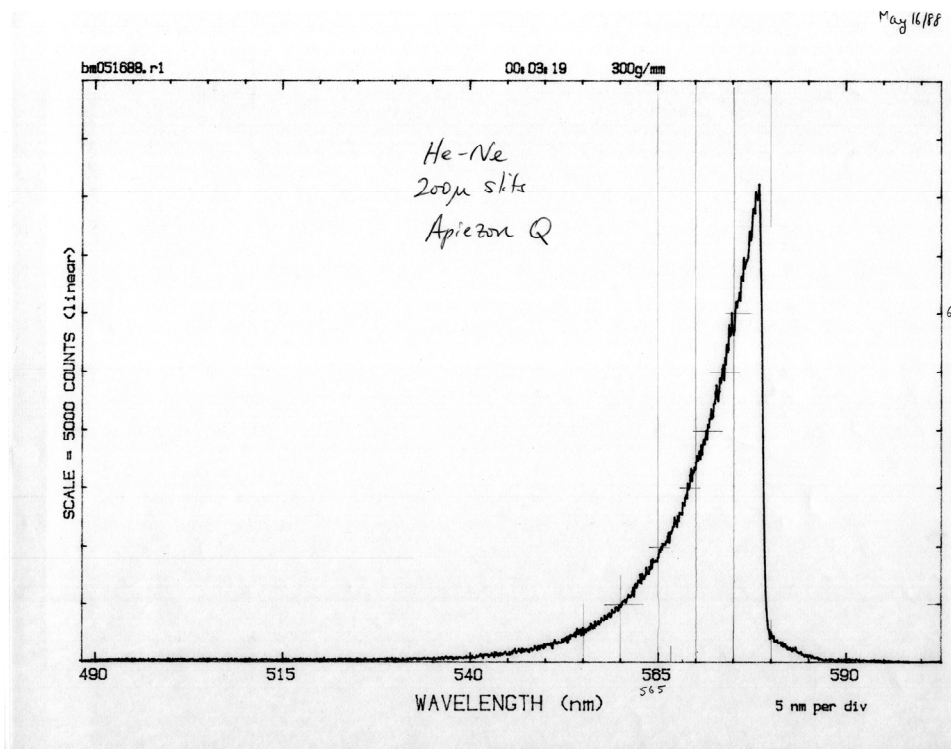
Figure 1: *Intensity vs wavelength for Raman scattering from Apiezon-Q using 1.96 eV (633 nm) excitation from a He-Ne laser. The spectrometer cut-off was at 580 nm*
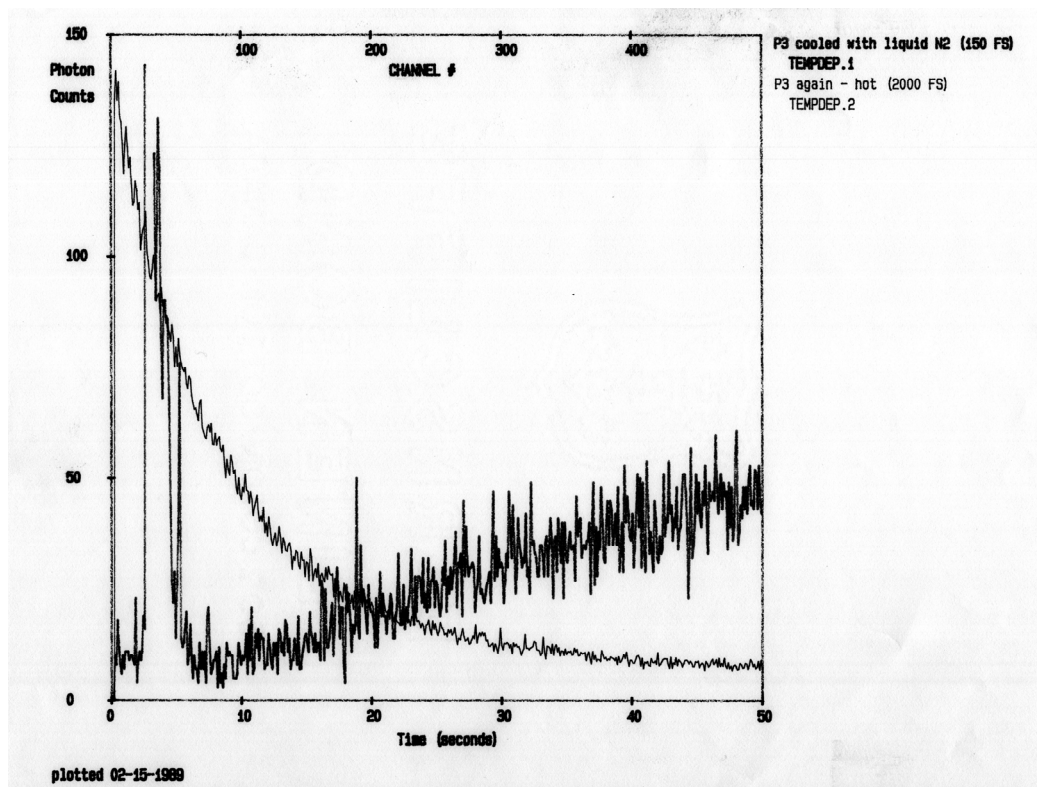

Figure 2: *Intensity vs time for Raman scattering from a plagioclase feldspar after it had been first cooled to liquid nitrogen temperature, showing the intensity increasing as it warmed, and then after it had first been heated on a hot plate, showing the intensity decreasing as it cooled*

were the motivation for our interpretation when we found the energy dependence to be about as expected for lattice scattering. Some of the raw data for Apiezon-Q are shown in the accompanying Figure 1. We also measured the plasticine with a 2.41 eV laser (Ar) and obtained a similar spectrum. In contrast, some black RTV (room temperature vulcanized) silicone on an aluminium disk gave nothing above background.

If our interpretation were to be correct there should be a very large temperature dependence, and we tested this using a sample chamber with a light-collection solid angle of ~ 0.96 sr. Samples were warmed or cooled and then quickly placed in the apparatus, where they slowly cooled or warmed to room temperature (hence we did not know the actual temperatures). Warming the plasticine on a hot plate increased the count rate over a factor of ~5 and cooling it in liquid nitrogen decreased the count rate a factor of ≥ 200 to background. We did a similar experiment with some feldspars, and again found a large temperature dependence; some data for a plagioclase are shown in Figure 2 (note the ordinate scales for the two data sets are different, being 150 and 2000 counts per 100 ms; the high count rate from 3-5 s probably occurred when the sample was loaded and light leaked into the chamber).

Jain and Lindvold have apparently missed our argument for the interpretation that was referred to and described in the accompanying paper by Godfrey-Smith et al. (1989) on zircons. Here, what we called the "Raman continuum" was ascribed to scattering from lattice vibrations in an imperfect crystal. Supporting evidence described was that the intensity had roughly the right energy dependence, a strong temperature dependence, and that it decreased with high-temperature annealing that improved the crystallinity.

Jain and Lindvold refer to the absence of any continuum in reports of Raman measurements on quartz and silica. Actually, Figure 1 of Hemley et al. (1986), to which they refer, shows a Raman spectrum of SiO_2 glass in which the background looks very much like our "Raman continuum", and has about the expected energy dependence.

All this fits in with the notion that the continuum arises from scattering from lattice vibrations in an imperfect lattice structure. Silica glass, plasticine and Apiezon-Q are disordered, feldspars are normally somewhat disordered, and zircons are often severely affected by radiation damage from internal U and Th decay; thus if our interpretation of the "Raman continuum" is correct one would expect it to be more

intense for these minerals than for less disordered crystals such as quartz.

The reader will now be wondering what we found for quartz. We did measure quartz sand-sized grains and observed the continuum, but a control experiment showed that it arose from the silicone oil used to mount the grains. We also saw the low-energy tail of what we now know is the quartz emission band; from this tail we deduced that the emission band was not in the blue as we had anticipated, but in the ultraviolet where the spectrometer was insensitive due to the coatings on its many mirrors. We thus abandoned measurement of quartz with the Raman spectrometer.

I would welcome any evidence that our interpretation of the exponential continuum is incorrect. I would also welcome alternative suggestions as to an explanation of the observations. Although I have consulted books and experts on Raman scattering, I have not found the subject discussed in the literature and would welcome any references.

In order to discuss the relevance of Raman scattering it is simplest to discuss it in terms of energies. For those who wish to use wavelengths or wave numbers, the conversions are:

$E.\lambda = 1240$ eV.nm   and $E/k = 1.24 \times 10^{-4}$ eV.cm,

where:

E = energy, λ = wavelength, and k = wave number

The largest Raman scattering energies are given in Table 1. I should emphasize that the figures given for the continuum are the largest reported values; because of the exponential energy dependence there is no fixed cut-off and the actual relevant value will depend on the conditions of the experiment; the higher the excitation power and the more sensitive the detector, the higher this energy will be.

The main portion of the emission band of quartz extends from 3.0 to 3.7 eV. Let us assume an experimental setup made to optimize the measurement of this band and ask what maximum excitation energy would lead to an absence of significant Raman scattering into this energy range?

Considering only Raman lines, the answer is 3.0 - 0.15 = 2.85 eV (435 nm). This energy falls in the range of likely emission from blue light-emitting diodes. If there is a significant Raman continuum then this energy would have to be lower.

Mineral	Line (eV)	Continuum (eV)	References
quartz	0.153	?	Shapiro et al. 1967
silica glass	≥0.15	>0.15	Hemley et al. 1986
feldspar	0.14	0.29	Smith and Brown, 1988
			Deer, Howie and Zussman, 2001
			Huntley et al. 1989
zircon	0.13	0.17	Godfrey-Smith et al. 1989
plasticine, Apiezon-Q	?	0.35	Us

Table 1: *Largest observed energy difference between excitation photon energy and Raman-scattered photon energy for several minerals*

There are two remedies for the problem. The first is to restrict the emission from the diodes; Jain and Lindvold indicate that they do this using Schott GG-420 filters, which have a cutoff at about 2.95 eV, depending on thickness. This, by itself, is clearly not adequate. Their second remedy is to use a filter in the measuring system that cuts out a portion of the quartz emission band; this Jain and Lindvold do using a Hoya U340 filter which cuts off sharply below about 3.15 eV. The difference between 2.95 eV and 3.15 eV is 0.2 eV. This would appear to be adequate to prevent measurement of any Raman lines, but one should be cautious because the cut-offs of the filters are not perfectly sharp and there is still the possibility of some overlap.

Jain and Lindvold argue another way that "Excitation of the quartz grains at 470 nm (excitation peak) and observation at 380 nm (emission peak) corresponds to an anti-Stokes shift of 5040 cm^{-1}. We do not expect any background due to Raman scattering at this wavelength." While this is so, it is not relevant because it ignores the fact that the emission bands of both the diodes and quartz are broad. What matters is the difference between the energies of the cut-offs of the U340 and GG-420 filters which is about 0.2 eV.

The numbers here are clearly critical; different filter combinations could yield a different conclusion, and only experimental tests will determine whether a particular combination is usable or not.

The situation for feldspar is different. The main emission for K-feldspar is in a band from 2.7 to 3.3 eV. If the measurement system incorporated a filter to encompass this then the excitation energy would need to be less than 2.55 eV (490 nm) or, if our measurement of a Raman continuum is considered, 2.4 eV (520 nm). Green or lower energy photons would be needed for excitation.

The experimental evidence provided by Jain and Lindvold that the effect is not significant for the quartz they tested and the particular set-up they used is reassuring. One does need to be alert however, because there may be situations for which the effect is significant. Reduction of their high background might do it. The use of different blue diodes or different filters could do it. So could a different quartz or quartzite or some other mineral, particularly one with a low emission intensity. In what may be an extreme case, ten years ago Olav Lian and I decided to measure a phytolith in a new Risø machine with green excitation from a filtered Xenon lamp; my recollection is that we observed about 200 counts/second above background, independent of time and a radiation dose. I attributed this to scattering from lattice vibrations in this non-crystalline material.

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Response to Huntley

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We find several errors in Huntley's reply:

1) Huntley relies on Kuhns et al. (2000) to argue that LM-OSL may yield different parameters than CW-OSL. LM-OSL by definition should originate from the origin (0, 0). All plots in the above study fail this requirement and therefore cannot be relied upon for comparison.

2) Huntley misquotes Poolton et al. (2003) by saying that 14 parameters were used for fitting. As can be seen in that paper, samples 1 and 3 used 10 free parameters and sample 2 used 12. The slow component is identical or varies by 5%, while the medium component by 15%. One should consider S/N effect while assessing precision.

3) Huntley claims a 'continuum' in Si-glass at >0.15 eV (his Table 1) based on Hemley et al. (1986, Fig. 1). However these are Stokes shifted spectra (pers. com. Hemley). The energy dependence discussed by Huntley (i.e. due to thermally populated excited levels according to the Boltzmann distribution) cannot by definition generate continuum in the Stokes mode. In fact, the claimed continuum in these

results arises due to 'diffuse scattering'. We suggest caution in use of the term Raman scattering (RS); it is a precise effect with definite predictions.

4) The choice of three commercial putty-like products (Apiezon Q, Plasticine and Black RTV) is inappropriate for comparison since these have no lattice, the exact chemical composition is proprietary, and the constituents (dispersed clay particles or carbon black) mainly generate multiple- or Rayleigh scattering.

5) Huntley advocates significant Raman scattering by relying on the tails of excitation and emission spectra. Our calculations show that only one scattered photon in 10 billion incident photons will be detected by the PMT in the antiStokes mode, therefore tails are unlikely candidates. Moreover, Huntley's result of 0.29 eV shift from feldspar (his Table 1) would predict significant RS photons observed through a U340; this was not seen in our experimental data (Figs. 3(a) and (b) in our previous letter).

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