Luminescence stimulated from quartz by green light : developments relevant to dating

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Abstract

Since the introduction, in 1985, of optically stimulated luminescence(OSL) for age determination, the technique has become increasingly common as a method of dating.

Light emitting diodes(LEDs) are a convenient and economical light source for the optical stimulation of luminescence. However for work with quartz, green light stimulation with an argon ion laser as light source is usual, particularly because of the low light intensity of light emitting diodes. Replacement of the original green light emitting diodes by newly developed high intensity green light emitting diodes allowed this limitation to be overcome. The new arrangement was shown to be of comparable sensitivity to the traditionally used argon ion laser system.

The optically stimulated luminescence dating method has been advanced with the introduction of the "single aliquot method", which uses one disc prepared from the sample to carry out all the measurements to determine the equivalent dose. A method based on a single aliquot has the advantages of avoiding normalization problems and reducing effort. The original version of this method concerned the infrared stimulation of feldspar and showed success with an additive dose method, in which correction was made for loss of luminescence signal due to repeated preheating and reading of the same aliquot. A similar single aliquot approach has been applied to the stimulation of quartz by green light, involving an alternative method of analysis of single aliquot data. This approach provides comparable accuracy to conventional equivalent dose determination by the multiple aliquot technique.

Declaration

This thesis has been composed by myself and it has not been submitted in any previous application for a degree. The work reported within was executed by me, unless otherwise stated.

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I dedicate this thesis to my father and mother.

Contents

Chapter 1

Introduction

1.1 Luminescence dating

Measurements of the luminescence signal from non-conducting, crystalline materials such as quartz or feldspar can provide a means of determining the time since the last heating of a piece of pottery or the last exposure of a layer of sediment to sunlight, the age of the pottery or sediment[1].

Although the mechanisms responsible for luminescence are not fully established, the basic principle can be explained in terms of a band model of the crystal, as shown in fig. 1.1.

Within the crystals, charge trapping due to exposure to ionizing radiation and long-term energy storage take place when an appreciable energy gap is present between the valence band and the conduction band, with excited states(or 'traps') between the bands due to impurities[2]. Observable luminescence is produced by electrons, released from traps by applied thermal stimulation, which recombine with lattice defects which act as luminescence centers, so called thermoluminescence(TL). The recombination luminescence of natural minerals can also be stimulated optically with a wide range of wavelengths, so called optically stimulated luminescence(OSL). For either of these

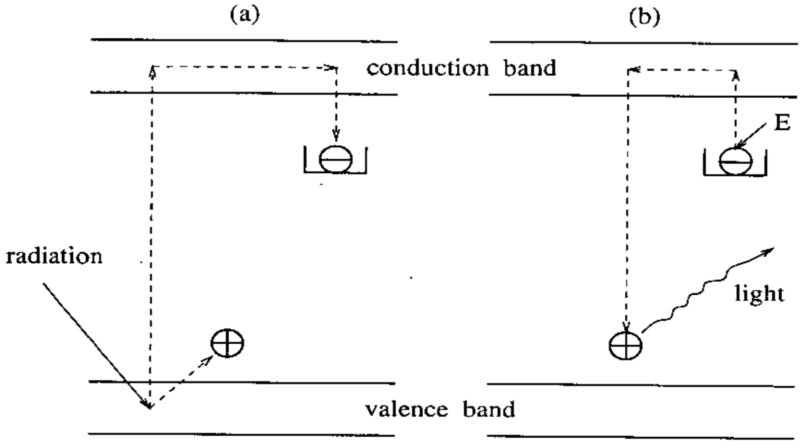

Figure 1.1. The simple model for the trapping of charge in semiconductors and insulators, assuming a single electron trap and single recombination center. (a) An electron is transferred to the conduction band by ionizing radiation and can be trapped at an electron trap, and a hole is trapped near the valence band. (b) The trapped electron is thermally(, or optically) activated and recombines with a hole, which can be accompanied with the emission of light. E = activation energy.

phenomena to be useful as a dating method, it is necessary for there to be a zeroing mechanism which empties out the electrons which had been stored at the time of interest. Generally several traps with different activation energies are involved, and possibly also deeper traps whose electrons are not transferred to the conduction band during TL or OSL measurement. Only luminescence signals originating from stable traps(stable for temperatures above about 300^0C), from which there has been no significant thermal leakage of charge during the timescale over which the sample has been buried, can be used to calculate an age. In practice, because of multiplicity of electron traps, the luminescence process for materials of interest in dating applications is more complicated than that displayed in fig. 1.1. A fuller discussion for the luminescence process can be found in elsewhere[3][4][5][6][7].

Wintle and Huntley[8] demonstrated that thermoluminescence (TL) dating techniques, originally applied to pottery, could be adapted for application to sediments. The latent luminescence in sediment could be bleached to some extent by exposure of the sediment crystals to light. Subsequent laboratory measurements, using thermoluminescence, must allow for the light insensitive components(or traps) which would not have been bleached by sunlight when the sediment sample was deposited. That the latent luminescence could be bleached to some extent by exposure of the crystals to light led to the development of techniques for dating the time of deposition of sediments, extending the interest in such dating methods from archaeology to geology. The development of optically stimulated luminescence(OSL) dating provided an elegant solution to the problem of dating sediments by probing only the light sensitive traps in the crystals. The optically stimulated luminescence, in contrast to thermoluminescence, has no unbleachable component and is reduced far more rapidly by exposure to natural light[9]. These two characteristics suggest that dating by OSL provides advantages over thermoluminescence both in dating the time of deposition of minerals zeroed by light during sedimentation, and for dating minerals exposed to only a limited amount of light prior to deposition.

The first optical luminescence measurements on sediments were introduced by Huntley et al.[10] who showed that light of 514nm wavelength could stimulate quartz grains to emit luminescence at around 400nm wavelength which could be used for sediment dating in a similar way to thermoluminescence. Since then, the exploitation of OSL from quartz for dating purposes has been extensively investigated[9][11][12][13][14].

During optical stimulation, particularly in the blue and green spectral region, of quartz grains which during sedimentation have been exposed to ionizing radiation, the trapped charges are released and as a result the luminescence signal(OSL) is produced, with photon emission occurring at higher energies. As optical stimulation continues, the OSL decays with time. The continuous stimulation results in charge being retrapped in the shallow traps e.g. 110^0C TL peak(photo-transferred TL(PTTL) peak)[13][15]. Recently, Wintle and Murray[16] discussed the effect of the trap responsible for the 110^0C TL peak upon the production of OSL for a sedimentary quartz at room temperature. They suggest that it would be an advantage to measure OSL of quartz at a temperature of 125^0C, so that the traps responsible for the 110^0C TL peak are kept empty.

Whereas in TL the glow curve provides a 'spectrum of trap stabilities' on the relevant geological timescale since heating to higher temperatures results in the emptying of progressively more thermally stable traps, there is no such intrinsic information provided in the course of an OSL measurement. In addition, the traps with low thermal stability resulting from an artificial dose by irradiation in the laboratory have to be emptied by preheating the sample[17]. The conditions of this preheating are mainly designed to isolate traps with adequate thermal stability. Further details of preheat procedures are given in Chapter 3.

There is some debate at present as to the origins of the quartz OSL signal. Smith et al.[11] studied the trap population giving rise to the OSL signal from quartz. They concluded that the trap responsible for the OSL signal was related to the TL glow peak at 325^0C. Using the bleaching studies of natural thermoluminescence(NTL) by selected wavelengths, Spooner et al.[18] found that the source traps of the 325^0C TL peak were the only traps readily bleachable by visible light. Later investigations characterised the OSL properties of quartz in more detail. Following the study of Ditlefsen and Huntley[19] who proposed that there are a number of different traps which can be emptied by exposure to light, Huntley et al.[20] concluded that a range of traps was responsible, each trap having a different excitation cross sections. Spooner[14] also mentioned the trivial contributions to the OSL signal from traps associated with the other NTL peak.

In dating based on luminescence, ages(in thousands of years) are assessed from the well-known age equation

$$Age\ (ka) = \frac{Equivalent\ \ Dose\ (Gy)^1}{Dose\ \ Rate\ (Gy/ka)} \tag{1.1}$$

where luminescence measurements are used to determine the *Equivalent Dose* of the sample. The *equivalent dose* comes from a mixture of alpha, beta and gamma radiation from the radioactive decay processes and from cosmic rays. One approach of determining the equivalent dose is to form an additive dose growth curve, of luminescence signal versus dose, with progressively higher artificial doses added to portions of the natural sample and to extrapolate to zero luminescence signal, see chapter 3 for details. In relation to the determination of equivalent dose, the development of optically stimulated luminescence dating has been reviewed by Wintle[21].

In addition to the use of the green light stimulation of quartz[10], much work has built on the observation of luminescence stimulated from feldspar by infrared[22].

The *dose rate* is obtained by measuring the radioactive contents of the samples. This is achieved either by direct measurements of the gamma activity in the field, and the beta and alpha activity in the laboratory, or by indirect measurement involving element analysis from potassium, thorium and uranium decay chains. More details on the various methods of radioactivity analysis can be found in Aitken[1].

In summary, the steps of the luminescence dating are as follows :

1. The heating or light exposure at the time of deposition removes the possibility of luminescence from the mineral crystals.
2. Latent luminescence then builds up with time due to exposure of the crystals to the natural radioactivity of the surroundings.
3. The luminescence intensity from a sample of interest is measured in the laboratory, either as thermoluminescence or optically stimulated luminescence.
4. The luminescence sensitivity to radiation of the crystals is determined using a calibrated beta particle or gamma ray source. The accumulated radiation dose

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[1] The gray(Gy, 1J/kg) is the SI unit of absorbed dose.

to produce the measured luminescence intensity(step 3) is deduced.

5. If the radiation dose per year can be determined, say by alpha, beta and gamma ray counting in the environment from which the mineral crystals came, age can be then calculated by eq. 1.1.

1.2 Aims and format of the thesis

Chapter 1 contains a brief overview of the production and measurement of luminescence signals as used in the dating of minerals which have had their signal zeroed by either heat or light at a time of interest in their history.

The aim of chapter 2 is to introduce a green light emitting diode system, originally designed by Galloway[23][24] as a light source for stimulation of luminescence from quartz and develop it into a improved system with higher ratio of luminescence signal to background. In this chapter, a brief overview of various light sources for luminescence stimulation including green light emitting diodes is presented. This is followed by the introduction of the original green light emitting diode system. Finally the design of the new Nichia green light emitting diode system is depicted and this is compared with the original green light emitting diode system and other systems.

Chapter 3 deals with the general dating procedures. In the first part of this chapter, general sample collection and preparation are presented. Later, a series of experiments relating to the dating methodology are investigated and discussed.

Chapter 4 concerns investigations carried out to determine whether a single aliquot additive dose method, similar to those reported for the infrared stimulation of feldspar[25] [26], is successful in the case of quartz stimulated by green light. Tests were undertaken with two kinds of quartz; quartz bleached by daylight, relevant to sediment dating and quartz drained by heating, relevant to pottery dating. Differences in behavior of bleached and heated quartz are noted. An alternative method of analysis of the single aliquot data is also considered.

In the following chapter(Chapter 5) the equivalent dose values of natural quartz using the single aliquot additive dose method are determined and the results compared with multiple aliquot equivalent dose estimates.

As an application of the single aliquot additive dose method, ceramic fragments are dated from Helike, a Greek city destroyed and submerged by earthquake and the results are presented in chapter 6.

The final chapter, chapter 7, summarises the main findings of the work presented in this thesis, with suggestions for future study.

Chapter 2

Instrument for luminescence stimulation

2.1 The stimulation wavelength

The first optical dating measurements on sediments were made with green light of 514.5nm from an argon ion laser to stimulate luminescence at about 400nm wavelength from quartz grains[10]. Since then, experiments have been undertaken to find an optimum stimulation wavelength by comparing optically stimulated luminescence signals obtained from quartz at a variety of stimulation wavelengths.

Godfrey-Smith et al.[9] used a dye laser tuned to provide stimulation wavelengths in the region 615~684nm. They described that a measurable luminescence in the blue-violet region was observed for both quartz and feldspar and there was a gradual increase in luminescence intensity per mJ of incident light as the energy of the exciting photons increased. A similar result has been reported by Botter-Jensen et al.[27] and Duller and Botter-Jensen[28], namely that at longer stimulation wavelengths a larger intensity is required to reduce the optically stimulated luminescence signal by a given proportion. Also, Godfrey-Smith et al.[9] chose to employ the wavelengths from infrared(799+753nm) to violet(413nm) using a krypton ion laser. They estimated the equivalent dose, 0.0±0.7Gy, for five different stimulating wavelengths on young quartz, but which showed a plateau in an equivalent dose versus photon energy plot. They have also observed the luminescence from older quartz with all the above different wavelengths that they have chosen for stimulation and found the equivalent dose to be independent of wavelength.

However, it is reported that infrared stimulation only produces luminescence from feldspar, not quartz and thus the response to infrared can be used as a test for the purity of quartz[29]. Wintle[21] pointed out that a weak luminescence stimulated by infrared from quartz in the above study of Godfrey-Smith et al.[9] results from the red 753nm excitation line from the krypton ion laser, rather than the near infrared 799nm line.

In association with the question of possible infrared stimulation of luminescence from quartz, the emission spectra from natural quartz using 950nm infrared wavelength for stimulation was reported by Short and Huntley[30]. However, they described that the emission did not seem likely from the quartz itself but could be from feldspar inclusions in the quartz grains[31] or from some other mineral as yet unidentified. Based on this result Huntley et al.[32] have dated using inclusions within quartz grains by infrared stimulation, and found consistency with the expected ages deduced from the oxygen isotope correlation. McFee[33] also described that a small luminescence signal stimulated by infrared (wavelength 880±80nm) was observed from a group of discs containing large numbers of coarse quartz grains. He indicated that this luminescence signal could have come from either contaminant feldspar grains deposited onto the disc along with the quartz grains or from inclusions of feldspars within the quartz grains themselves.

Relevant to the influence of stimulation wavelength on quartz is a study by Spooner et al.[18] who investigated the bleaching of thermoluminescence by selected wavebands (UV-free ‘white light’, 500±20nm, 370±12nm and 322±12nm) obtained using suitable filters within a solar simulator. They found that the 325^0C thermoluminescence peak from quartz has an extraordinary susceptibility to light. Further measurements showed active bleaching continuing to ~ 700nm, but indicated that near infrared(> 750nm) is incapable of untrapping electrons from any of the NTL(natural thermoluminescence luminescence) traps.

Feldspars, however, behave very differently from quartz regarding stimulation, there being a marked peak in stimulation sensitivity in the infrared[22][27] even though they can also be stimulated by green light. The high yield and ease of separating luminescence from stimulating light has led to most dating using feldspars employing infrared stimulation which can be provided conveniently by GaAs light-emitting diodes[23][34][35][36].

2.2 Emission spectra

Information on emission characteristics is very important not only for understanding the physical mechanism occurring in minerals, but also for aiding in the choice of optical filters in dating applications[37][38].

Several papers have been published concerning the emission spectra of thermally and optically stimulated quartz. In respect of the thermoluminescence emission spectra, it was reported that the 110^0C peak emission was a band at about 360 ~ 380nm, while the 300 ~ 400^0C emission yielded bands at ~ 470nm and ~ 630nm[39][40][41][42]. A similar result was reported by Hashimoto et al.[43] who, using colour photographs, showed a red emission band as well as a blue one from quartz separated from beach sands.

For optically stimulated luminescence, Huntley et al.[44] have investigated the emission spectra for quartz from dune sands of various ages using two stimulation wavelengths(514nm and 647nm) from lasers. They observed a single emission band at 365nm(fig. 2.8), which looked similar to that of the 110^0C thermoluminescence peak emission. As a result, the quartz emission of optically stimulated luminescence is a single band at 365nm in distinct contrast to the blue emission band($\sim$ 470nm) seen in the high temperature thermoluminescence.

However, the emission of feldspars is quite different from that of quartz[45]. Feldspars generally give emission bands at 330nm, 400nm and 570nm, the 400nm band being particularly strong for K-feldspars and 570nm band being strongest for Na-rich plagioclase feldspars[27][44]. These bands appear to be the same as are observed in thermoluminescence($\sim$ 300^0C peak) emission spectra.

2.3 Light sources for optically stimulated luminescence

Following from the original work of Huntley et al.[10], much work on quartz using green simulation has employed an argon laser as light source[11][46][47].

Alternative, more economical and convenient sources of green light for stimulation have been investigated. One approach has been to use powerful white light from which, by use of filters, the green part of the spectrum has been selected for stimulation. A filtered xenon arc lamp(transmission 500-550nm) was used for luminescence stimulation from quartz[29][48]. Botter-Jensen and Duller[49] constructed a filtered 75W halogen lamp which has an output in the region 420-550nm for the study of quartz. In preliminary dating results with an archaeological quartz sample from burnt stone, they found a good agreement within 2% in the thermoluminescence date. Also, in a geological quartz sample from dune sands they found consistency within 5% with previous ^{14}C and clay-varve dates. The latter system is being used increasingly[50][51]. Galloway[24] introduced a compact arrangement of 16 green light-emitting diodes for luminescence stimulation which has been in routine use ever since(section 2.4 and 2.5).

Each stimulation system has advantages and disadvantages. The argon ion laser has the advantage of providing an appropriate intensity of monochromatic light at the sample with the disadvantages of technical complexity and consequent expense. The filtered light from the halogen lamp is also of appropriate intensity and the system can readily be altered by a change of filters to measure luminescence stimulated by colours of light other than green. The green light emitting diode system is the most compact and simplest of the three, but has hitherto provided a much lower intensity of stimulating light(by almost two orders of magnitude). This was compensated by longer measuring times, but inevitably resulted in a poorer ratio of luminescence signal to background with a consequent limitation to the lowest absorbed radiation dose that could be detected from quartz or feldspar crystals[52]. Newly available LEDs have allowed this limitation to be overcome(see section 2.5 for details).

2.4 Green light emitting diode system

A versatile 40-sample system for thermoluminescence and optically stimulated luminescence was designed by Galloway[23], its main components being a precision rotatable wheel controlled by optical sensor, a heater assembly for preheating, beta source for dosing, LED array for optical stimulation and photomultiplier for luminescence measurement.

The 40 samples can be carried on the wheel to any of four positions which give a versatile means of mounting and changing the facilities required. Details of this system can be found elsewhere[23][53], but a brief description will be provided for the sake of completeness since this system was used for most of the measurements reported in this thesis.

2.4.1 The 40-sample carrying wheel

The samples are moved from position to position by a precisely constructed and controlled wheel. The system was designed for carrying stainless steel discs, 12mm in diameter and 0.2mm thick, with the central 10mm depressed by 1mm(fig. 2.1(a)). The dished shape aids both the retention of grains on the disc and the positioning in the carrier on the wheel(fig. 2.1(b)). The wheel position is detected by diffuse reflective

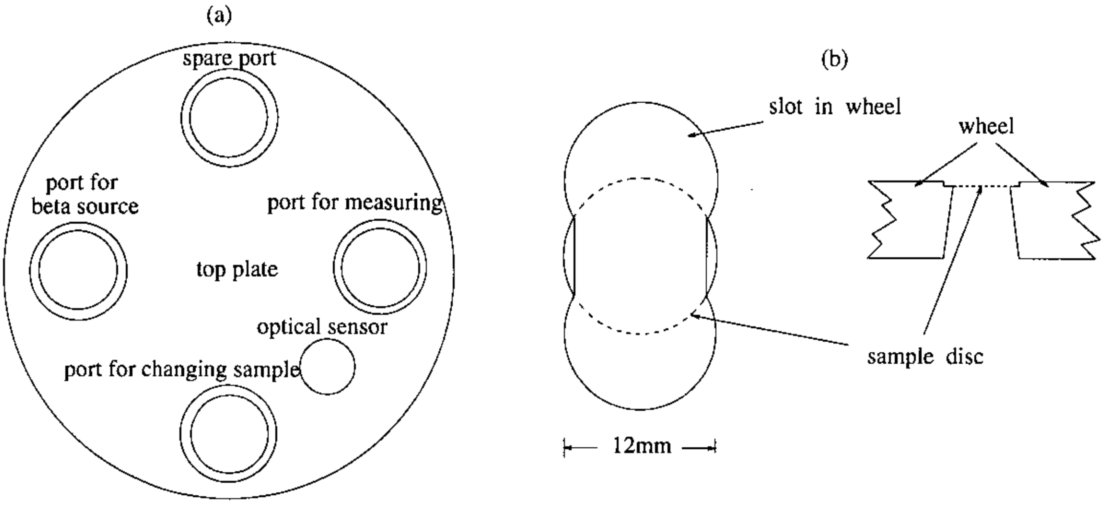

Figure 2.1. The port arrangement of the 40-sample carrying wheel(a) and an example of one sample disc carrier(b).

optical sensors. The angular position of each sample is indicated by a short radial line onto the wheel surface which is blackened and so can be detected by an optical sensor. A longer line, detected by two sensors, indicates the reference orientation of the wheel('position 1') and any other required orientation is found by counting the number of lines which pass under the optical sensor as the wheel rotates, the motor being switched off when the desired position is located. A gentle friction brake applied continuously to the rim of the wheel improved the smoothness of rotation and precision of stopping.

2.4.2 The heater assembly

The heater assembly is developed from the design used for a manual single sample thermoluminescence system[53], illustrated in fig. 2.2. Linear increase in heater temperature with time is controlled by a 20kHz signal from a 120W audio amplifier as the source of power for the nichrome heater strip. Fig. 2.3 shows the linearity of heater temperature with time. The secondary of the transformer made from solid copper serves also as the mechanical mounting for the heater strip. The knife-edge of the two copper blocks onto which the heater is clamped is chosen to prevent excessive conduction of heat away from the top surface of the heater strip by the copper and to facilitate easy heater replacement while ensuring accurate location of the heater.

Vertical movement of the heater assembly is achieved by a slide mechanism and cam wheel drive. The copper transformer secondary(i.e. the heater mounting) is fixed by an insulating block to a vertical metal slide. The lifting mechanism comprises a cam wheel, the angled top face of which on rotation pushes the slide upwards or allows the slide to come back down. Rotation of the cam wheel is by synchronous motor and gear box at 10 rpm, the limits of motion of the slide being controlled by optical sensors.

Before raising the heater to make a measurement, the computer program tests that the heater has cooled down to less than 30^0C, as otherwise a build-up in starting temperature occurs in a sequence of measurements that are not interspersed by beta exposures or other delays between use of the heater.

2.4.3 Beta source

A controlled radiation dose was administered to a sample in position on the wheel by a shielded ^{90}Sr beta source(d:19mm, h:12.2mm) mounted on the top plate. The source is stored at the center of a cylindrical shield, comprising an outer layer of lead 16mm thick, an aluminium layer 23mm thick and a 114mm diameter core of perspex. The source is mounted on a wheel to provide easy rotation from the storage position to the exposure position by motor drive under computer control with an external disc on the drive shaft indicating to optical sensors the position of the source.

A disc of aluminium is inserted between the beta source and perspex in order to avoid radiation damage of perspex due to immediately facing the surface of the beta source in its storage position. The wheel carrying the source is made of aluminium, except for a lead section which completes the outer lead layer when in the closed position. The dose rate to quartz grains on the 0.2mm thick stainless steel disc routinely

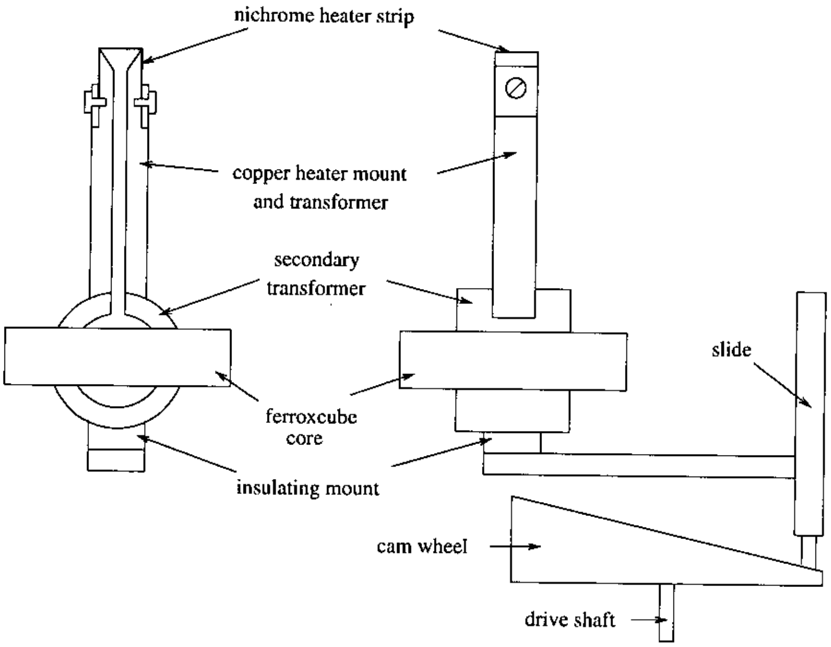

Figure 2.2. The heater assembly mounted on the chamber bottom plate.

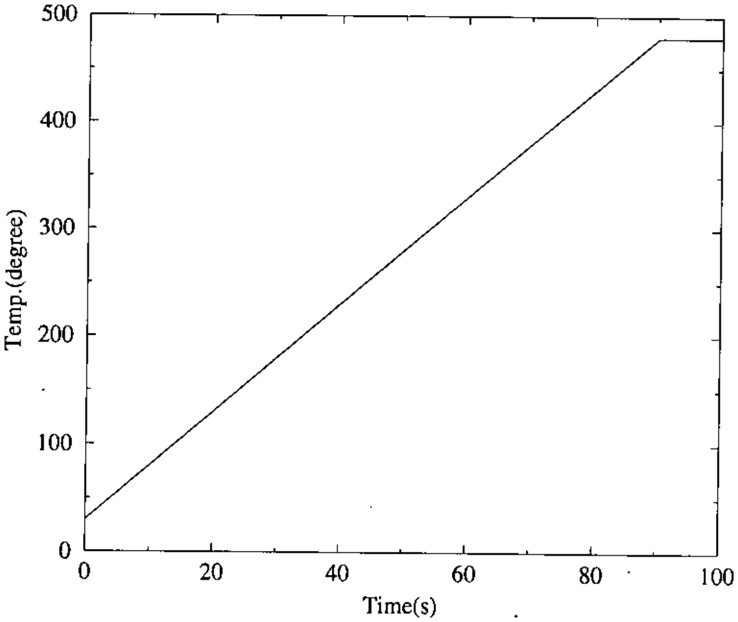

Figure 2.3. A diagram for linearity of heater temperature with time.

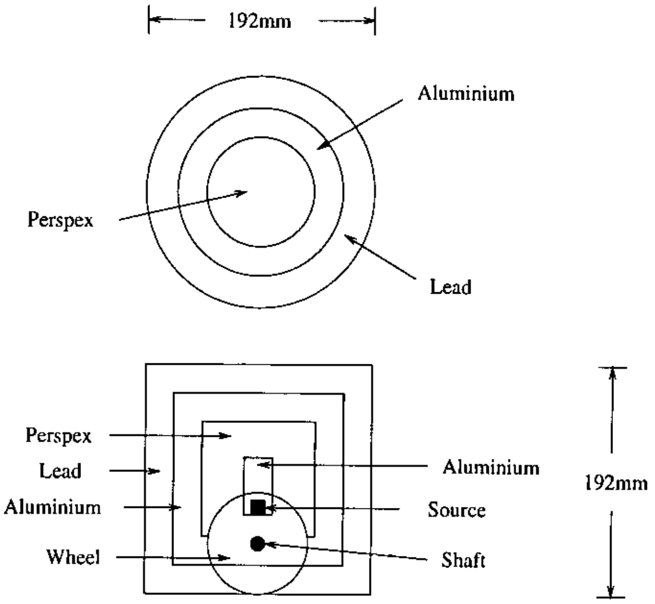

Figure 2.4. A diagram of the shielded beta source.

used with the system is 240±7 $mGys^{-1}$ when in the exposing position[23]. The 'spillage' to immediately neighbouring discs is 0.03%, while the dose rate to a disc when the source is in the storage position is not more than $0.2\mu Gys^{-1}$. Fig. 2.4 is the diagram of the shield beta source.

2.4.4 System control

A BBC Master computer controls the 40-sample system as well as storing the data from the system. Fig. 2.5 represents the simplified schematic diagram of the data collection and control circuitry associated with the 40-sample system.

Interfacing is to the 1MHz bus on the computer which can input or output an 8-bit word as well as providing a 4-bit "device-identifying" code. The latter 4-bit code is fed to a 74154 decoder while the eight input/output lines are connected to two 6522 versatile interface adapters(VIAs). Only six of the outputs from the decoder are

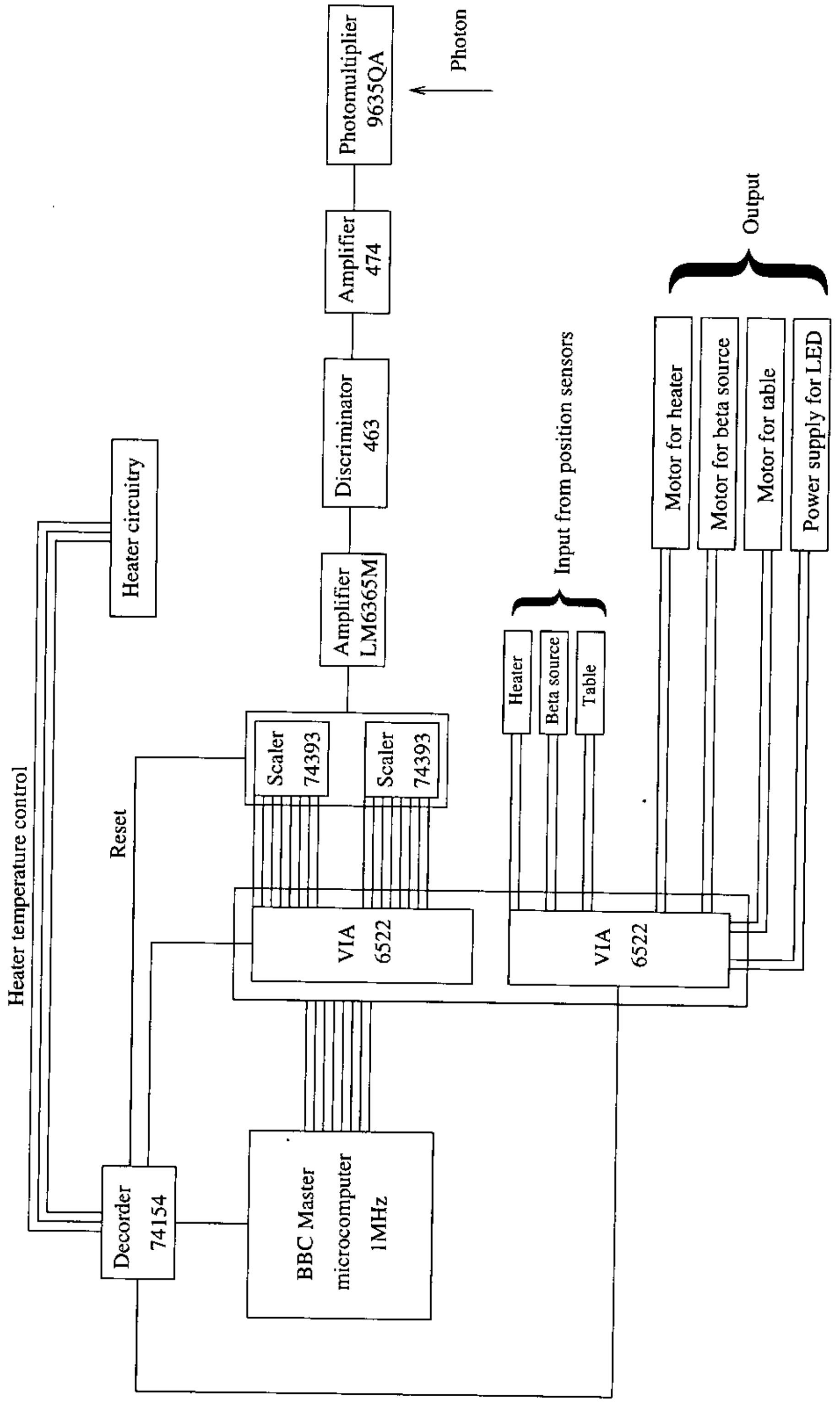

Figure 2.5. Simplified schematic diagram of the data collection and control system.

required at present, three to control the heater circuitry, one to reset the 16-bit scaler used for photon counting, two to identify which VIA is to be enabled. One VIA is used to transfer the scaler contents to the 1MHz bus, the other served to input the signals from the optical sensors indicating the wheel, heater and beta source positions and to output controlling signals to the motors which moves these devices and to switch the LED power supply.

2.4.5 Photomultiplier

The photomultiplier is a device used to convert the extremely weak light output of a scintillation pulse into a corresponding electrical signal by multiplication or amplification. As is denoted in its name, it absorbs a small amount of light from the scintillator, amplifies it many times, and delivers a strong pulse at its output. The photomultiplier used in all measurements is the EMI type 9635Q photomultiplier which is highly sensitive in the blue region and also has a low electrical background level(12 counts s^{-1}). The capability of amplification is nearly the order of 10^8(Amplifications of the order of 10^6 are commonly used.) and quantum efficiency[1] is 26.5%.

2.4.6 Photon counting

Photons which pass through the filters(fig. 2.6) are detected by an EMI 9635QA photomultiplier connected to a standard nuclear fast pulse amplifier(ORTEC 474) and discriminator(ORTEC 463). The NIM standard pulses from the discriminator are inverted using a fast operational amplifier(LM6365M), counted using two binary scaler chips(2N74393) and the resulting 16-bit word read in two bytes into a BBC Master computer which records the data[53]. Pulses separated by more than 30ns are counted without loss up to a maximum of 2^{16}-1(i.e. 65535) counts per channel of recorded data.

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[1] The ratio of number of photoelectrons produced to number of incident photons

2.4.7 Green light emitting diodes for optically stimulated luminescence

Since the first exploration that feldspar could be stimulated by infrared radiation[22], infrared light emitting diodes(LEDs) have provided the most convenient and effective light source for feldspar stimulation for dating purposes, because of the high yield and simplicity of separating luminescence from stimulating light[23][34][35][36]. However, for work with quartz, green stimulation with an argon ion laser as light source is usual due to the insensitivity of quartz to infrared. Replacement of the argon ion laser by LEDs is difficult. The reasons are as follows.

- The output light intensity of LEDs is considerably lower than that of an argon ion laser.
- The optically stimulated luminescence of bleached quartz is less intense than that of feldspar for the same radiation dose.
- The spread in wavelengths emitted by the LEDs makes more critical the filtration of the luminescence from the scattered light compared with an argon ion laser.

Despite these difficulties, a system using green LEDs for the optically stimulated luminescence dating of quartz and feldspar was devised[24] to provide an alternative to the argon ion laser system. Details of the original green LEDs system can be found elsewhere [23][24][54][55] but a brief description will be provided here as an introduction to the new green LEDs system.

The arrangement of green LEDs follows that already used with infrared diodes[23][34] and is illustrated in fig. 2.6. Black 'Q-compound' is packed round the filters to prevent light leakage reaching the photomultiplier.

Sixteen LEDs, fitted in an accurately machined Dural holder, are connected in parallel and illuminate the sample which is carried on a stainless steel disc 12mm in diameter. The LEDs, manufactured by III-V, are type TLMP 7513 which have a

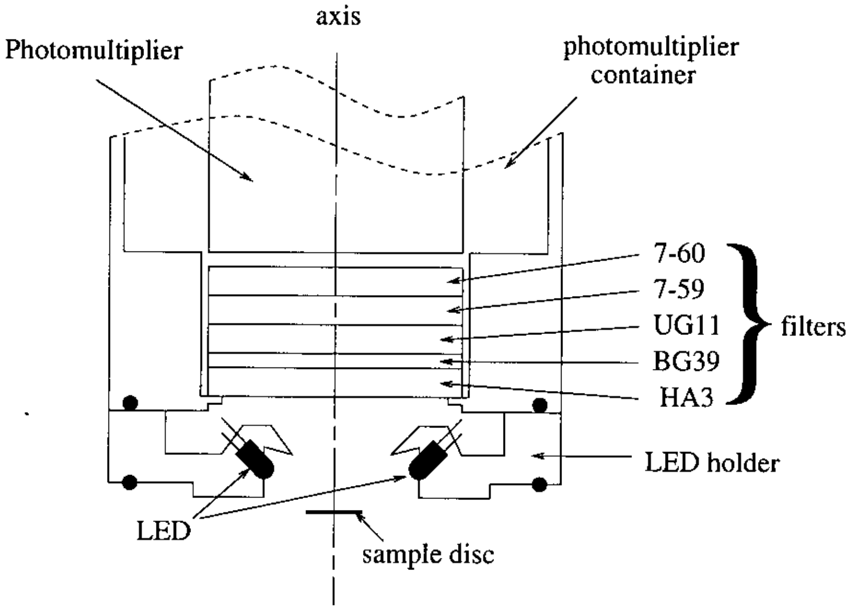

Figure 2.6. The arrangement of 16 green light emitting diodes which is cylindrically symmetrical about the axis.

25^0 emission angle, providing 300mcd at 20mA current with a peak in the emission spectrum at a wavelength of 565nm(full width at half maximum 30nm).

In luminescence measurement, the scattered green light from the LEDs is rejected by a carefully chosen filter stack comprising Chance HA3, Corning 7-59, 7-60, Schott UG11(each 4mm thick) and BG39(0.5mm thick) in front of the photomultiplier(EMI type 9635QA). The BG39 filter also plays an important role in removing red fluorescence, namely 700 ~ 800nm in fig. 2.7. The HA3 heat absorbing filter is included to protect the filters from heat(during pre-heating). The dependence of the transmittance of the filters on wavelength is illustrated in fig. 2.7.

For elimination of scintillations in the filter stack induced by low intensity bremsstrahlung radiation from the nearby shielded beta source, a shadow shield of 100mm thickness lead was included[54].

The microcomputer system records the photon counting rate as a function of time of exposure to the light from the LEDs as well as switching on and off the constant current supply which feeds the LEDs. The current through the sixteen LEDs in parallel is 0.35A, i.e. 22mA per LED which is safely within the maximum rating of 25mA. The intensity of illumination of the sample is about 0.2mW/cm^2.

For compensation of low intensity, luminescence intensity was integrated over first 100s for measurements on bleached quartz and a time of 12.5s on the heated quartz because of its greater sensitivity. Table 2.1 summarises the principal properties of the reading system. The old green LEDs system was used for all measurements over the first 24 months of my research, prior to the change to the new green LEDs system.

Recently, McFee[33] attempted to use similar diodes, which emit green light at a wavelength of 565nm, along with an imaging photon detector(IPD) for the purpose of investigating the behaviour of optically stimulated luminescence using single grains of quartz. In his measurements, 8mm of Schott 7-59 filters and 2mm of BG 39 filters in the beamline was chosen to prevent exposure of the IPD to a high illumination, which would cause irreversible damage. Several discs of coarse grained quartz were given beta doses

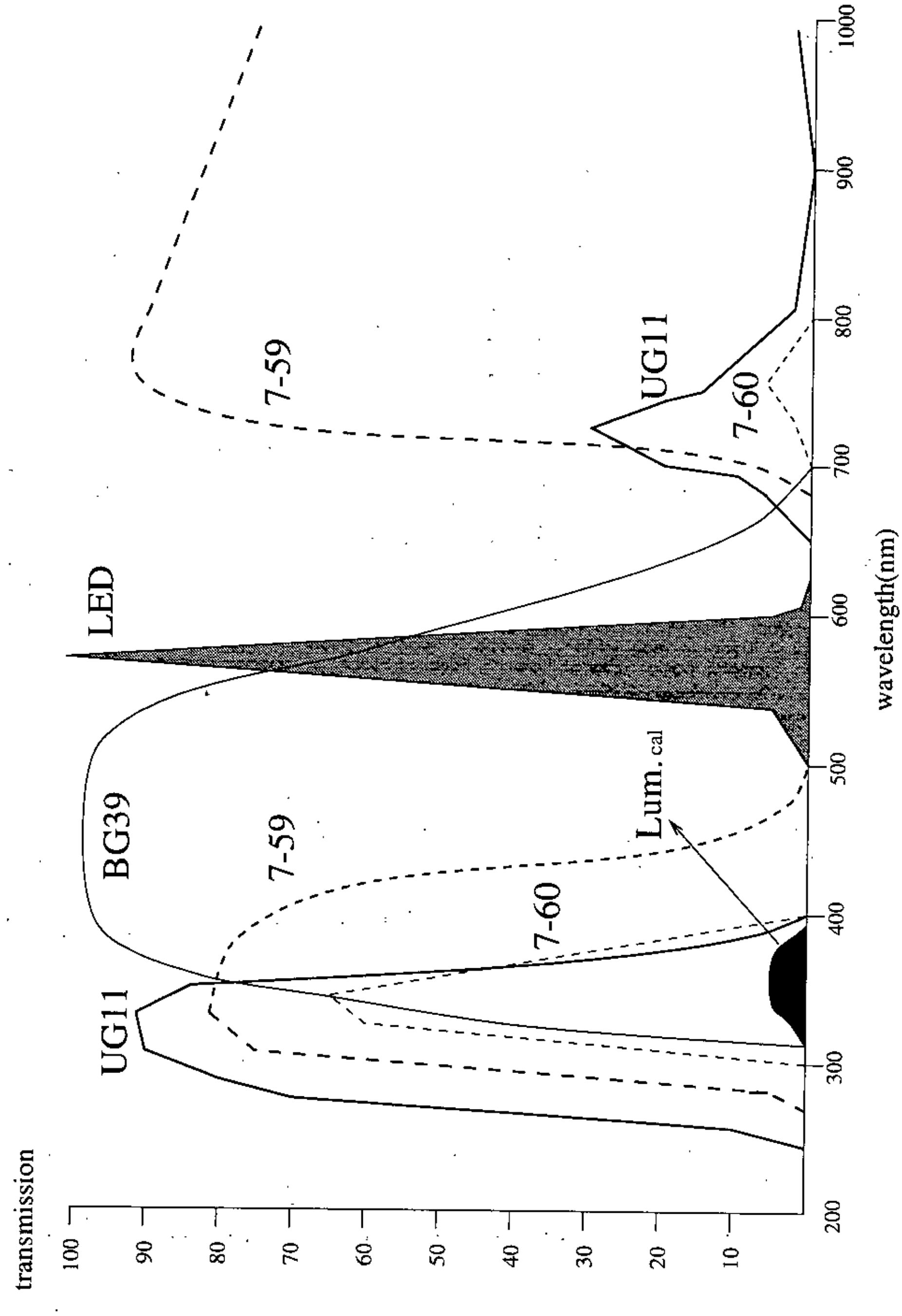

Figure 2.7. The transmittance of the 7-60, 7-59, UG11 and BG39 filters compared with the LED emission spectrum. Lum.$_{cal}$ is the transmission of the filter combination.

Table 2.1. Properties of the 16 old green LEDs system.

LED type	Emission peak (nm)	Approx. power at sample	Filters	Transmission peak (nm)
TLMP7513	565	0.2mWcm^{-2}	BG39, UG11, 7-59, 7-60	360, 1% 330-390

of 300Gy, followed by a preheat of 220^{0}C for 1 minute. No observable luminescence was found from any of the discs while the diodes were operated for 300seconds. He pointed out that this was considered to be due to a combination of the low power output from the diodes, and more importantly to the large number of filters which had to be incorporated into the beamline to remove the green light excitation. In relation to the latter, it is also indicated that the significant low luminescence intensity presumably originates from relatively thick 7-59 filters. As an example, Rhodes[56] attempted the interposition of additional thickness of the 7-59 signal transmission filter in order to reduce the time independent signal level at high laser beam power.

However, in the case of the red rejection BG 39 filter the thickness is not critical. There is no noticeable difference in luminescence detected whether using 0.5mm of BG 39 or 2mm of BG 39 filter. For comparison, the photon counts using these two filter thicknesses are listed in table 2.2. The measurements were made using bleached quartz with the same filter stack except for different thickness of BG 39 filter. Beta doses of 23Gy, 230Gy and 460Gy were used for the tests. Preheating was for 1 minute at 220^{0}C. The values shown in table 2.2 represent in each case the average of three measurements with the error indicating the spread. Note that the photon counts in table 2.2 are not linear with dose because of the saturation effect[1].

Table 2.2. The luminescence using different thicknesses of BG 39 filter.

Beta dose	Photon counts using BG 39(0.5mm)	Photon counts using BG 39(2mm)
23Gy	2250±285	2296±418
230Gy	11089±535	11037±1017
460Gy	15890±608	15292±889

2.5 New green light emitting diode assembly

2.5.1 Characteristics of the diode

Although various measurements using quartz have been made successfully using the old green LEDs[24][54][55], they have been hampered, particularly in case of young sediment dating, by the low light intensity from the LEDs. A dramatic improvement has been achieved by replacing the old LEDs with the new Nichia green LEDs(Nichia Chemical Industries Ltd of Japan type 110104 LED)[2]. According to the manufacturer's specification, the new LEDs have an emission angle of 15^0 and provide 3-6cd at 20mA current(30mA absolute maximum current) with a peak in the emission spectrum at 525nm(full width at half maximum 40nm). Table 2.3 epitomizes a comparison of the old green LEDs with the new green LEDs.

2.5.2 A green long pass filter

The optically stimulated luminescence is observed while the light source is operated and the signal decays as the trapped electrons are progressively released with the light exposure time.

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[2] supplied by MI Cables Ltd, 53 Carsegate Road, Inverness IV 6EX, UK

Table 2.3. The comparison of the old green LED with the new green LED.

LED type	Emission angle	Maximum current	Lum. intensity (I=20mA)	Emission wavelength	FWHM*
Old green LED (TLMP 7513)	25^0	25mA	300mcd	565nm	30nm
New green LED (110104)	15^0	30mA	3-6cd	525nm	40nm

*FWHM : full width at half maximum.

In the process of detecting optically stimulated luminescence it is necessary to exclude scattered stimulating light from the photomultiplier detecting the luminescence, by use of suitable filters in front of the photomultiplier. The quartz luminescence is peaked at about 365nm wavelength with a full width at half height of about 60nm[44]. In so far as the dependence of the sensitivity on the stimulating wavelength is concerned, the stimulated luminescence intensity from quartz falls exponentially as the wavelength increase, at least from 400nm[27][14]. Thus for the efficient detection of optically stimulated luminescence from quartz, the stimulating wavelength should be as close as optical filter properties permit to the luminescence wavelength. Hence the use of green light for stimulation which can be blocked from the luminescence detecting photomultiplier by blue filters which can pass only the luminescence.

Initial tests with one Nichia LED showed that the spread in the emission spectrum into the blue region($<$ 400nm) is sufficient to penetrate the original filter stack, comprising Chance HA3, Corning 7-59,7-60, Schott UG11(each 4mm thick) and BG39(0.5mm thick) filters, which preceded the photomultiplier(EMI type 9635QA) used to count luminescence photons. The capability of the photomultiplier, designed to be highly sensitive to the blue region, could be overloaded. Placing a green long-pass filter(Schott

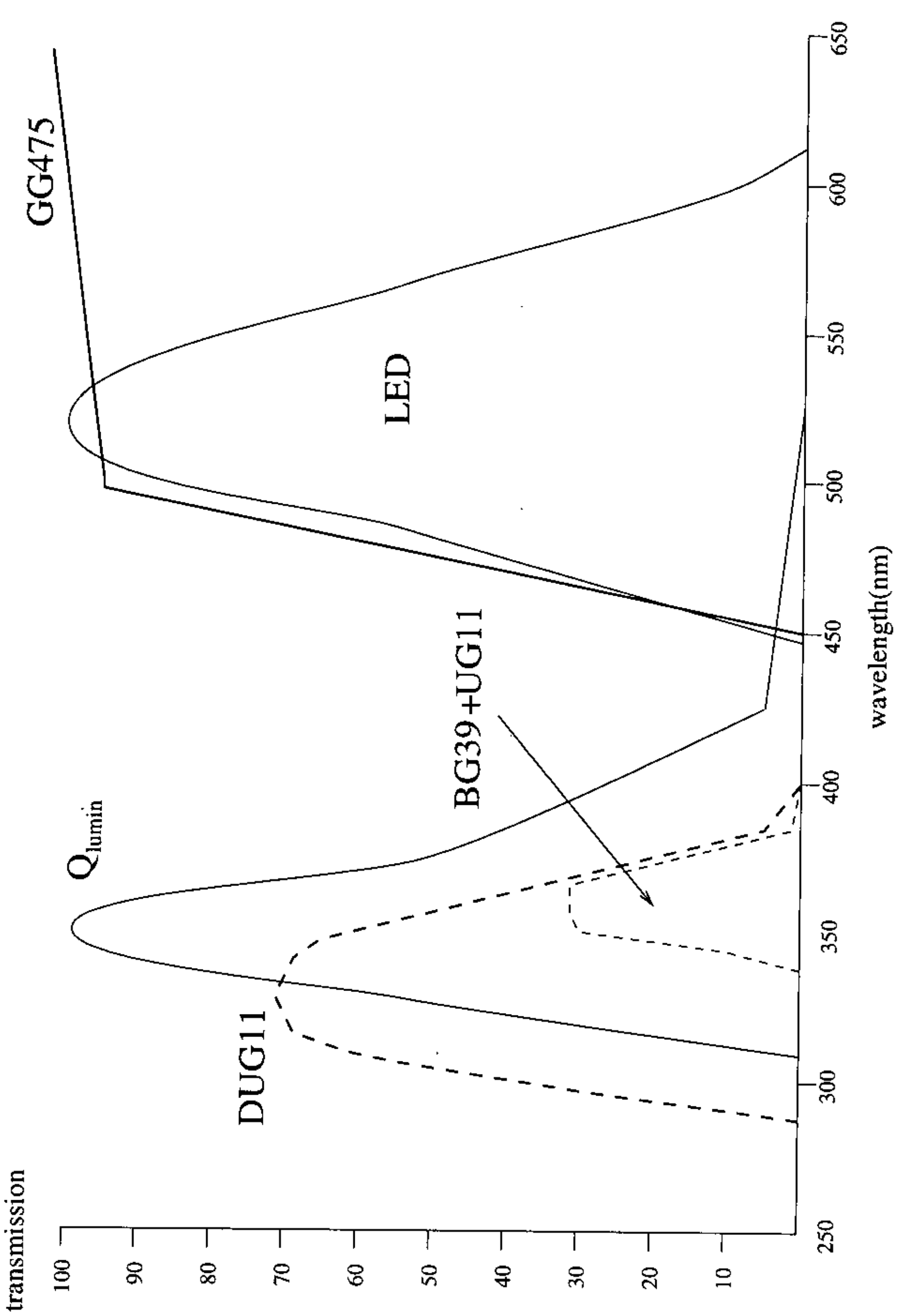

Figure 2.8. The transmission characteristics of filter combinations, based on the manufacturer's data(Schott and Corning).

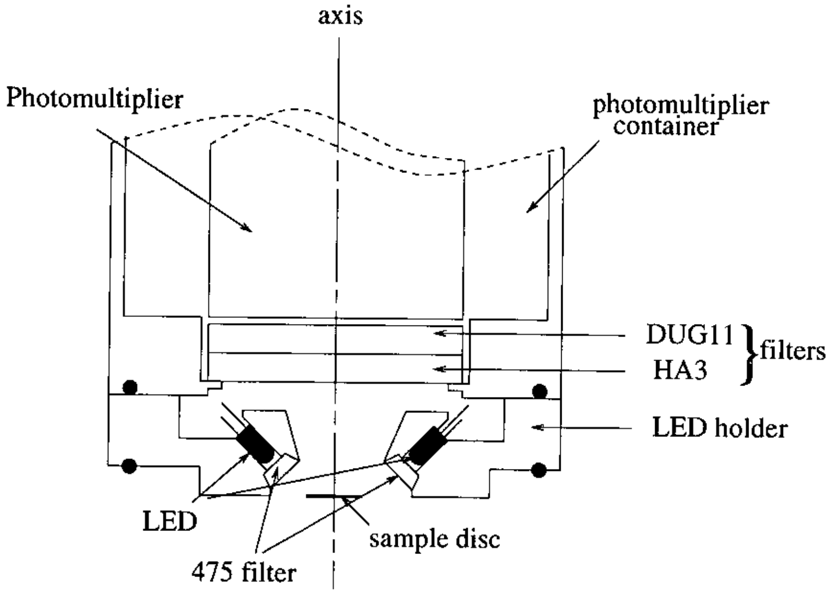

Figure 2.9. The mounting assembly, which is cylindrically symmetrical about the axis, for the Nichia LEDs and associated GG475 filters.

GG475) of 3mm thickness in front of the LED removed the troublesome 'tail' of blue light with no significant influence on the green emission of interest for stimulation of luminescence. The transmission properties of the filters used and the emission spectrum of the LEDs are illustrated in fig. 2.8. Also, superimposed in fig. 2.8 is the quartz luminescence emission spectrum(Q_{lumin}) from Huntley et al.[44] and the Nichia LED emission from the manufacturer's data.

The LED arrangement for luminescence stimulation, fig. 2.9, is based on that used previously with the addition of a 5mm diameter, 3mm thick GG475 filter in front of each LED. An accurately machined Dural holder can accommodate 16 LEDs, each with a filter. The LEDs are connected in parallel and operated from a constant current source, which is switched on and off as required by the computer which also records the luminescence photon-counting rate.

2.5.3 The tests

In the control arrangement the LEDs are connected to the constant current supply by program command from the computer and simultaneously the counting of pulses from the photomultiplier commences. Conversely, the LEDs are switched off at the end of the data collection period.

The constancy and reproducibility of the light output from the LEDs during measurement should be emphasized. This stability of the stimulating light intensity with time has been investigated by scattering the light from stainless steel in the sample position and replacing the colour filters in front of the photomultiplier by sufficient neutral density filters to attenuate the intensity of scattered light entering the photomultiplier to a level at which photon counting of the scattered light was possible.

After connecting the 16 Nichia LEDs, measurements of the variation of light intensity with time were made over periods of 250 consecutive measurement intervals of 0.1, 1, and 10s with the recommended maximum current of 30mA, so that the stability over durations of 25, 250 and 2500s was investigated. Fig. 2.10 is a typical example of the time dependence of the intensity of the light emitted by the LEDs measured in this way covering 25s(a), 250s(b) and 2500s(c) respectively. The light output intensity is constant within 2% for continuous operation(tested up to 42 minutes operation) and from run to run. In order to confirm the stability of light output from the LEDs, further measurements have been made while the LEDs are repeatedly switched on and off. Following these sequences with approximately 2 second intervals between successive measurements, the photon counts for 125 seconds were integrated, and then compared. Fig. 2.11 displays the five consecutive measurements. The integrated photon count is constant within 0.1% for continuous five operations , with no particular control of room temperature.

There is a small overshoot of intensity at switch on of about 5%(the average of five measurements) in magnitude, which falls to half this value after 2s and is imperceptible

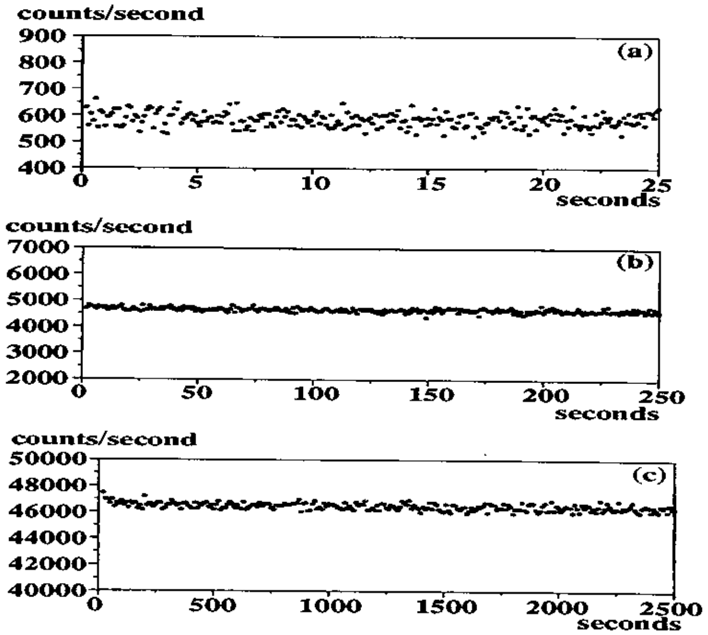

Figure 2.10. The light output from the 16 Nichia LEDs measured through neutral density filters by the photomultiplier, with measurement time (a) 25s, (b) 250s and (c) 2500s.

after 6s. This phenomenon also appeared with the old green LEDs although there is a little difference in overshooting level[24]. Further tests have been made with the new green LEDs to confirm this behaviour. The light output of the LEDs being in proportion to the current, the light output characteristics of the LEDs were examined with increasing current. The current range from 10mA to 50mA which is beyond the recommended maximum operating value(30mA) was selected, measuring over a period of 250s(fig. 2.12). There is no noticeable overshoot up to 20mA, but it starts to appear from 30mA, and is particularly significant for the highest current of 50mA. This type measurement has been made with different green LEDs(figs. 2.13, 2.14 and 2.15). Repeated measurements using the different green LEDs, of the kind illustrated in fig. 2.12 made from time to time over a day while the system was in continuous use, gave similar curves. Similar results can be found in experiments with infrared diodes[33][34]. It is worth while to mention that the Nichia green LEDs give a much less level of the overshoot, compared with the other tested green LEDs for the highest

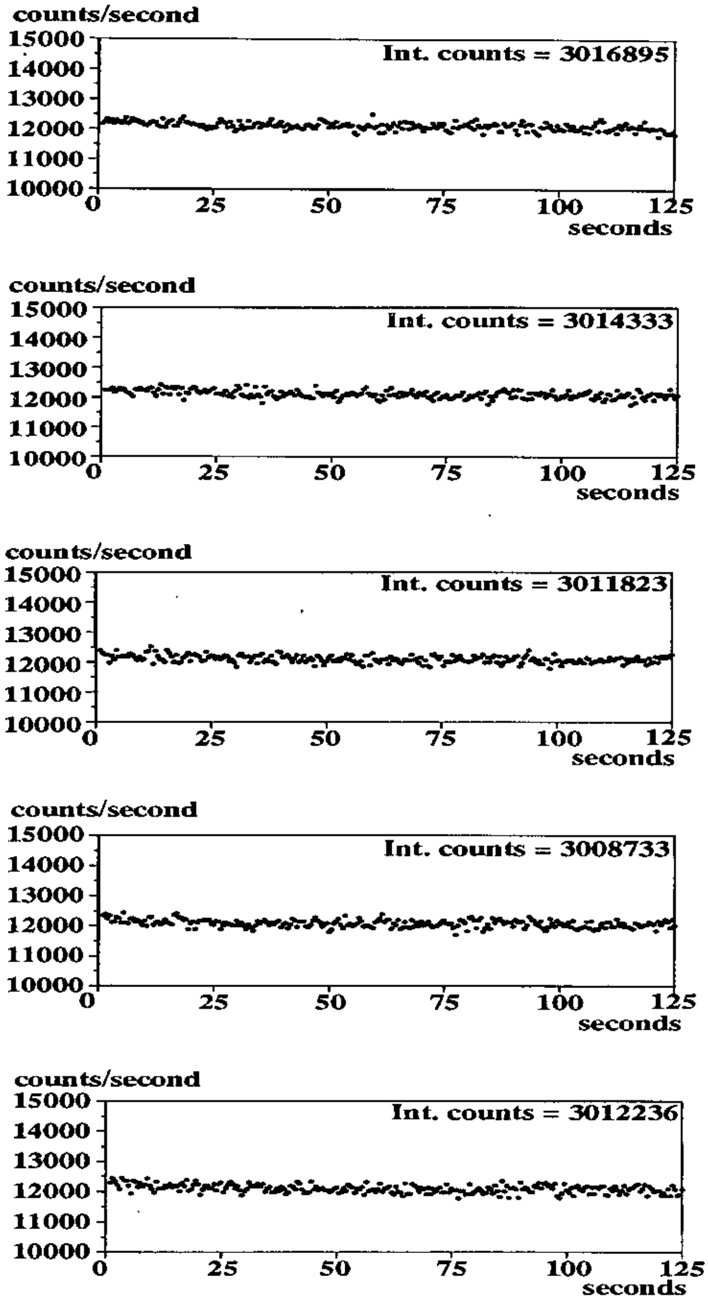

Figure 2.11. The integrated light output of the consecutive five measurements.

given currents(figs. 2.12, 2.13, 2.14 and 2.15).

Note that the neutral density filters were changed between measurements and therefore the observed intensities in fig. 2.10, fig. 2.11 and fig. 2.12 do not correlate with each other.

2.5.4 Measurements on quartz

Quartz, which had been bleached by daylight and given a known dose in the laboratory, was used for the tests. The quartz samples were prepared from 'acid washed sand'(BDH Ltd.), further treated with 40%HF and HCl, and sieved to $\sim 125\mu m$ before deposition of about 15~25mg per sample on 12mm diameter stainless steel discs. A random selection of samples was tested to confirm negligible feldspar contamination by looking for infrared stimulated luminescence[35][54]. Quartz bleached by daylight was used because it provides a more critical test of the system than quartz which has had luminescence removed by heating. The latter has a luminescence sensitivity(luminescence intensity per unit radiation dose) 30 or more times that of bleached quartz[49][55].

The time dependence of the luminescence stimulated from quartz by the new system is shown in fig. 2.16. The quartz was dosed to 75Gy, stimulated by the 16 Nichia LEDs each with GG 475 filter as in fig. 2.9. The quartz sample was preheated for 1minute at 220^0C prior to measurement. The luminescence counting rate falls to half of the initial value in 18 seconds. The time taken to reduce the luminescence signal to half of its initial value provides a basic comparison of the effectiveness of the new system with any other and is presented in table 2.4.

In this regard the new system is a factor of 70 better than its predecessor and comparable in performance to an argon ion laser. The energy per unit area required from an argon ion laser to reduce the green stimulated luminescence to half intensity is about $150mJcm^{-2}$[12] and $250mJcm^{-2}$[9]. It may be that this range of values results from a dependence on the mineralogy of the quartz or on the duration of any heating prior to

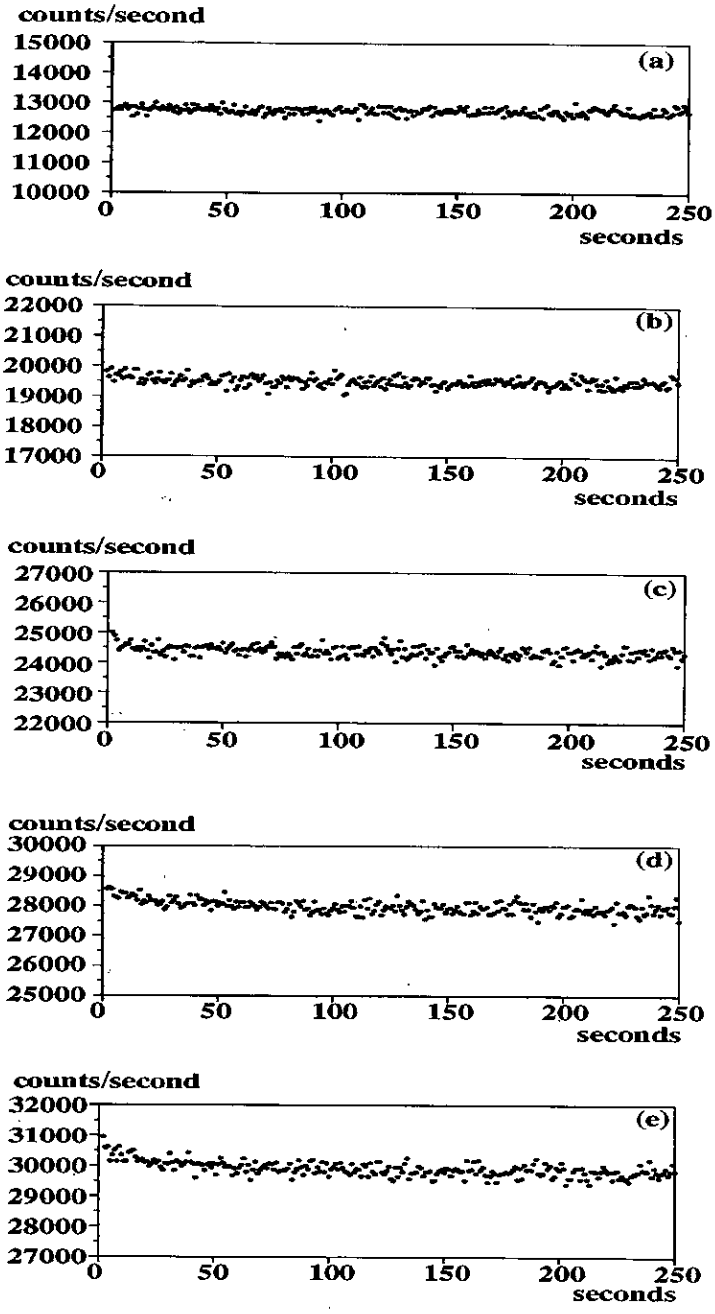

Figure 2.12. The light output characteristics of the 16 Nichia LEDs with increasing current (a) 10mA, (b) 20mA, (c) 30mA, (d) 40mA and (e) 50mA.

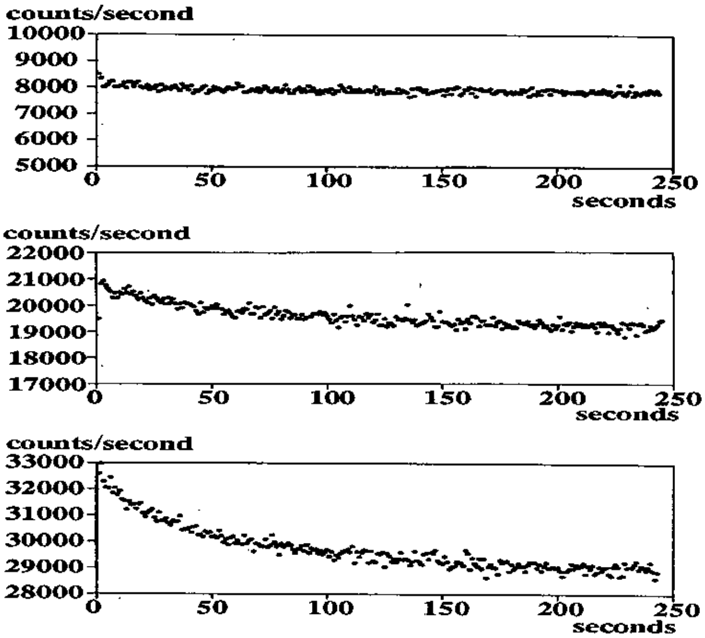

Figure 2.13. The light output from the 16 Toshiba LEDs(recommended maximum operating current(25mA)) measured through neutral density filters by the photomultiplier, with measurement time 10mA(top), 20mA(middle) and 30mA(bottom).

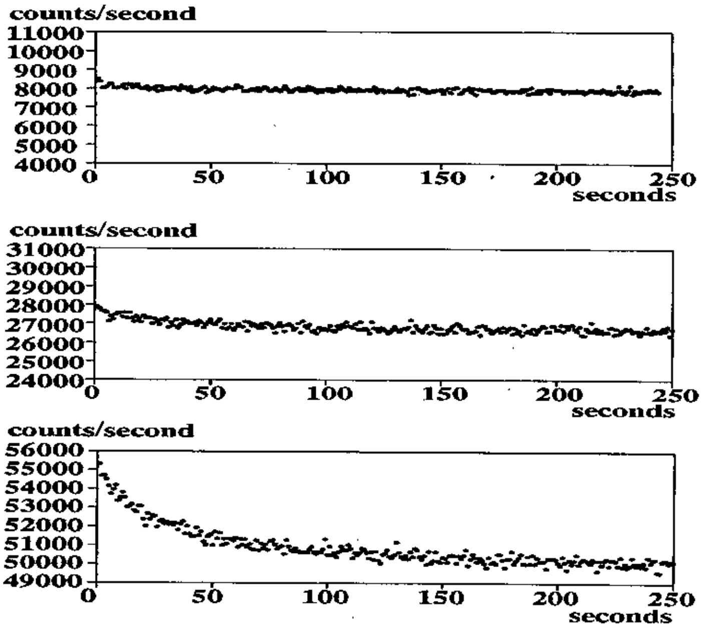

Figure 2.14. The light output from the 16 TLMP LEDs(recommended maximum operating current(25mA)) measured through neutral density filters by the photomultiplier, with measurement time 10mA(top), 20mA(middle) and 50mA(bottom).

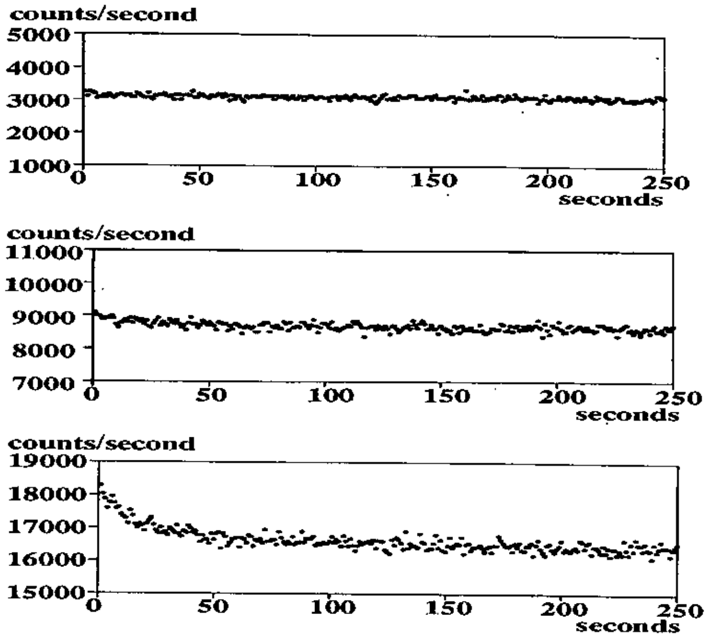

Figure 2.15. The light output from the 16 VOL LEDs(recommended maximum operating current(25mA)) measured through neutral density filters by the photomultiplier, with measurement time 10mA(top), 25mA(middle) and 50mA(bottom).

green stimulation. However, from these values the present LED system must be producing about 10mWcm^{-2}, which is within the power range commonly used for dating with sedimentary quartz. Stokes[46], for example, refers to the use of an argon ion laser system which provided a power density at the sample in the range 5~50mWcm^{-2}, in the context of dating the deposition of young sediments using quartz. Smith et al.[12] refer to the power at the sample being usually in the range 5~10mWcm^{-2}. The filtered halogen lamp system of Botter-Jensen and Duller[49] has a short time to half intensity in relation to the power density at the sample due to the stimulating light extending to shorter wavelengths than the other systems.

2.5.5 Luminescence pass filter development

First tests of the new LED system were made with the same combination of filters in front of the photomultiplier as was used with the original LED arrangement of Galloway[24]. It is however appropriate to consider whether any advantage can be

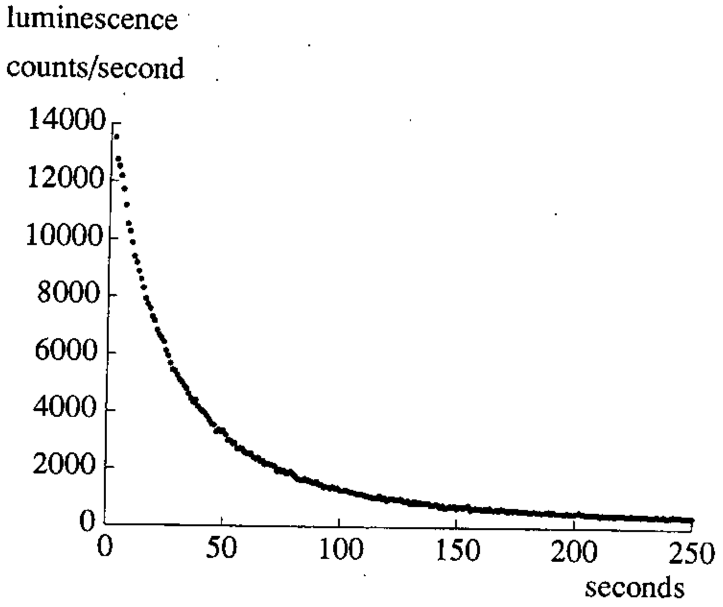

Figure 2.16. The decay in luminescence with time of exposure to the stimulating light. The quartz was dosed to 75Gy, stimulated by the 16 Nichia LEDs each with GG 475 filter as in fig. 2.9.

Table 2.4. The time taken by different green stimulation sources to reduce the luminescence from quartz to half of its initial value.

Stimulation source	Power at sample ($mWcm^{-2}$)	Wavelength (nm)	Time (s)	Reference
16 LEDs(TLMP7513)	0.2	565(30 FWHM)	1200	Galloway[24]
16 LEDs(Nichia 110104)	10	525(40 FWHM)	18	Present work
Argon ion laser	50	514.5	≃2	Huntley et al.[10]
	10	514.5	25	Godfrey-Smith et al.[9]
	45max	514.5	≃4	Smith et al.[12]
	5-10 usual	514.5	40-20	Smith et al.[12]
Filtered halogen lamp	16	420-550	2.5	Botter-Jensen and Duller[49]

gained by use of a different filter combination, since the new system has a GG475 filter in front of each LED to cut off any light near the luminescence wavelength, fig. 2.8. Basically it seemed that a UG11 filter should be suitable for passing the quartz luminescence more efficiently than the original combination while still retaining discrimination against scattered green light. However the UG11 filter, in common with most colour filters which transmit in the violet or ultra-violet region of the spectrum, also transmits in the red region. To suppress this red transmission, the UG11 filter was used in combination with a BG39 filter and the transmission of the combination is also shown in fig. 2.8. A possibly more efficient alternative investigated was the DUG11 filter, fig. 2.8, which comprises a 2mm thickness of UG11 filter glass with red absorbing metal oxide layers deposited on both sides of the filter. Comparison of the effectiveness of these possible filter choices was made using a preliminary test system which contained only 4 Nichia 110104 LEDs. The choice of filters in front the photomultiplier depends only on the emission spectrum of the LEDs(each with associated GG475 filter), and not on the number of LEDs. The comparative measurements are given in table 2.5.

A heat absorbing HA3 filter was always included since, in eventual routine use for dating work, it may be convenient to be able to heat the sample in the measuring position without concern for the possibility of damage to the filters. The UG11 and BG39 combination improved the photon counting rate from the photomultiplier by a factor of 4 compared to the original filters, without worsening the background counting rate in which photomultiplier noise predominates. The DUG11 filter provides a factor of 16 improvement in signal compared to the original filters, with a doubling of the background rate in which scattered light now contributes more than the photomultiplier noise. Accordingly the DUG11 was adopted for use with the Nichia 110104 system.

2.5.6 Overall system performance

Also included in table 2.5 are data on the original and the complete new 16 LED systems. The overall improvement in sensitivity to quartz luminescence stimulated by

Table 2.5. A comparison of performances with different filter combinations in front of the photomultiplier.

	Filter combination				
	7-60(4mm) 7-59(4mm) UG11(4mm) BG39(0.5mm) HA3(4mm)		UG11(4mm) BG39(2mm) HA3(4mm)	DUG11(2mm) HA3(4mm)	
	16(TLMP7513) (Galloway, 1992)	4(Nichia 110104)	4(Nichia 110104)	4(Nichia 110104)	16(Nichia 110104)
Photomultiplier noise(cs^{-1})	9	9	9	9	9
+ filter phosphorescence(cs^{-1})	11	11	11	10	10
+ scattered light(cs^{-1})	16	16	15	30	100
Measured relative luminescence signal*	1	20	80	320	≃1000
Relative filter transmission		1	4	16	
Signal to noise ratio improvement	1	20	80	160	160

* Average from measurements on quartz samples given a range of beta doses, with a measurement time of 100s for the original system [24] and 1s for the new systems.

green light is about three orders of magnitude, a factor of 70 resulting from the change in LEDs used and a further factor of 16 resulting from the change in luminescence selecting filters.

Before any measurements using the 40-sample wheel system, it was tested whether the light from the LEDs affects the sample in the neighboring positions, because of the much stronger intensity of the new LEDs. Tests were made with both bleached quartz samples and with heated quartz samples, given 230Gy beta dose. The time-dependent luminescence signal from the samples was compared. One set of measurements was made with the samples placed in consecutive positions on the wheel. The other set was made with the samples in alternate positions with an empty position between pairs of samples. In no case was any noticeable difference of the time-dependent luminescence signal observed.

An indication of the performance of the new system in determining the dependence of luminescence on dose is given in fig. 2.17. Each point was provided by a measurement of the luminescence for only 1 second, whereas 100 seconds measurement times were used with the original system[24]. Fig. 2.17(a) displays the response of bleached quartz up to a dose of 150Gy, showing the typical influence of approaching saturation. Fig. 2.17(b) illustrates the approximately linear response at much lower doses(up to 10Gy only), the finite luminescence response for zero dose being due to the recuperation phenomenon[57]. For comparison fig. 2.17(c) exemplifies the much higher luminescence emitted by quartz previously heated to 500^{0}C for 5 minutes.

2.5.7 Conclusion

The system described for the stimulation of luminescence from quartz by green light from 16 Nichia 110104 LEDs each with its own small GG475 filter provides comparable sensitivity to the traditionally used argon ion laser systems, being 70 times as sensitive as the previous LED system. When used with a DUG11 filter to select the stimulated luminescence, the overall performance is about 1000 times better than the previous

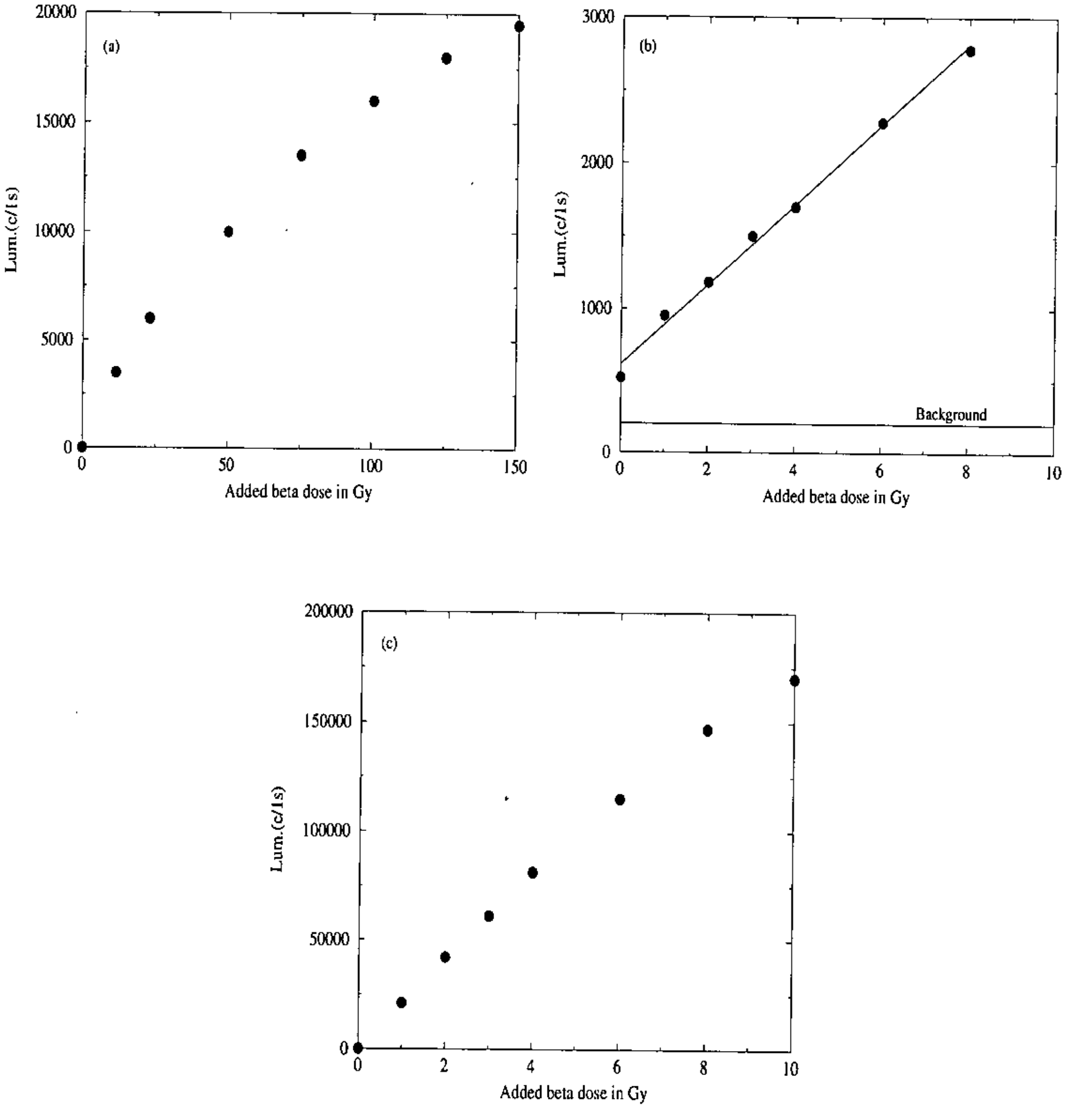

Figure 2.17. The dependence of luminescence on added dose. Quartz bleached by daylight was used for (a) and (b) with quartz drained by heating to 500^0C for 5 minutes used for (c).

LED system. It is the most compact and economical system for green light stimulation and so should provide a most convenient tool for luminescence dating with quartz.

2.6 Peripheral systems

2.6.1 Luminescence test system

A simple one sample system which can easily be altered was used for many experiments. The system is made up of the photomultiplier and LEDs assembly connected to the computer. The advantage of this system is that changing of the LEDs assembly is very easy and convenient. Hence it was useful for checking for contamination of feldspar in quartz samples and testing of the filter choice. With this system a lot of time was saved.

2.6.2 Solar simulator

A Honle SOL-2 'solar simulator' was used for studying the effects of optical bleaching and for equivalent dose determination by the regeneration technique. According to the manufacturer's specification, the SOL-2 uses metal halide high pressure lamps and can produce up to 6.5times the intensity of natural sunlight.

Chapter 3

Methodological investigations of dating procedure on quartz

3.1 Sample considerations

3.1.1 Sample collection

Samples of sediment in the field were typically collected by hammering steel cylinders into a sediment face. After being removed from the section, the steel cylinders were immediately covered tightly at both ends with thick tapes. Considerable care was taken to avoid exposure to direct daylight in the case of samples for luminescence analysis and to avoid contamination by water for samples for dosimetry. In the laboratory's dark room, the material in both ends of the steel cylinders, which may have been exposed to daylight during wrapping, was extracted for beta and gamma dosimetry measurement. The sample material remaining in the steel cylinders was processed for luminescence analysis.

In case of a pottery sample, it can be obtained from its origin irrespective of exposure to sunlight because a 2mm layer from each surface should be removed to avoid the bleaching effect of daylight, soil contamination and variations of the beta dosage between the radioactivity within pottery(internal beta dosage) and the radioactivity surrounding soil(external beta dosage), for details see Aitken[1]. However, similar attention as in sediment is paid to the water content of pottery fragments for internal beta radiometric analysis.

3.1.2 Sample preparation

All sample preparation was undertaken under subdued red light which has been shown not to affect the dating signal from quartz [58][59] and never focused directly onto the sample, to avoid bleaching the luminescence signal. The pottery fragment was gently crushed to suitable size in an agate mortar after removing the 2mm outerlayer.

After removal of ferrous materials(such as ilmenite, magnetite and titanomagnetite) by stirring with a ferrox magnet within a plastic bag, clay-rich samples were washed thoroughly with water and sodium hexametaphosphate($(NaPO_3)_6$) to remove the clay and then grains in the size range 125 to 150μm were separated by sieving. With the selected sample grains, solutions of sodium polytungstate of different densities were used to separate the heavy mineral($\geq$2.70 gcm^{-3}), quartz(2.60$\sim$2.70 gcm^{-3}) and feldspar($\leq$2.60 gcm^{-3}).

In the adoption of the quartz inclusion technique[60] it is necessary to etch away the outer layer of the quartz grains to remove the alpha dosed layer of the grains. The alpha particle contribution to the thermoluminescence from a 100μm quartz grain is within the 4$\sim$12% range of the total thermoluminescence for the 'typical' pottery and soil specified by Aitken[1]. Hydrofluoric(HF) acid is commonly used for the purpose of the etching. Besides reduction of the alpha-particle contribution, HF treatment eliminates the feldspar, the most probable contamination in quartz, and improves the transparency of the quartz grains. Although etching is highly recommendable, it remains questionable as to whether the assumption of isotropic etching is possible. Lang and Miuscov[61] mentioned that the quartz had a tendency to etch preferentially along dislocation lines in the crystal lattice structure, so that it could be erroneous to use the observed loss of weight during etching to calculate how much of the alpha-irradiated surface layer has been removed. A similar result was discovered in feldspar[62] that the surface etching of a feldspar grain does not occur regularly but preferentially along crystal planes. Recently it is reported that the etching behaviour of quartz is different from that of feldspar[48]. This is reflected in different HF treatment time for etching of quartz grain from researchers to researchers; some people choose an hour[1][46][63], others 40 minutes[32][18][48]. In regard to HF treatment time, Valladas and Valladas[64] have demonstrated the failure of 45 minutes of HF treatment(at 40^0C) to eliminate completely the alpha dose from quartz grains. Stokes[65] also mentioned that 40 minutes HF etch to remove non-quartz minerals is not adequate, referring to the cause of scatter in the course of a normalization study. Aitken[1] has described that even for very long etching time it could not be guaranteed that the remaining material would not contain some grains which still carried an alpha contribution, and this resulted also in uncertainty in the beta attenuation factor.

Apart from above different views on the etching behaviour of quartz, measurement has been made with quartz(the average size $\sim$137.5μm) from 'acid-washed sand'(BDH Ltd), assuming spherical grains and isotropic etching. This measurement concerns how much of the quartz surface layer is removed by means of calculation from the loss of weight using different concentrations of HF acid and duration time. The results are presented in Table 3.1. Before the treatment with HF the same tests were performed using water for confirmation that there is no weight loss due to removal of dust from quartz grains or loss of grains during washing. There was no difference between after and before water treatment.

The purity of the quartz after HF treatment was tested by verifying, for some randomly selected samples, that no luminescence was stimulated by exposure to infrared radiation. Any such signal would have indicated the presence of feldspar, the most probable contaminant. However, one should bear in mind that not all feldspar minerals exhibit infrared stimulated luminescence[66].

For the etching in the hope of removal of feldspar grains, extended (30~50 hours) etching using fluorosilicic(H_2SiF_6) acid has been recommended as a technique for removing any residual feldspathic minerals after HF treatment[67]. A similar experiment as in HF treatment mentioned above was made with different concentrations of H_2SiF_6 acid(20~25 wt. % solution on water)[1] by adding water and varying duration time, assuming the same condition as above. Table 3.2 shows the results. For confirmation of feldspar removal, 100mg of microcline feldspar was treated with 33% dilute H_2SiF_6. No feldspar was detected after 18 hours.

Quartz treated following the above procedure was rinsed with 3N HCl to remove fluorides formed during HF treatment and then washed by water. After drying, the quartz was deposited as a monolayer onto stainless steel discs with a thin coating of silicone oil. Fig. 3.1 is the schematic outline of the procedure used for quartz separation in this study.

3.2 Preheating

Over the relevant geological time period, thermally-unstable(or 'shallow') trapped electron populations are not retained, but they are re-created during the laboratory irradiations required for equivalent dose determination. If this unstable component is not removed, the equivalent dose, and hence the age of the sample, will be underestimated. Therefore, emptying of these is necessary before dating measurements can be made. Basically, there are two possible methods which could be used to remove this unstable charge population; one is by means of the optical bleaching of the thermally unstable component by choosing a suitable wavelength, the other is the use of the thermal treatment, so called 'preheating', for this purpose.

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[1] quoted by specification on the bottle

Table 3.1. The degree of etching for quartz(~137.5μm) for different concentrations of HF and different duration time

HF	Time	Sample mass(mg) before HF	Sample mass(mg) After HF	Average outlayer(μm) removed after HF
40%	40min	101	67	10.3±1.9
		80	47	
		126	75	
40%	1hr	102	50	13.8±1.4
		86	44	
		114	60	
48%	40min	101	41	17.6±1.6
		121	51	
		108	44	

* Error is due to both variations of grain size and scatter of measurement.

Table 3.2. The degree of etching for quartz(~137.5μm) by H_2SiF_6(20~25 wt. % solution in water, average 22.5%) treatment

H_2SiF_6	Time	Sample mass(mg) before H_2SiF_6	Sample mass(mg) After H_2SiF_6	Average outlayer(μm) removed after H_2SiF_6
H_2SiF_6 (22.5%)	2hr	97	93	1.6±0.2
		101	95	
	4hr	100	88	2.6±0.3
		101	91	
Dilute(33%) H_2SiF_6 (22.5%)	24hr	101	98	0.7±0.1
		97	94	
	48hr	100	97	0.6±0.1
		100	98	

* Error is due to both variations of grain size and scatter of measurement.

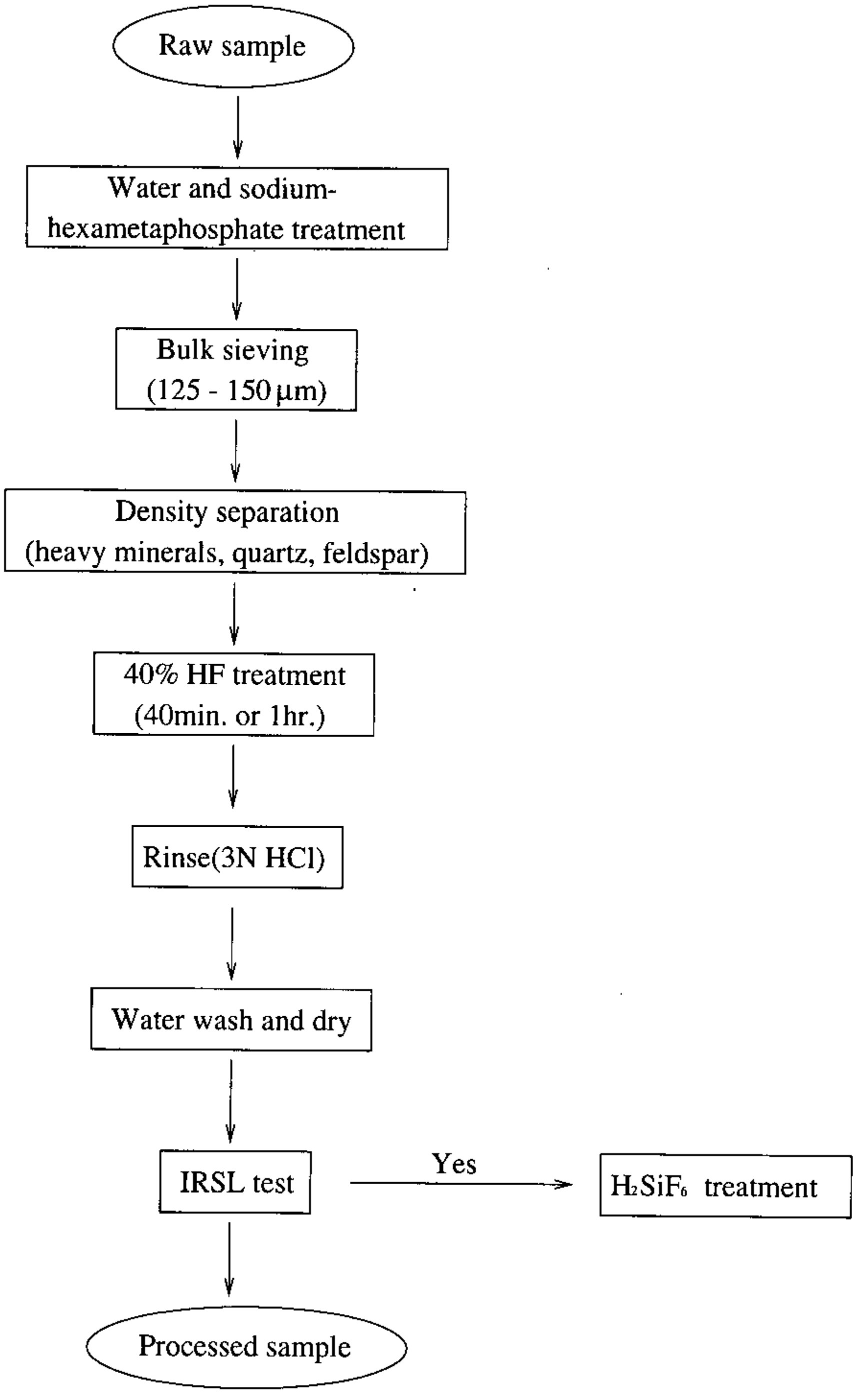


Figure 3.1. A schematic diagram of the procedure used for quartz separation.

Spooner et al.[18] attempted to use an exposure to long wavelength illumination in the hope of removal of unstable charge populations with quartz from sediment deposits. The result gave no encouragement to the notion that these unstable components can be emptied without depletion of the 325^{0}C traps. Additionally, trials to isolate specific wavelengths of light for selective optical bleaching of thermally unstable electrons have been unsuccessful[68].

As a result, the use of preheating for removal of thermally unstable charge has been universally employed. Since the introduction of 250^{0}C preheating for quartz samples in the first demonstration of optical dating by Huntley et al.[10], two typical preheatings for quartz have been generally used, 5 minutes at 220^{0}C[69] and 16 hours at 160^{0}C[46].

There has been some debate on equivalent dose determined by optically stimulated luminescence between the two preheatings for coarsed-grained quartz sample. Roberts et al.[70] suggested that a short preheating time at temperatures above 200^{0}C(i.e. 220^{0}C/5minutes) produces correct equivalent dose, whereas long preheating time at temperatures below 200^{0}C(i.e. 160^{0}C/16hours) results in equivalent dose underestimation, when comparing with the age obtained by thermoluminescence dating and by ^{14}C dating of associated charcoal. However, it has since been reported that there is no tendency for one or other of the preheating regimes to give a systematic over or under estimation, by intercomparison of long versus short duration preheating on 45 samples which range from a few hundred to approximately 125000 years[71][72].

The determination of appropriate preheating temperature is based on the change of the optically stimulated luminescence signal or the erosion of the associated thermoluminescence peak with increasing the temperature. One method for this, suggested by Huntley et al.[10], is the plateau test in which a series of additive equivalent dose determinations are made with preheatings of increasing duration or temperature until a plateau of equivalent dose values is obtained. This approach was applied to Heliki samples in this study(see chapter 6), using a preheating temperature of 220^{0}C.

Rhodes[69] observed that the optically stimulated luminescence level of the quartz given a laboratory beta dose decreases with increasing preheating temperature up to around 100^0C, which can be interpreted as being due to the removal by the heating of a component of the optically stimulated luminescence which has a low thermal stability, but there is a subsequent increase in optically stimulated luminescence from around 140^0C until 210^0C in both natural and laboratory-irradiated quartz, of particular significant in the latter quartz. He suggested that the increase is due to transfer of charge to easily bleachable, thermally stable, traps from traps which are less stable and harder-to-bleach, and that the smaller increase in optically stimulated luminescence of the natural sample is presumably because the lower stability traps are empty due to natural thermal fading during burial. This phenomenon is referred to as 'thermal transfer'(, or recuperation Type C ; Aitken[73], see section 3.4 for details). Similar observations can be found elsewhere [9][46][54][74].

As a result, the preheating is an indispensable process for optically stimulated luminescence dating because, for a laboratory-irradiated sample it simulates the thermal transfer, the removal of charge from unstable traps as well as the charge redistribution, which occurred for the natural sample during the period of burial.

3.3 Normalization

When measurements on many aliquots are used for estimating an equivalent dose, aliquot to aliquot scatter is observed because the aliquots, in practice, are not usually sufficiently homogeneous nor equal in radiation dose to luminescence conversion efficiency. The luminescence variations from those intrinsic causes which can be explained in terms of the differences in the physical characteristics between aliquots(such as different trap and recombination center concentrations, transparency and extents of bleaching at deposition) should be compensated in order to achieve accurate equivalent dose assessment; the normalization should precede determination of equivalent dose.

Several normalization methods, most of which were originally developed for thermoluminescence dating, have been tested and employed in quartz[65]. Weight(or mass) normalization, that is the normalization of sample aliquots by dividing the luminescence signal from each aliquot by its weight, is problematic in conventional thermoluminescence dating[1] and has been equally unsatisfactory in quartz optically stimulated luminescence applications [56][68]. For most cases this lack of success has been explained in terms of the difference of the light collection efficiency between aliquots, in the way in which the sample is spread, and more importantly the variations in the brightness of grains [56][75][76]. The reason for the latter is that because the luminescence signal is derived from only bright grains which constitute a small part of each aliquot, the mass of the aliquot is not directly proportional to the intensity of the optically stimulated luminescence.

Alternatively, normalization may be achieved by the use of the luminescence intensity resulting from a brief exposure of each natural sample to stimulating light prior to the addition of any laboratory dose(so-called 'natural normalization'[11]). The brief normalizing exposure must be so short as not to affect significantly the total optically stimulated luminescence signal. The natural normalization is a very attractive approach, not only because the normalization signal is primarily derived from the same traps as those used for the equivalent dose determination, but also because the examination of scatter in a growth curve gives information about the completeness of bleaching at deposition[56]. Indeed this procedure has been much used with the infrared stimulation of feldspar[21][77]. However the accuracy achievable from natural normalization must become less as the natural dose approaches zero and the method cannot be applied to investigations of the dose response properties of bleached materials. In these circumstances normalization must be by an appropriate second measurement on the sample and Stokes[46], using an argon ion laser for stimulation of young quartz, reduced the luminescence to about 1% of the initial value and then applied a dose of 5Gy to each sample for normalization(so-called 'dose normalization').

The concern in this section is with one particular aspect of dose normalization for additive dose optically stimulated luminescence dating, namely sample to sample normalization when stimulating quartz of low natural dose with green light. Variations on second dose normalization are compared, involving the use of light or heat for bleaching before the second dose and looking for any indication of second dose sensitivity being dependent on the magnitude of the first dose.

3.3.1 The samples and measurement system

The quartz samples(~125μm) were prepared from BDH "acid washed sand" treated according to the procedure outlined in fig. 3.1. Some of the quartz was bleached by exposure to daylight for at least one week and some by heating for 5minutes at 500°C before further use. The multi-sample system equipped with the original 16 green light emitting diodes[23] was used for the measurements(see section 2.4 for details).

3.3.2 Method of measurement

First of all for each sample the time independent signal due to scattered light and photomultiplier noise was measured. A beta dose was then given, the sample preheated for 1minute at 220°C to remove any unstable signal component and the luminescence measured. A 100s exposure time to the green LEDs was chosen for the bleached quartz and a 12.5s for the heated quartz. This was repeated for three samples for each dose and for eight doses ranging from 12.5Gy to 175Gy and the samples were then normalized to generate a growth curve showing the dependence of luminescence on dose. A separate set of 24 samples was processed in this way for each of the normalization procedures considered.

Normalization required that the samples be bleached prior to application of the normalizing beta dose and bleaching was either by placing the samples in a Honle SOL-2 "solar simulator" for an hour or by heating the samples to 450°C for 1minute. The sensitivity to the normalizing beta dose might depend on the dose to which the samples had been exposed before bleaching, as can occur in the case of thermoluminescence[1]. To allow for this possibility the normalized dose response was compared for samples which had a second beta dose added to bring all to the same total dose before bleaching, with samples which had not; this was applied in both the SOL-2 and the heat bleaching procedure. In addition to these four normalization methods, one further procedure was investigated, based on a "single aliquot" approach developed for infrared stimulation of feldspar[25][62] and tested to a limited extent with green stimulation of quartz[55]. In this variant, each sample had a second beta dose added so that the sum of the two beta doses equalled the maximum beta dose applied to any of the set of samples to be normalized. The sample was then preheated, read and compensation applied in the single aliquot manner for loss of signal due to the first preheating and reading(see chapter 4 for detail). This can be mathematically expressed as

$$N = I_1 + I_2 + I_1(1 - r) \tag{3.1}$$

where N is a normalization factor, I_1 is a response from the first beta dose for constructing an additive growth curve, I_2 is a response from the second beta dose for a normalization and r is a ratio for the loss of signal due to the first preheating and reading.

3.3.3 The normalized dose response measurements

(a) Quartz bleached by daylight

Following the procedures outlined above, dose response curves for quartz initially bleached by daylight have been constructed using four different normalization methods(fig. 3.2).

- The first procedure adopted is that samples were brought to the same total beta dose(175Gy) before bleaching in the SOL-2 and application of the normalizing dose, indicated by squares in fig. 3.2.

- The second method used is that samples were brought to the same total beta dose(175Gy), preheated and read for normalization with correction in the single aliquot manner, indicated by circles(which are indistinguishable from the squares on which they are superimposed) in fig. 3.2.
- The third method used is that samples were bleached in the SOL-2 without bringing to the same total beta dose and the normalizing dose applied, indicated by upward pointing triangles in fig. 3.2.
- The final attempt is that samples were brought to the same total beta dose(175Gy) then bleached by heating to 450°C before application of the normalizing dose, indicated by downward pointing triangles in fig. 3.2.

Each point in fig. 3.2 represents the mean of three measurements while the error bars indicate the spread in the measurements. It is immediately clear that one of the methods of normalization, involving heating of the samples to 450°C before applying the normalizing dose, is not successful in reducing the scatter in the data. It is indicated that in bleached quartz the ratio of the sensitivity change between aliquots after annealing is not constant, showing larger scatter in the higher dose region. The two procedures which involved giving all samples an equal dose before normalization, one with bleaching by the SOL-2 and the other developed from the single aliquot approach, show an essentially identical dose response with little scatter in the normalized data. The procedure in which the samples were not given equal doses before bleaching and normalization gives a response which shows little scatter but falls below the others. This could be due to the sensitivity after bleaching increasing with previous dose. That preheating can cause thermal sensitization analogously to the thermoluminescence pre-dose effect has been observed by Godfrey-Smith[17]. The data in fig. 3.2 were measured with a 100s exposure time to the green LEDs. The more encouraging normalization procedures, that is excluding the one involving 450°C heating as a bleach, were investigated further using green light measurement times of 50s and 12.5s

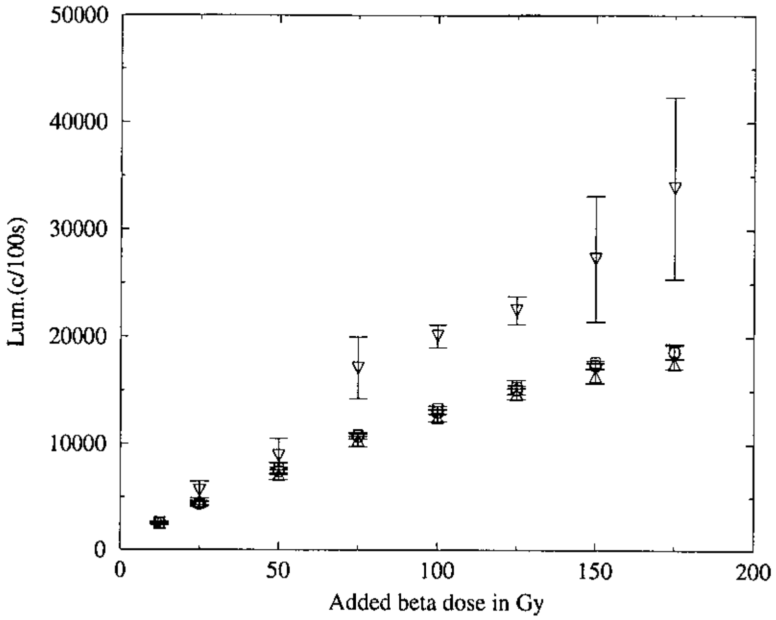


Figure 3.2. The dependence of the green light stimulated luminescence on beta dose for quartz previously bleached by daylight. (1) samples were brought to the same total beta dose before bleaching in the SOL-2 and application of the normalizing dose, indicated by squares. (2) samples were brought to the same total beta dose, preheated and read for normalization with correction in the single aliquot manner, indicated by circles(which are indistinguishable from the squares on which they are superimposed). (3) samples were bleached in the SOL-2 without bringing to the same total dose and the normalizing dose applied, indicated by upward pointing triangles. (4) samples were brought to the same total beta dose then bleached by heating to 450°C before application of the normalizing dose, indicated by downward pointing triangles. A 100s exposure time to the green LEDs was used.

with the results shown in figs. 3.3 and 3.4. It is interesting to note that the predose effect is more noticeable in shorter measurement time.

These measurements confirm that the two procedures which involved giving all samples an equal dose before normalization show an essentially identical dose response with little scatter in the normalized data, while the procedure in which the samples were not given equal doses before bleaching and normalization gives a response which falls below the others.

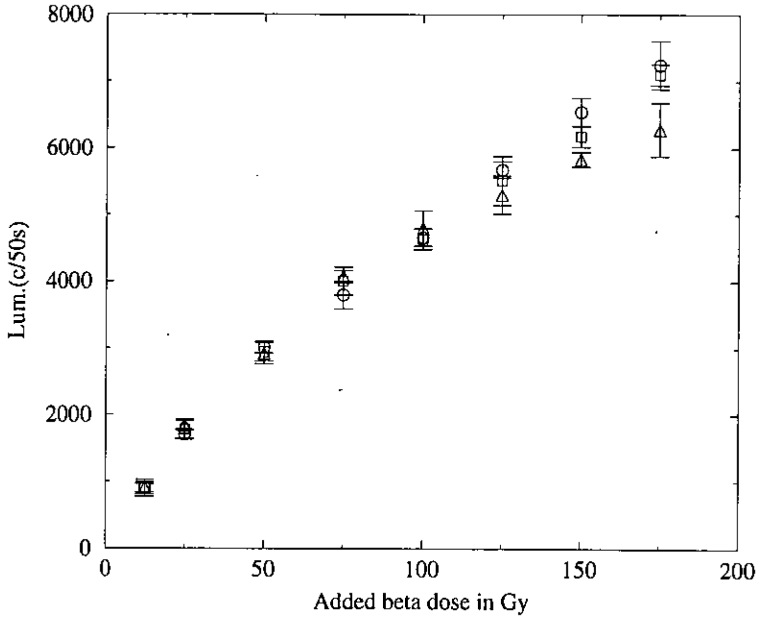


Figure 3.3. As fig. 3.2 but for 50 seconds green light stimulation, omitting the least successful normalization procedure involving heating to 450°C.

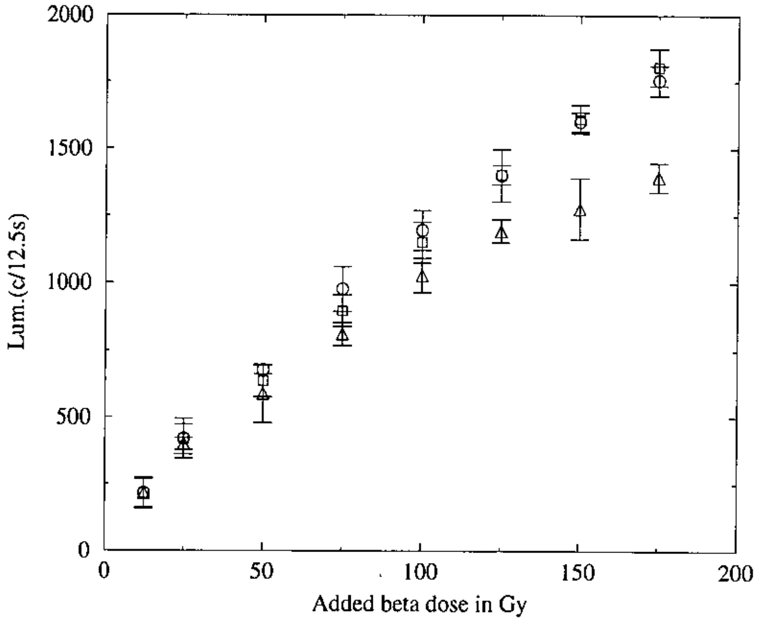


Figure 3.4. As fig. 3.3 but for 12.5 seconds green light stimulation.

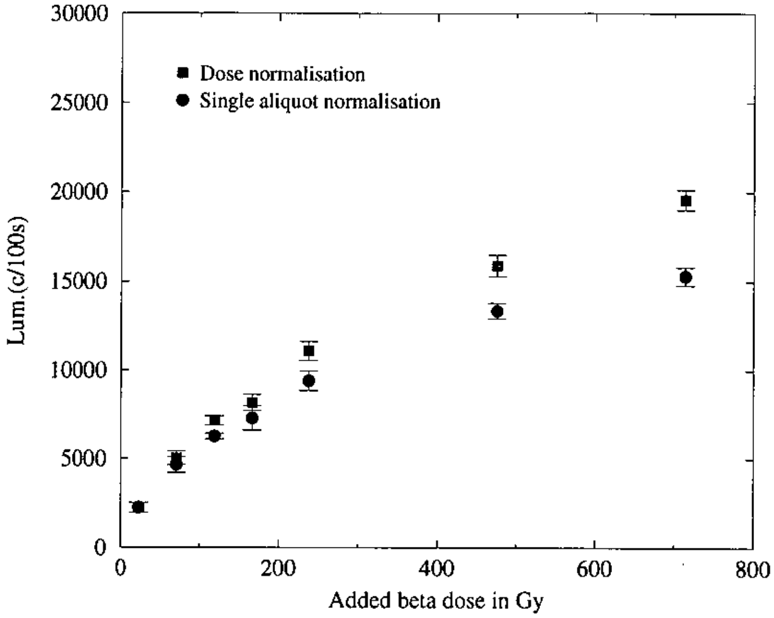


Figure 3.5. The dependence of the green light stimulated luminescence on beta dose for quartz previously bleached by daylight, as in fig. 3.2 but extending to higher doses at which saturation becomes more significant.

However extending the investigation to higher doses at which saturation becomes more significant shows that normalization based on measurements corrected in the single aliquot manner is no longer satisfactory. An example of additive growth curve using those two different normalization procedure is displayed in fig. 3.5. Indicated by squares are samples which were brought to the same total beta dose(720Gy) before bleaching in the SOL-2 and application of the normalizing dose. Indicated by circles are samples which were brought to the same total beta dose(720Gy), preheated and read for normalization with correction in the single aliquot manner. As shown in fig. 3.5, the difference in the results from the two normalization methods is noticeable in the high additional dose region showing a saturating response. The reason for this is discussed in chapter 5. As a result, the normalization approach based on single aliquot technique is strictly applicable only when the luminescence response to dose is linear.

(b) Quartz bleached by heating at 500°C

The tests on quartz initially bleached by daylight should be relevant to sediment dating; for completeness, similar tests were carried out on quartz which had all luminescence removed by heating, which should be relevant to the dating of pottery. Five different normalization procedures have been investigated and results shown in fig. 3.6.

- The first procedure used is for samples that were brought to the same total beta dose(175Gy) before bleaching in the SOL-2 and application of the normalizing dose, indicated by squares in fig. 3.6.
- The second method used is for samples that were brought to the same total beta dose(175Gy), preheated and read for normalization with correction in the single aliquot manner, indicated by circles in fig. 3.6.
- The third method used is for samples that were bleached in the SOL-2 without bringing to the same total beta dose and the normalizing dose applied, indicated by upward pointing triangles in fig. 3.6.
- The fourth method is for samples that were brought to the same total dose then bleached by heating to 450°C before application of the normalizing dose, indicated by open circles in fig. 3.6.
- The final attempt is for samples that were bleached by heating to 450°C without being brought to the same total beta dose before normalization, indicated by downward pointing triangles in fig. 3.6.

Each point in fig. 3.6 represents the mean of three measurements while the error bars indicate the spread in the measurements. In fig. 3.6 the data were measured with a 12.5 seconds exposure time to the green light because of the greater sensitivity of previously heated quartz. Note that due to overlap not all symbols are individually distinguishable.

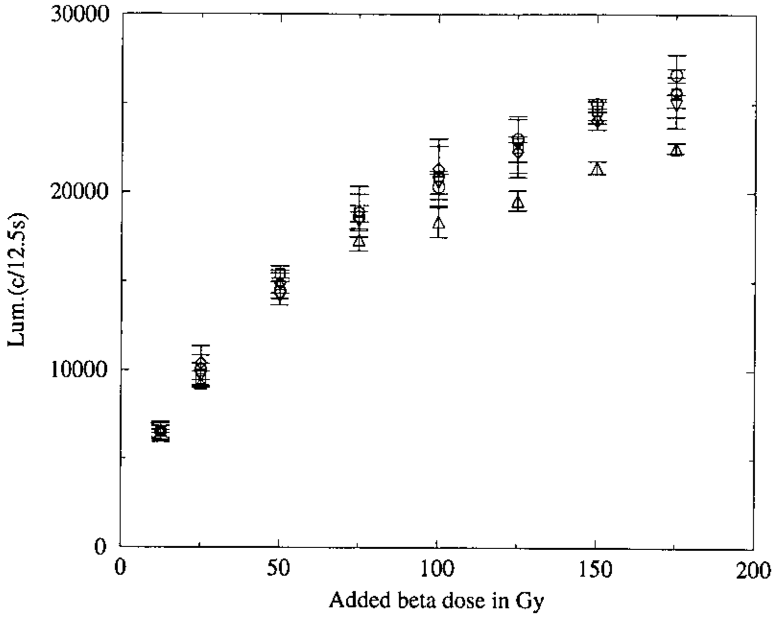


Figure 3.6. The dependence of the green light stimulated luminescence on beta dose for quartz previously bleached by heating to 500°C. A 12.5s exposure time to the green LEDs was used.

Considering the scatter in the normalized luminescence values there is nothing to choose between the procedures. Four out of the five procedures give consistent results and only the procedure in which the samples were not given equal doses before bleaching by the SOL-2 and normalization gives a response which differs by falling below the others. This procedure showed the same tendency in the tests on daylight bleached quartz in fig. 3.2, fig. 3.3 and fig. 3.4. The initially heated quartz behaved differently from the initially daylight bleached quartz discussed in section above when heating to 450°C was used as a bleach prior to application of the normalizing beta dose, in that entirely acceptable normalization resulted(compare fig. 3.2 and fig. 3.6). Further, when 450°C heating was used as a bleach the normalization was not dependent on whether the samples had received the same dose before normalization, in contrast to the situation when the SOL-2 was used for bleaching.

It is interesting to point out that the dose response curves for the daylight bleached quartz show a different relationship between luminescence and dose from those for the 500°C heated quartz. Initially the response of the former is approximately linear, up to 25Gy say, whereas the latter is clearly non-linear in this region, which is quite analogous to the previous result of Galloway[24]. A slightly supralinear dose response has been observed in the region of less than about 2Gy for heated quartz[78]. It is also worth while to note that in bleached quartz, after preheating the dose response does not give zero optically stimulated luminescence at zero added dose which can be explained in terms of incomplete emptying of the optically stimulated luminescence traps during the bleaching, and/or more possibly recuperation of the optically stimulated luminescence signal(recuperation Type A or C[57]).

3.3.4 Conclusions

Two alternative normalization methods were investigated for quartz zeroed initially by daylight and heating. They were dose normalization and normalization based on a single aliquot approach.

As a result, normalization involving sample bleaching by SOL-2 prior to application of the normalizing dose was successful on both types of quartz provided all samples had been given the same total dose before bleaching. However, normalization involving bleaching the sample by heating prior to application of the normalizing dose was only successful for quartz which had been zeroed originally by heating irrespective of equal pre-dose before bleaching. Finally a variant of the single aliquot method also provided a successful procedure for normalization.

3.4 Recuperation

Although optically stimulated luminescence has a very much lower signal level than with thermoluminescence after exposure to light, there still exists a residual signal.

This component can be divided into two parts ; one is the component that is not completely bleached during the process of deposition, the other is the component which has developed subsequent to deposition. The former can be detected by means of the shine-plateau test[10], namely if the bleaching at deposition is insufficient to empty traps the equivalent dose will progressively increase with longer shine-time due to sampling of the optically stimulated luminescence from poorly bleached traps. The component which has developed subsequent to deposition is referred to as recuperation, the optically stimulated luminescence signal increasing during subsequent storage or preheating [11][57][73][79].

Aitken[73] mentioned the recuperation signal from quartz and classified it by three types, Type A, B and C. He proposed that the Type A recuperation is produced due to some transfer of charge from bleachable traps(responsible for the dating signal) to shallow, unbleachable traps during optical bleaching with retrapping in the dating traps during preheating or storage. Therefore the optically stimulated luminescence level after bleaching increases and is substantially reduced by successive cycles of bleaching because of loss of charge during the repeated transfer processes. However, even if an attempt is made to produce a zero optically stimulated luminescence signal sample through heating to above 325^0C, a signal still remains. This Type B recuperation is interpreted as due to the charge in deep, hard to bleach traps either undergoing a sensitization(as with the 110^0C pre-dose effect for quartz in thermoluminescence) or a redistribution of the charge into deep, easy to bleach traps. The Type C recuperation is due to thermal transfer from unbleachable traps into the bleachable dating traps by preheating, so that the signal increases as progressively higher preheating is administered. Rhodes[69] suggested that this type recuperation presumably occurs while the sample is buried.

The recuperation for quartz has been reported approximately equivalent to a dose of the order of 1Gy[57][69]. Also, it has been reported that only for fairly young sites is the recuperation liable to be relevant. Rees-Jones[80] investigated the recuperation of the infrared stimulated luminescence signal for feldspar(varies from 0.58Gy to 1.21Gy) and concluded that the recuperation is mainly due to preheating, but is not developed significantly at room temperature.

In this section the recuperation for quartz bleached by daylight and heated quartz was briefly investigated.

3.4.1 Samples and measurement system

The coarse grained quartz(~125μm) was prepared with the procedure described in section 3.3.1. The measurement was made with the same multi-sample automatic system as used in section 3.3, except for replacing the original green light emitting diodes by new green light emitting diodes(see section 2.5).

3.4.2 Measurement and result

First of all the recuperation for the quartz initially zeroed by daylight was investigated. This investigation is primarily for the recuperation Type C. Since the quartz samples used were bleached, any equivalent dose(see section 3.5) deduced from an additive dose growth curve must result from recuperation. The conventional multiple aliquot additive dose method was used to construct the growth curve, over a dosage range from 0 to 32Gy. Preheating was for 5 minutes at 220^{0}C and the measuring time 1s. Fig. 3.7(a) shows the growth curve to determine the equivalent dose due to the recuperation for the bleached quartz. The recuperation was 1.5±1Gy when the level of recuperation was expressed as a dose equivalent.

A similar approach has also been made in respect of the heated quartz. This measurement was aimed at examining the recuperation Type B. The growth curve was made in the same dosage range as in the bleached quartz(fig. 3.7(b)) and the equivalent dose resulting from the recuperation effect was then determined. The recuperation was 0.6±0.8Gy when the level of recuperation was expressed as a dose equivalent.

Each point in fig. 3.7 represents the mean of three measurements while the error bars indicate the spread in the measurements. The data points were fitted by the single saturating exponential function(eq. (3.3), see section 3.5).

As a result, the recuperation in the bleached quartz showed a similar value to those published before[57][69].

The recuperation of the heated quartz showed a smaller effect(statistically insignificant) than that of the bleached quartz. It implies that the recuperation Type B for the quartz used is not significant compared with the recuperation Type C.

3.5 Equivalent dose determination

The equivalent dose determination is an essential aspect of the calculation of an age(eq. 1.1). One method for the evaluation of equivalent dose is that after measuring the natural signal all portions of sample are bleached, laboratory doses are administered to construct a growth curve and then the natural signal is interpolated to the dose axis(so called 'regeneration method'). The regeneration method has the advantage that besides being the simplest and easiest approach, it is not necessary to make an intercept correction which may occur in the additive dose method due to nonlinear growth(see below). However, a drawback of this technique is the possibility that laboratory bleaching is accompanied by change of sample's luminescence characteristics[65], so that the regenerated growth does not truly reproduce the growth during antiquity.

Alternatively, equivalent dose can be assessed by the additive dose growth curve, which can be produced by giving progressively higher doses in addition to the natural dose, with extrapolation of the growth curve towards intersection with the dose axis(so called 'additive dose method'). For an accurate dating, the equivalent dose value obtained from the additive dose growth curve may require an intercept correction to allow for any supra-linear growth and for any residual signal[81]. As a technique to avoid this correction, Prescott et al.[82] has described the "Australian slide method" based on the regeneration method.

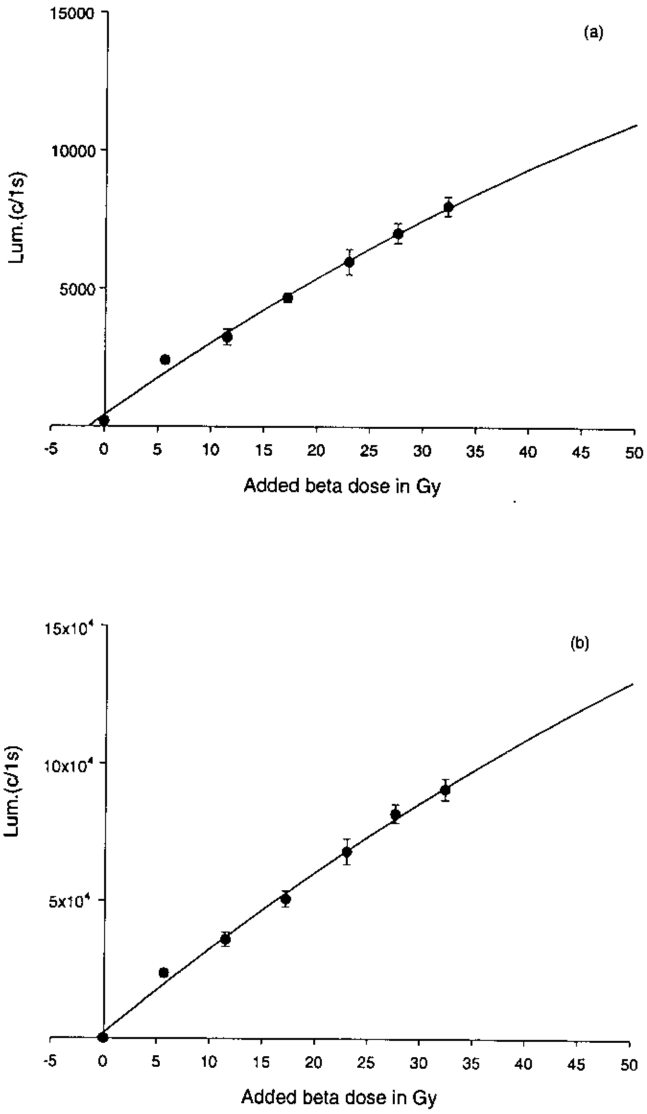


Figure 3.7. The additive growth curve for the recuperation effect for the bleached quartz(a) and the heated quartz(b).

In adopting the additive dose method for the equivalent dose determination, it is very important to find a function which adequately describes the form of the growth curve. Various approaches, which were originally developed for thermoluminescence dating, have been discussed. Three functions for fitting of growth data were investigated in this study.

The simplest form is the linear fitting of the growth curve, which can be described as

$$L = m(\beta + E_D) \tag{3.2}$$

where L is the luminescence intensity measured for an added beta dose β, E_D is the initial dose(equivalent dose) to be deduced from fitting a set of measurements with zero initial dose and m is a constant of proportionality.

This approach is very convenient when the experimental data does indeed behave linearly. It has been reported that the application of linear fitting has produced internally more consistent results than that of exponential curve fitting[83][84]. Conversely, Rhodes[69] has discussed that with increasing laser exposure time a linear fit produces a steady increase in equivalent dose value while exponential extrapolation gives a constant. Grun[85] also suggested that the linear fitting should be avoided in dating studies because it results in larger systematic and random errors over a very wide range of the dose response curve, although the systematic application of linear fitting may under certain circumstances produce internally more consistent results than exponential fitting. In order to reduce the applicable possibility of linear fitting, he recommended to avoid the term "apparent linear part" of the dose response curve.

As a rule, the growth curve exhibits a significant nonlinear response in old samples or high irradiation dose region since the electron traps contributing to the luminescence signal become filled. Therefore, the approach of a single saturating exponential function has been introduced[86]. The function can be represented as

$$L = a[1 - exp\{-b(\beta + E_D)\}] \tag{3.3}$$

where the term b was determined from fitting a set of measurements with zero initial dose and a is a constant of proportionality for the purpose of fitting.

Alternatively, the utilization of a single saturating exponential with the optional addition of a linear term was suggested to accommodate a steady increase at large dose in the growth curve, which can be explained in terms of the creation of new traps simultaneously with trap filling during artificial irradiation in thermoluminescence[32][82][87][88]. Prescott et al.[82] have mentioned that this model is satisfactory over a wide range of samples.

Using equation (3.3), the modified fitting function can be expressed as

$$L = a[1 - exp\{-b(\beta + E_D)\}] + m(\beta + E_D) \tag{3.4}$$

where m is a constant of proportionality for the purpose of fitting.

The equation (3.4) may represent continual creation of defects throughout the burial history[89]. The usual assumption of defect creation is that it is not significant except at very high doses, so that the dose response curve does not exhibit saturation at high applied doses. This implies that the mechanism of the trap-filling and emptying processes are generally more complicated than those described by only one or two traps because of the occurrence of processes such as competition during read-out and irradiation, charge transfer or trap production and destruction.

As an example, Rees-Jones[90], in a dating study of fine grain quartz extracted from young sediments, mentioned that the equivalent dose determined by the additive dose method was dependent upon the dose range fitted when the growth curve is clearly sub-linear from very low doses. She found a successive reduction of the equivalent dose value obtained by fitting using a saturating exponential function, from 10.4±1.2Gy to 6.0±0.4Gy by removing the highest dose points. However, there was little difference between equivalent dose values after reaching the equivalent dose of 6.0±0.4Gy even if further dose points were removed.

Determination of the natural equivalent dose was simulated using bleached and heated quartz. This simulation involves whether the growth curve obtained is well represented by a selected function. Similar preliminary simulation for quartz samples has been mentioned by Galloway[55] to test the green light emitting diode system for a dating application.

3.5.1 The samples and measurement system

Coarse grained quartz samples($\sim$125μm) were prepared with the procedure described in section 3.3.1. The measurement was made with the same multi-sample automatic system as previously used in section 3.4.

3.5.2 Method of measurement

First of all two different artificial beta doses, 11.5Gy and 23Gy, to be simulated as natural dose were administered to the quartz bleached by daylight and all samples then preheated for 5minutes at 220^0C to remove unstable signal. The measurements were made following the standard procedure of multiple aliquot additive dose method and normalized by dose normalization, as described in the previous section 3.3. A preheating of 5 minutes at 220^0C for all measurements was chosen, along with 1 second green light exposure time. Similar measurements were also carried out on quartz which had all luminescence removed by heating.

Comparison of the given initial dose with the value deduced from the additive dose procedure gives an indication of how well a fitting function used can perform.

(a) Linear fitting

With the bleached quartz samples dosed for simulation, the growth curve was constructed over a dosage range from 0 to 23Gy, which looked an apparently linear response, by adding increments of 4.6Gy beta dose. The simulated equivalent dose was then determined by the linear function(eq. (3.2)) and the results shown in fig. 3.8. The equivalent doses determined were 14.0±0.3Gy and 29.4±0.3Gy. Compared with the actual given initial dose for simulation, the extrapolated dose values were overestimates, particularly so for the higher dose. This suggests that the shape of the "missing part" from zero dose to dose portion given for the simulation in the growth curve is not linear. Similar procedures were applied to the heated quartz and the equivalent doses determined were 13.7±0.4Gy and 31.8±0.7Gy, respectively(fig. 3.9). Similar to the bleached quartz the values were overestimated. It implies that the linear fitting is not suitable to describe the growth curve of either the bleached or the heated quartz used, although the dose response apparently looks linear. Each point in figs. 3.8 and 3.9 represents the mean of the three measurements while the error bars indicate the spread in the measurements.

(b) Single saturating exponential fitting

The same experimental data sets were fitted by the single saturating exponential function(eq. (3.3)) and the results shown in fig. 3.8. Two computer programs were used for fitting of the single saturating exponential function, one was developed by Galloway and the other "SigmaPlot(version 4.0)" commercially purchased. The latter was useful for error analysis. For confirmation of the computer programs used, a test has been made with published data by Berger and Huntley[91] before use(summarized in table 3.3).

As seen in table 3.3, the estimated equivalent doses calculated using the two programs show little difference with published results when the error limits are considered,

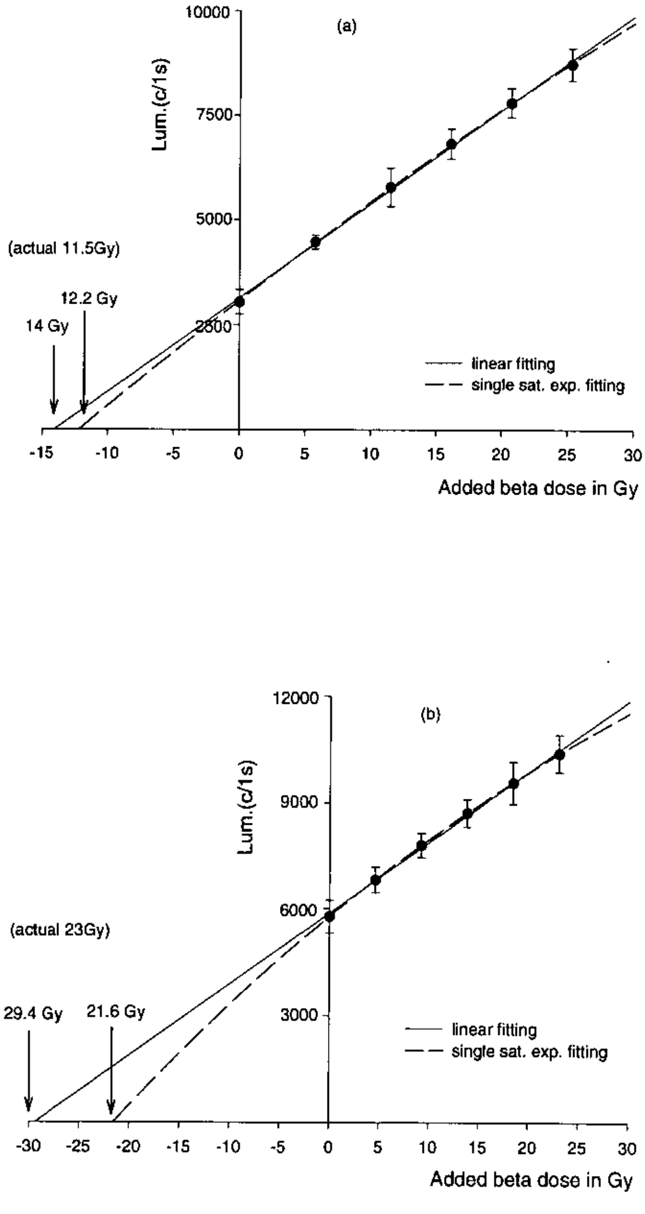
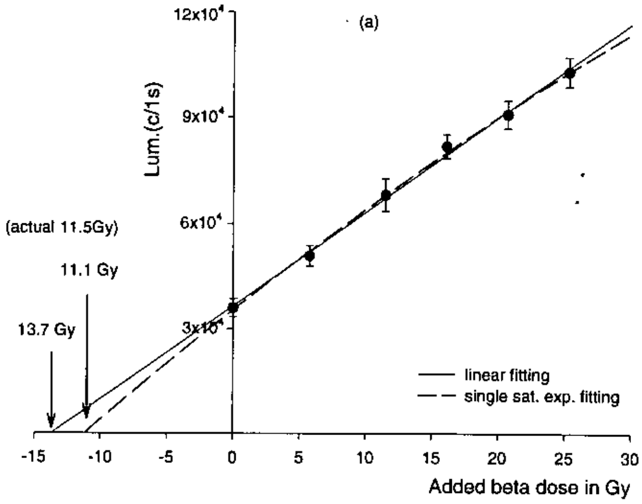


Figure 3.8. Simulated additive procedure applied to two sets of bleached quartz samples, one with an initial beta exposure of 11.5Gy(a) and the other 23Gy(b).



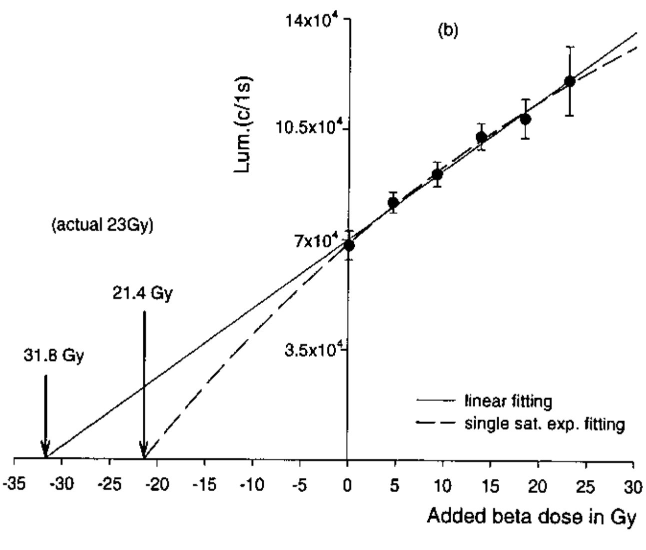


Figure 3.9. Simulated additive procedure applied to two sets of heated quartz samples, one with an initial beta exposure of 11.5Gy(a) and the other 23Gy(b).

Table 3.3. A comparison of the regression analysis of Berger and Huntley with that of programs used, based on the same data published by Berger and Huntley[91]

Data set	Estimated equivalent dose		
	Berger and Huntley(1987)	Galloway	SigmaPlot
QNL 84-2 unbleached(16pt)	123±7	124	125±8
QNL 84-2 bleached(13pt)	193±19	200	208±29
STRB 87-1 unbleached(19pt)	0.58±0.02	0.6	0.62±0.07
STRB 87-1 bleached(16pt)	0.68±0.02	0.6	0.63±0.07

although the two programs used gave a slightly larger equivalent dose value and error. Both programs used were useful in the verification of each result.

Following the encouraging test results for the fitting programs, the simulated equivalent doses were determined in the same dosage region as used in linear fitting. The equivalent doses resulting were 12.2±0.6Gy and 21.6±0.2Gy in the bleached quartz, and 11.1±1.6Gy and 21.4±1.7Gy in the heated quartz. This fitting is clearly more satisfactory than the linear fitting although it gave a relatively larger error in the heated quartz.

More measurements have been made to investigate whether the extrapolated equivalent dose value depends on the dosage range. Increments of 23Gy beta dose were added up to 184Gy, fig. 3.10. The equivalent dose was determined for each increase of 23Gy in dose range. Table 3.4 and fig 3.11 show the equivalent dose values determined from each dose range. As seen in fig 3.11, the equivalent doses could be considered as a constant value without any particular behaviour until about 110Gy dosage range, but they tend to a steady increase with adding data points from about 110Gy dose range. Although one should consider the spread in the measurements a similar tendency is shown in all cases(fig. 3.11) so this may well reflect a genuine effect. This also confirms the findings of Rees-Jones[90] who discussed dosage range dependence of the equivalent dose. The reason may be that the dose response does not saturate in high dose region(see below).

(c) Single saturating exponential with linear fitting

With small increments of beta dose, growth curves were constructed in the same dose region as discussed above in order to see whether the dose response became saturated in the high dose region(fig. 3.12). For both the quartz samples, while the dose response apparently indicated saturation around the 110Gy dose region, continuing to higher doses showed that saturation did not occur.

Following the assumption of the single saturating exponential with the addition of a linear component, the same data set as used in the single saturating exponential fitting was applied to the modified function(eq. (3.4)). Contrary to the result from single saturating exponential fitting, the value extrapolated was relatively constant in the whole dose range investigated, except for a few values which could be explained as random scatter in the measurements(fig. 3.11). Fig. 3.10 is an example of the equivalent dose determined from different dosage ranges using the single saturating exponential function and the single saturating exponential with the addition of a linear function. The equivalent dose determined by the latter function shows a similar value irrespective of dose range, although it gave a larger error in the extrapolation compared with the former function. In order to reduce the error of the equivalent dose obtained by the single saturating exponential with the addition of a linear component, Berger[87] suggested that considerably more data may need to be generated than for the simple exponential model.

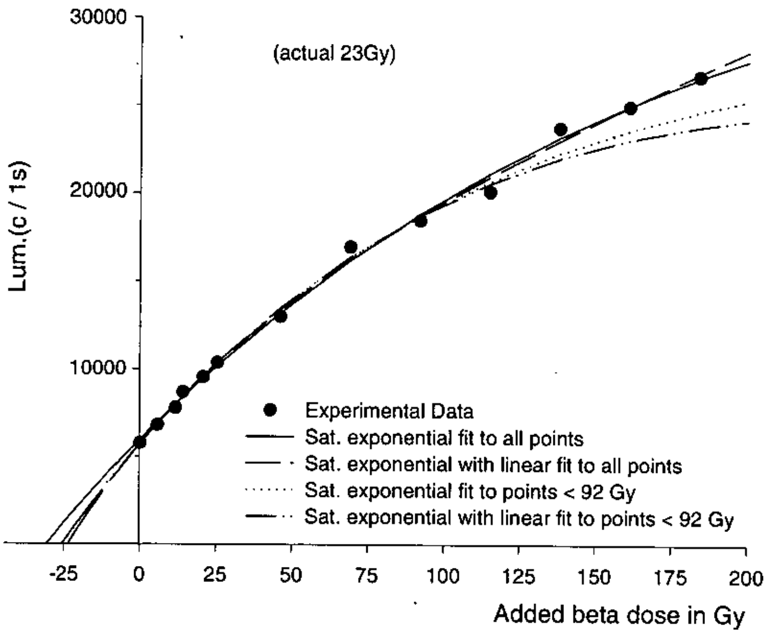


Figure 3.10. An example of growth curve for bleached quartz sample showing all dose points with the curve fits to all dose points and to the dose points below 92Gy. There are four curves; 1) Sat. exp. fitting to dose points < 92Gy(x-axis intercept : 25.1±3.4Gy), 2) Sat. exp. with linear fitting to dose points < 92Gy(x-axis intercept : 21.7±5.8Gy), 3) Sat. exp. fitting to all dose points(x-axis intercept : 33.1±3.6Gy) and 4) Sat. exp. with linear fitting to all dose points(x-axis intercept : 21.5±4.9Gy).

Table 3.4. A comparison the regression analysis using two fitting methods.

Sample	BDH quartz bleached by daylight (BDH heated quartz, 500°C/5min)			
Simulated ED*	11.5Gy		23Gy	
	fitting method			
Added beta dose range	sat. exp.*	sat. exp. lin.*	sat. exp.	sat. lin. exp.
0 ~ 23Gy	12.2±0.6 (11.1±1.6)	11.3±0.8 (11.1±6.4)	21.6±0.2 (21.4±1.7)	20.5±1.1 (21.9±1.5)
~ 46Gy	10.3±0.4 (9.2±0.9)	10.5±1 (9.5±2.2)	18.4±0.7 (20.5±0.9)	19.3±2.4 (20±2.1)
~ 69Gy	12.7±1.6 (10.9±1.5)	8.5±2.1 (8.4±2.1)	27.4±5.2 (27.8±4.4)	18.8±7.4 (27.9±6.2)
~ 92Gy	11.3±1.3 (12.5±1.7)	11.6±2.3 (10.4±1.6)	25.1±3.4 (25.7±2.3)	23.5±4.9 (25.6±8.2)
~ 115Gy	11.4±1.1 (14.4±1.9)	11.5±1.8 (8.5±1.3)	24.4±2.6 (27.7±3.3)	24.6±5.6 (24.6±5.5)
~ 138Gy	12.5±1.3 (15.1±1.7)	10.6±1.7 (11.7±1.5)	31.6±5 (32.2±3.3)	18.5±6.8 (18.5±6.8)
~ 161Gy	14.3±1.8 (16.1±1.6)	9.9±1.7 (10.5±1.5)	32.4±4.2 (32.2±2.6)	19.5±4.5 (19.5±6.2)
~ 184Gy	15.2±1.7 (16.5±1.5)	10.2±1.6 (11.8±1.6)	33.1±3.6 (33±2.3)	23.7±5.8 (23.8±5.9)

1) ED* : equivalent dose, 2) sat. exp.* : single saturation exponential fitting and 3) sat. exp. lin.* : single saturation exponential with linear fitting.

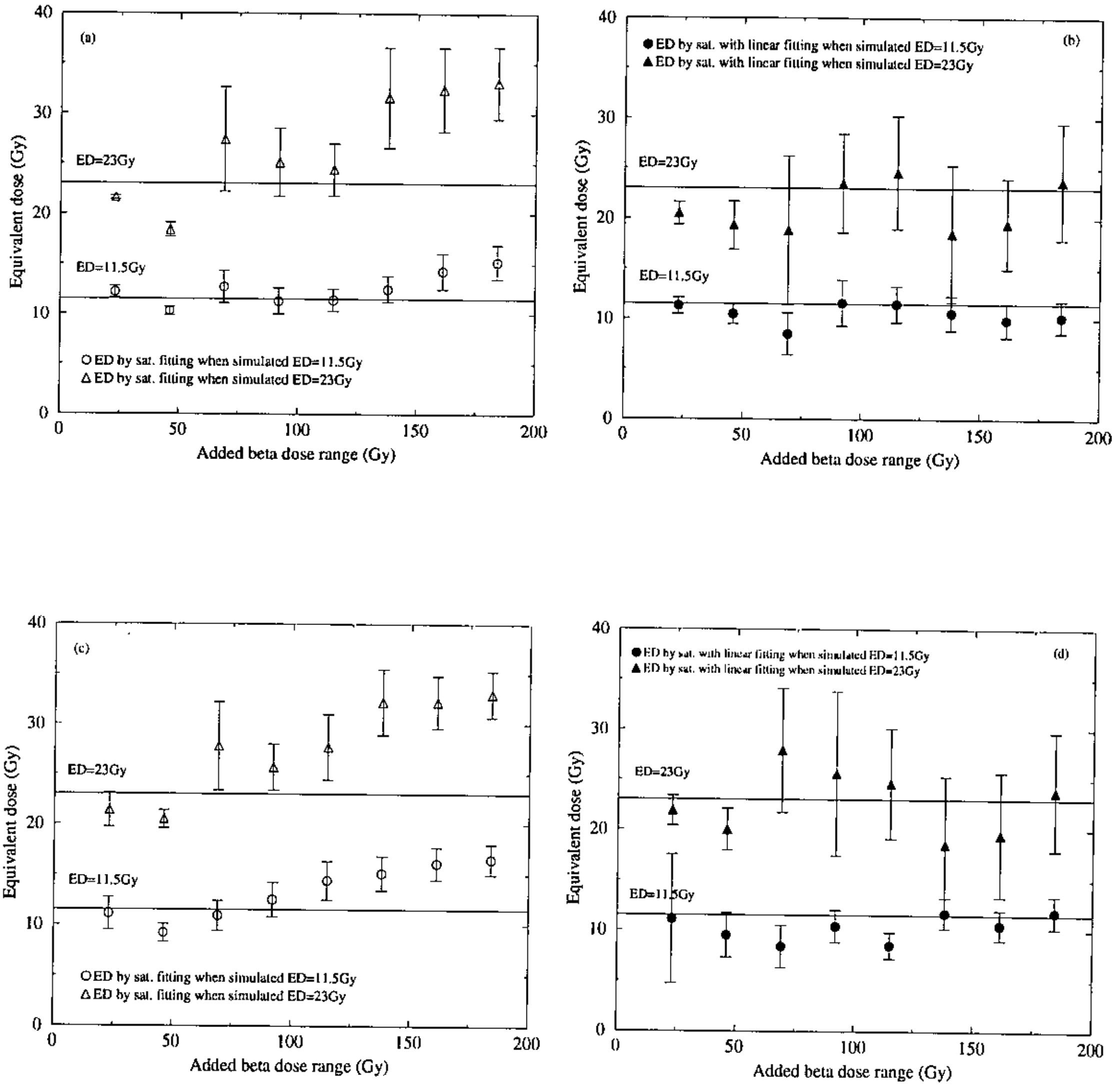


Figure 3.11. The plot of equivalent dose determined using two different fitting functions against selected dosage range, for bleached quartz((a) and (b)) along with heated quartz ((c) and (d)). Figs. (a) and (c) are for the single saturating exponential function and figs. (b) and (d) for the single saturating exponential with linear function.

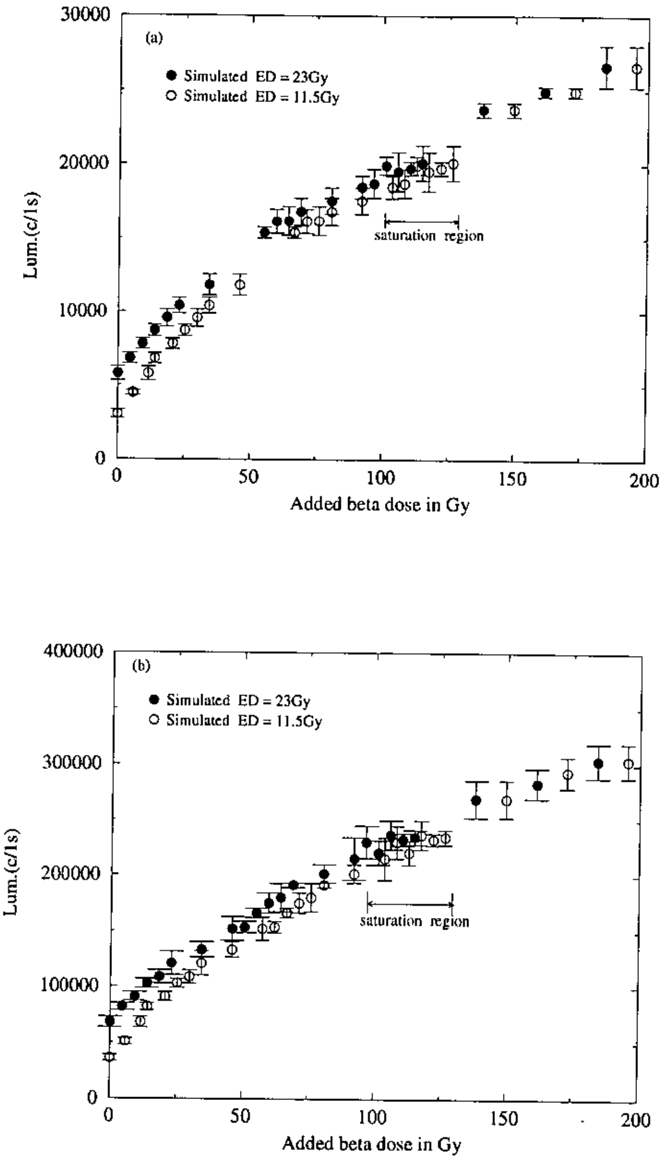


Figure 3.12. The growth curve showing all dose points, (a) bleached quartz and (b) heated quartz. Each point represents the mean of the three measurements while the error bars indicate the spread in the measurements.

3.5.3 Result and discussion

Through the simulated equivalent dose determination, three different functions for fitting of growth data were investigated. The linear fitting gave an overestimated equivalent dose value in spite of superficially showing a linear response on beta dose in the growth curve. It means that apparent linearity in growth curve cannot be generally taken as justification for linear fitting although under certain circumstances, such as a very young sample, it could be considered as a genuine effect.

The single saturation exponential fitting gave an extrapolated values close to the value given initially. However, the size of the extrapolated value was critically dependent on the selection of the maximum irradiation dose. Grun[85] suggested that for the exponential fitting, the selection of a dosage range of D_{max}(maximum irradiation dose) $\approx 10D_E$(equivalent dose) leads to very small systematic and random errors for a wide range of the growth curves. In this study the equivalent dose was close to the given initial dose in dosage range of $D_{max} \approx 10D_E$ when the simulated equivalent dose was 11.5Gy, but in case of the given initial dose of 23Gy the optimum dose range was $D_{max} \approx 5D_E$. In a study of young sediments, Rees-Jones[90] selected the highest dose point of 32Gy for dosage range because the equivalent dose value calculated differed little even if that dosage range was reduced. This case is $D_{max} \approx 5D_E$(The equivalent dose value determined was ~6Gy). It implies that the optimum dose range may vary from sample to sample. For finding of the optimum dosage range a plateau test is suggested for equivalent dose against dose range, as exemplified in fig. 3.11.

Finally, the single saturation exponential with the addition of a linear function gave a similar value to the given initial dose as well as a constant result independent of the dosage range. However, the drawback of this fitting was seen in the somewhat larger error compared to the single saturation fitting. The larger error may result from there being less data in the higher dose part of growth curve, but further study should not be excluded.

Chapter 4

Tests of single aliquot measurement ....

4.1 Introduction

Among the established methods for equivalent dose determination, the additive dose method has usually been employed because the regeneration technique results in sensitivity changes in the sample after bleaching. In adopting the additive dose method, many separate aliquots of sample are required, each aliquot being used only once. Measurements are made of the luminescence from aliquots of the natural sample and also from aliquots to which various radiation doses have been added. The radiation dose equivalent to the luminescence from the natural sample material is then determined by extrapolation. In practice, the 'aliquots' are not usually sufficiently equal in radiation dose to luminescence conversion efficiency, so that aliquot to aliquot normalization is required. This is very time consuming and may bring about an additional source of systematic error.

In the past 10 years attempts have been made to develop a method such that all the measurements necessary for equivalent dose determination can be made on the same single aliquot. Conventional thermoluminescence measurements are not generally suitable as the basis for a single aliquot approach because heating the samples to 400^0C or more involves the complete removal of the signal during measurement and causes the luminescence sensitivity to change[92]. That each reading of luminescence in the optically stimulated luminescence technique may involve only a brief stimulation which removes only a small fraction of the total luminescence available, so called 'partially destructive method', led to the development of the single aliquot method.

Although there were some previous mentions of the possibility of a single aliquot method[10][11][56], Duller[25] was the first to show the feasibility of carrying out the equivalent dose determination using only a single aliquot, considering both additive dose and regeneration methods. The work by Duller[25] was undertaken using coarse-grained potassium feldspar stimulated by infra red. Making all measurements on a single aliquot would have advantages over the conventional multiple aliquot method, as follows.

- Normalization between measurements is not necessary since the same aliquot is used for all measurements.
- The difference in the equivalent dose determined using each aliquot can be a tool to assess the uniformity of bleaching at deposition.
- The amount of sample required for analysis is reduced and a rapid measurement of samples can be provided. The former is of particular importance for archaeological samples in situations where the amount of material available for measurement is limited.
- The effort involved in sample preparation is greatly reduced.

The single aliquot method which Duller[25] favoured was an additive dose method, with correction of the measurements for loss of signal due to repeated preheating and reading of the same aliquot. The essence of the single aliquot additive dose method is that the luminescence due to each component of added dose is reduced by successive preheating and reading in the same way independently of the other components. The information necessary for correction of the additive dose measurements, that is the decay of signal with repeated preheating and reading, is obtained separately on other aliquots of the same sample material. Comparable results have been obtained by an alternative way of determining the correction for compensation for the loss of signal due to successive preheatings and infrared readings[93]. This offers some advantages that enable all the necessary information to be obtained from only one aliquot. Further, Duller[26] has proposed that a different approach, the dose correction method, is necessary if the additive dose curve shows significant nonlinearity.

In contrast to the success of the additive dose procedure, Duller[25] reported that the regeneration-based single aliquot process failed because of changes in sensitivity in the feldspar. Stokes[65] and Mejdahl and Botter-Jensen[63] have attempted to apply a regeneration approach to quartz, but the same conclusion was reached. Work has been done by Mejdahl and Botter-Jensen[63] towards overcoming this problem with regeneration. They developed a new "single aliquot/regeneration and added dose(SARA)" procedure. The method is based on a typical regeneration technique, but at least three different beta doses are given to three aliquots on top of the natural radiation dose before the regeneration is applied to each of them. A graph is plotted of the regeneration equivalent dose obtained from the aliquots against the amount of radiation dose added to it before regeneration and the regression line is then extrapolated for true equivalent dose at zero added dose. The SARA technique was tested by Mejdahl and Botter-Jensen[63] on a number of samples, which were predominantly quartz extracted from heated materials, with ages up to 4000 years and gave good agreement with between the ages obtained using this approach and those by various dating techniques. This technique has an advantage over the Australian slide method[82] because of considering the possibility of a changes in sensitivity after bleaching, but requires that the changes in sensitivity are independent of the dose given before applying regeneration.

Concerning application of the single aliquot additive dose method to the stimulation of quartz and feldspar by green light, Galloway[55] presented a preliminary indication that for heated quartz consistent functional forms resulted for the dependence of luminescence on dose when determined by single aliquot and multiple aliquot methods, but the corrected single aliquot measurements showed an increase in sensitivity with re-use in the case of feldspar[94].

This chapter concerns whether a single aliquot additive dose method, similar to those reported for the infrared stimulation of feldspar[25][26][93] , is successful in the case of quartz stimulated by green light.

Two requirements must be met; the decay of the signal due to repeated preheating and reading should be independent of radiation dose and the luminescence sensitivity should not change during repeated cycles of dosing, preheating and exposure to green light. Regarding the latter, Liritzis et al.[95]and Stokes [65] have reported for quartz that the optically stimulated luminescence incremental sensitivity is not strongly affected by repeated dosing, preheating and reading by green light.

The tests described below are aimed at answering the fundamental question, does the single aliquot method reproduce the same form of relationship between green stimulated luminescence and radiation dose as a conventional multiple aliquot method? The tests were undertaken using the 16 original green light emitting diodes for stimulation and later the 16 new green light emitting diodes developed recently, with quartz bleached by daylight which should be relevant to sediment dating and with quartz drained by heating which should be relevant to pottery dating.

4.2 Tests using the 16 original green light emitting diodes

4.2.1 Equipment and samples

All single and multiple aliquot measurements were made using an automated system[23] equipped with the 16 green light emitting diodes for stimulation, as described in chapter 2.

The quartz samples($\sim$125μm) were prepared from "acid washed sand"(supplied by BDH Ltd) treated with the procedure outlined in chapter 3. On confirming the absence of feldspar contamination, the quartz was divided into two parts. Before measurement some of the quartz was bleached by exposure to daylight for at least one week while the rest of the quartz was heated for 5 minutes at 500°C.

4.2.2 Methodology

First of all for each sample the time independent signal due to scattered light and photomultiplier noise was measured. A beta dose was then given and the sample was preheated for 1minute at 220°C prior to each measurement to remove any unstable signal component. The measurement time of exposure to light from the green LEDs was chosen so as to achieve an adequate yield of stimulated luminescence to ensure that statistical fluctuations in the number of photons counted were not a cause of significant uncertainty (no more than a few percent, say) in the results. It is, however, an assumption of the single aliquot additive dose method that only a small part of the latent luminescence, less than a few percent, is stimulated on each exposure to the green light. In order to meet these criteria, an exposure time of 100s was chosen for measurements on the daylight bleached quartz. For measurements on the heated quartz, because of its greater sensitivity, a time of 12.5s was chosen. The optical power at the sample with the original green LED system is two orders of magnitude less than with a typical argon ion laser system, consequently the measurement time required with the LED system is about 100 times that required with a laser[24].

The sequence of beta dosing, preheating and measuring was repeated for eight doses ranging from 12Gy to 167Gy to generate a growth curve using a single aliquot, as exemplified in figs. 4.5 and 4.6.

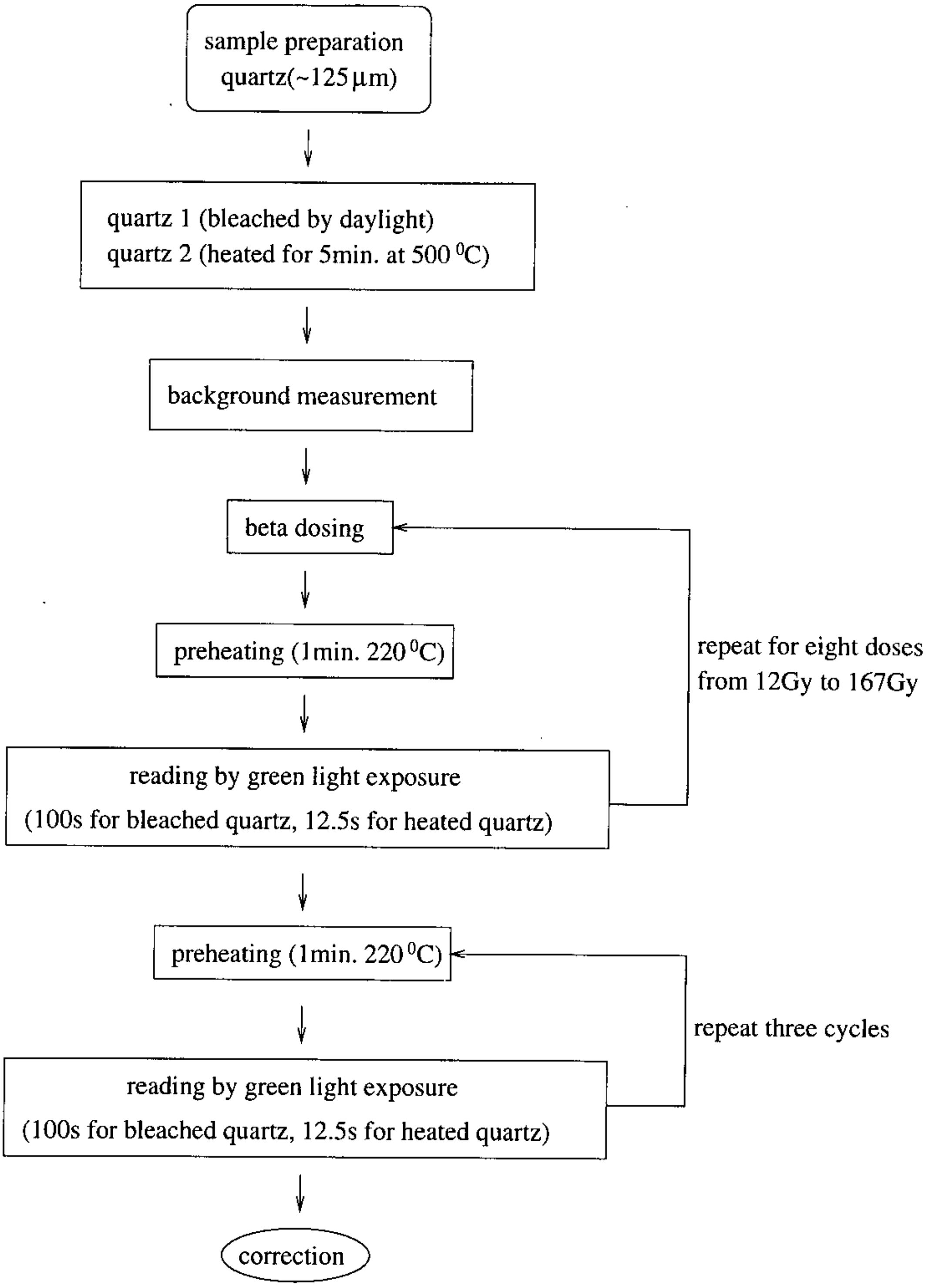


Figure 4.1. A schematic diagram of the procedure used for single aliquot measurement.

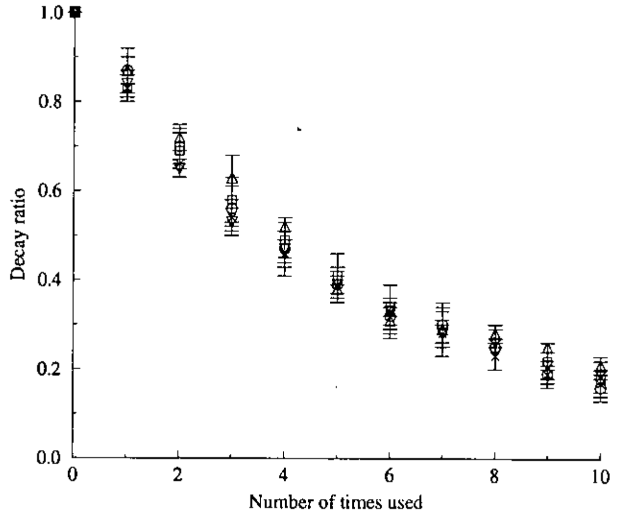


Figure 4.2. The decay in luminescence signal due to successive preheating and measurement sequences relative to the first measurement for quartz bleached by daylight dosed to each of 12Gy(o), 48Gy(△), 119Gy(▽), 190Gy(□) and 238Gy(×). Preheating was at 220°C for 1 min. and measurement was for a 100s exposure to the green LEDs.

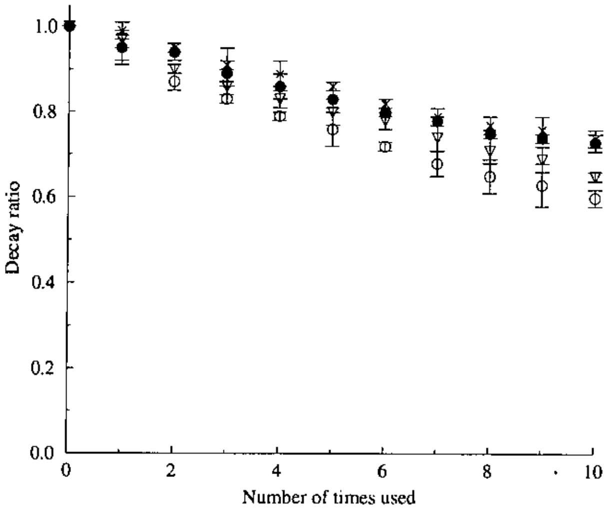


Figure 4.3. The decay in luminescence signal due to successive preheating and measurement sequences relative to the first measurement for heated quartz dosed to each of 12Gy(o), 119Gy(▽), 238Gy(×) and 476Gy(•). Preheating was at 220°C for 1 min. and measurement was for a 12.5s exposure to the green LEDs.

Three further measurement cycles of preheating and reading of luminescence without adding any beta dose were carried out and are also included in figs. 4.5 and 4.6. The procedure used in this study is summarized in fig. 4.1.

The four measurements at maximum beta dose serve as a test of the efficacy of the Duller[25] type of correction to the measured data and are essential for the correction procedure proposed by Galloway[93], as will be discussed below.

Since each preheating removes not only the unstable component of the signal but also part of the stable component, it is necessary to compensate for the loss of stable signal due to repeated preheating and reading. This loss of stable signal can be assessed using an initially dosed aliquot, by repeatedly preheating and measuring the green light stimulated luminescence remaining without irradiation of the aliquot between each measurement. Figure 4.2 concerns quartz bleached by daylight prior to dosing and shows the decay of the signal due to repeated preheating and reading for aliquots dosed to 12Gy, 48Gy, 119Gy, 190Gy, and 238Gy. Three aliquots were measured for each dose. The decay curve is independent of initial dose. Figure 4.3 concerns quartz heated to 500°C for 5minutes before use and shows the decay of luminescence due to repeated preheating and reading for aliquots dosed to 12Gy, 119Gy, 238Gy and 476Gy, with three aliquots measured for each dose. In figs. 4.2 and 4.3, each point is the mean of three measurements and the error bars indicate the spread in the measurements. In contrast to the behaviour of bleached quartz, the heated quartz shows a slight dependence of decay rate on initial dose. The lower dosed samples decay more rapidly than the higher dosed samples. Accepting that the scatter in the measurements prevents the drawing of a definitive conclusion, it seems that the decay rate becomes less as the initial dose increases from 12Gy to 119Gy with no detectable change from 238Gy to 476Gy. There is a similar trend, although within the measurement uncertainty, in the luminescence decay due to repeated preheating and reading of sedimentary feldspar stimulated by infrared[25]. Further investigations for the decay rate were made in section 4.3.3.

4.2.3 The correction for loss of signal

The single aliquot additive dose measurements have to be corrected for loss of signal due to re-use of the aliquot in order to produce, it is hoped, the true relationship between luminescence and dose. Four correction procedures are considered, all introduced originally for the correction of single aliquot measurements on feldspar with infrared stimulation. They are the 1^{st}, 2^{nd} luminescence correction methods of Duller[25], the iterative least squares fitting procedure of Galloway[93] and the dose correction method of Duller[26].

(a) The 1^{st} luminescence correction method

The 1^{st} luminescence correction method[25] considered assumes that after irradiation the distribution of trapped charge will be similarly affected irrespective of the number of preheats or irradiations that have occurred previously. In this case each preheating and reading will cause the previous signal to decay by the ratio of the 2^{nd} to 1^{st} reading in figs. 4.2 and 4.3. This is summarized in the expression

$$S_{\beta n} = I_n - (I_{(n-1)} \times F) \tag{4.1}$$

where n=measurement number, $S_{\beta n}$=the luminescence signal due to beta irradiation number n, I=the measured green light stimulated luminescence and F=the ratio of the 2^{nd} to 1^{st} reading(the 2^{nd} ratio) in figs. 4.2 and 4.3. The single aliquot measurements on bleached quartz were corrected in this way using F=0.85 from fig. 4.2 and the resulting corrected dose response is shown in fig. 4.5. Of particular interest at this stage are the four repeated measurements at the maximum dose. If the correction for loss of luminescence due to repeated use of the aliquot is successful, it would be expected that the repeated measurements at the same dose should correct to the same luminescence value, which does indeed happen in fig. 4.5. In this regard quartz stimulated by green light behaves quite differently from feldspar stimulated by infrared, since Duller[25] rejected his 1^{st} luminescence correction method on the grounds that such repeated measurements on a single aliquot at the same dose did not correct to give equal luminescence values(This fact led to proposing the 2^{nd} luminescence correction method, discussed further below.). Turning to the single aliquot measurements on heated quartz, they were corrected in the same way using F=0.98 from fig. 4.3 and the correction was successful according to the criterion that the repeated measurements on the same maximum dose should correct to equal luminescence values, fig. 4.6. The value of F used for correction is the average of the two higher dose(and statistically more accurate) values in fig. 4.3 and is within the error limits of the two lower dose values. It should be noted that the magnitude of the correction to the heated quartz measurements(fig. 4.6) is much less than in the case of bleached quartz(fig. 4.5), which means that the corrected dose response of the heated quartz is less sensitive to uncertainty in value of F.

(b) The 2^{nd} luminescence correction method

Now consider the 2^{nd} luminescence correction method of Duller[25], which implies that the trapped charge induced by each dose administered behaves independently of the trapped charge induced by all other dosing stages. To correct for this effect, one should isolate each component of the signal and then correct each component independently for signal loss, through the decay ratios of the various preheat and read cycles. Mathematically this can be expressed by

$$S_{\beta n} = I_n - \sum_{i=1}^{n-1} (S_{\beta i} \times F_{(n-i+1)}) \tag{4.2}$$

where n=measurement number, $S_{\beta n}$=the luminescence signal due to the current n^{th} irradiation, $S_{\beta i}$=the luminescence signal due to a previous irradiation number i, F=the appropriate decay ratio from figs. 4.2 or 4.3 and I_n is the measured luminescence. The single aliquot measurements on bleached quartz were corrected in this way, using the decay data in fig. 4.2, with a very similar result to the previous correction method, as shown in fig. 4.5. This is in marked contrast to Duller[25] in which the 1^{st} and 2^{nd}

luminescence correction methods gave distinctly different results for the infrared stimulation of feldspar, the 2^{nd} method being preferred. The single aliquot measurements on heated quartz were also corrected by the 2^{nd} method(fig. 4.6), using the mean of the two higher dose decay curves in fig. 4.3. The result was indistinguishable from the previous correction (fig. 4.6). Consideration of possible dose dependence in the decay data is deferred.

(c) Least squares fitting correction method

As an alternative correction method the iterative least squares fitting procedure of Galloway[93] was considered. This procedure, developed for the infrared stimulation of feldspar, relies on the fact that the decay factors can be represented by a simple function dependent on only one parameter and that this parameter can be found by applying an iterative least squares fitting procedure to the measurements with no added dose after the maximum dose has been reached, with the assumption that these measurements should correct to be equal. For the infrared stimulation of feldspar the decay factors are given by the function

$$f(n) = 1 - a\ln(n) \tag{4.3}$$

where n is the number of times the aliquot has been measured, $f(n)$ is the fraction of signal remaining and a is a parameter dependent on the preheating and reading conditions. This is not an appropriate function for fitting the decay data(figs. 4.2 and 4.3) for quartz stimulated by green light. Alternative plotting of the decay from figs. 4.2 and 4.3 with a logarithmic axis for the fraction of signal, fig. 4.4 shows the correction factors to be well represented by

$$f(n) = \exp[-c(n-1)] \tag{4.4}$$

where n is the number of measurements on the aliquot, $f(n)$ is the fraction of initial signal remaining and c is a parameter which will be dependent upon the preheating temperature and duration.

Alternatively, the exponential form of decay may be written $f(n) = r^{(n-1)}$, where $r = \exp(-c)$ is the ratio of any reading in the decay curve to the immediately preceding reading. It follows from regarding $f(n) = r^{(n-1)}$ that the 1^{st} and 2^{nd} luminescence correction methods of Duller [25] should give the same result. The small differences between points corrected by the two methods in fig. 4.5 and fig. 4.6 can be attributed to scatter in the measurements of the decay curves in figs. 4.2 and 4.3 about the exponential form. The exponential form for the decay curve was used in the iterative least squares fitting approach previously used for feldspar[93]. The single aliquot measurements were corrected assuming an arbitrary starting value for the parameter r. For the repeated measurements at maximum dose which are intended to correct to equal luminescence values, the mean luminescence and the sum of the squares of the deviations from the mean were evaluated. This sum should go to a minimum as the parameter r is varied to find the most appropriate value. The results from this correction procedure, fig. 4.5 and fig. 4.6, are very close to the values from the two luminescence correction methods.

(d) Dose correction method

Duller[26] observed that the equivalent dose was underestimated when the luminescence correction method was applied to feldspar with a nonlinear growth curve. He proposed a dose correction method which was effectively identical to the luminescence correction method for a linear growth curve but which, for a nonlinear response, gave equivalent dose values in better agreement with those obtained by standard multiple aliquot methods. This new dose correction method considers the effect of the preheat as a negative dose because it reduces the luminescence signal rather than increasing it. Thus the total applied radiation dose is adjusted as a correction instead of altering the size of the measured luminescence signal(as in the luminescence correction). An equation similar to that for the luminescence correction method is used to calculated the dose

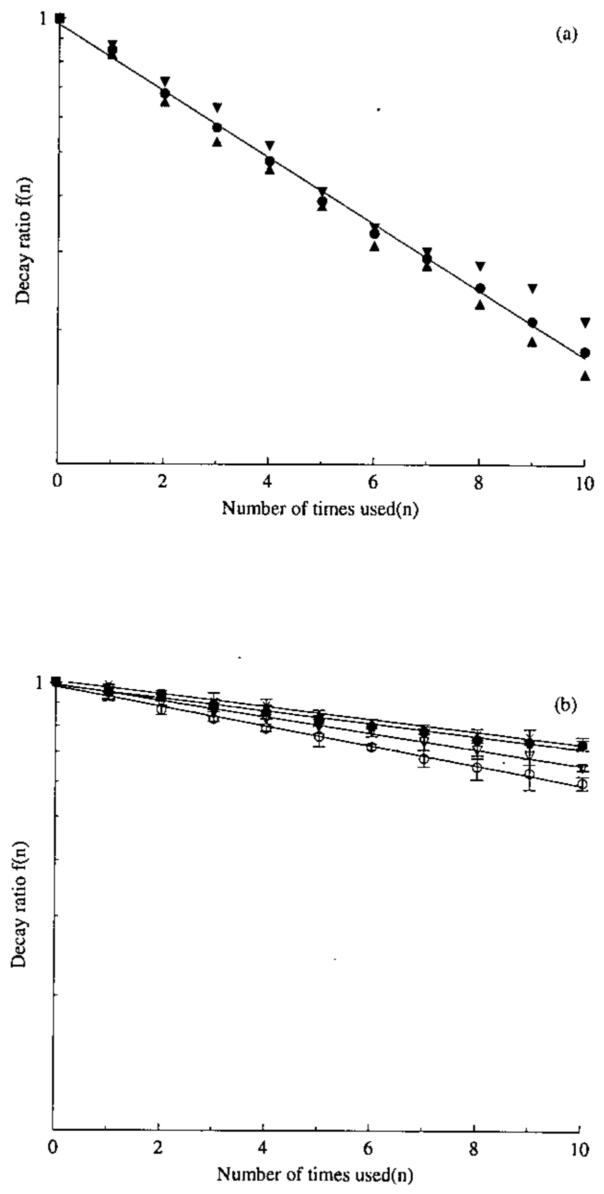


Figure 4.4. (a)The decay data of fig. 4.2, for bleached quartz, exemplifying the relationship $f(n) = \exp[-c(n-1)]$, for the fraction of initial signal $f(n)$ in terms of the number of times n that the aliquot is used. (b)Similar relationships for the heated quartz data of fig. 4.3. Stimulation times were 100s(a) and 12.5s(b).

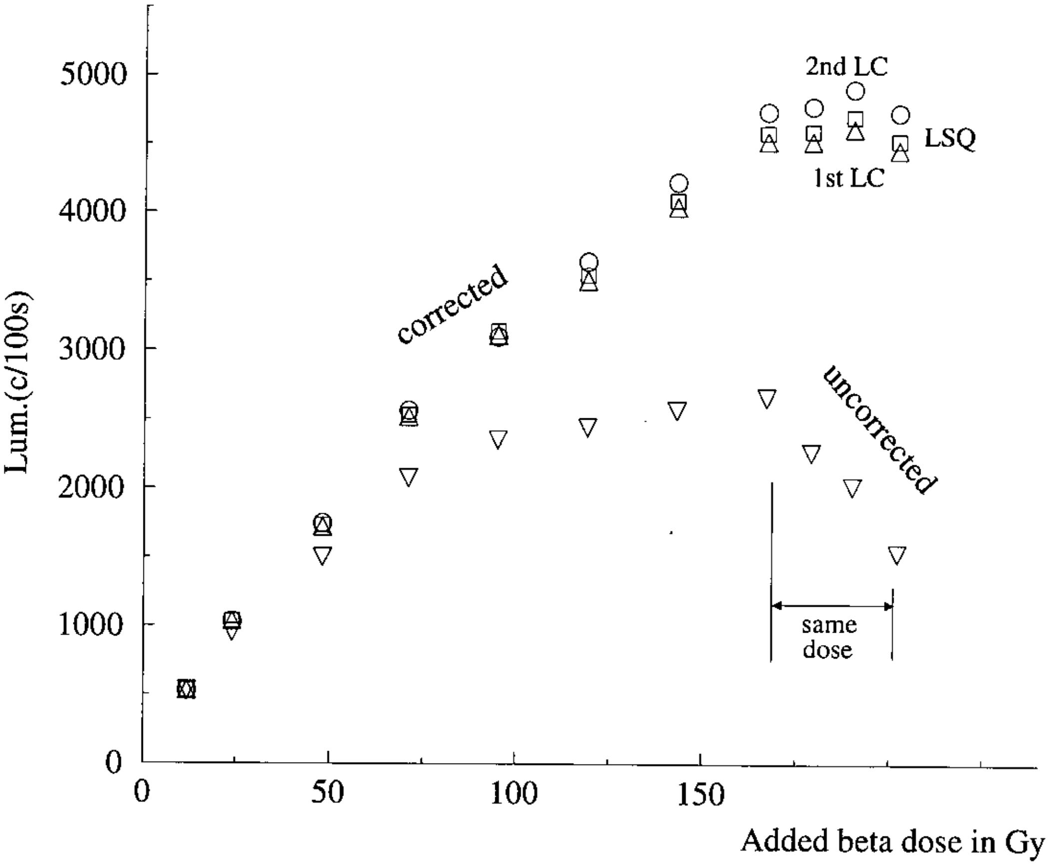


Figure 4.5. An example of single aliquot measurements for quartz bleached by daylight which were corrected by the 1^{st} luminescence correction method(△), 2^{nd} luminescence correction method(○), the least squares fitting procedure(□) along with uncorrected data(▽).

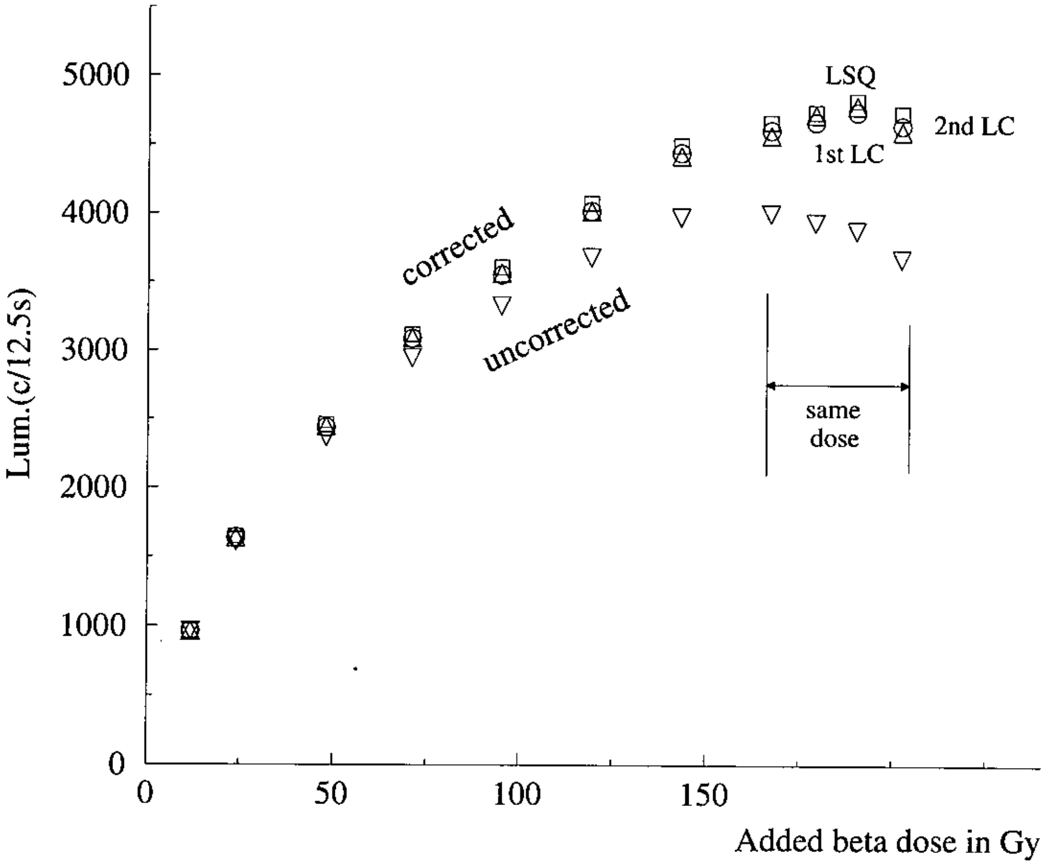


Figure 4.6. An example of single aliquot measurements for heated quartz which were corrected by the 1^{st} luminescence correction(△), 2^{nd} luminescence correction method(○), the least squares fitting procedure(□) along with uncorrected data(▽).

$$\text{EAD} = \sum_{i=1}^{n-1} (D_i \times F_{(n-i+1)}) - D_1 \tag{4.5}$$

where for measurement n the corrected 'effective added dose'(EAD) can be calculated by subtracting the natural dose D_1 from the sum of the previous component doses D_i multiplied by the appropriate correction factors $F_{(n-i+1)}$. This procedure is very similar to that for the luminescence correction method, except that the component doses unlike the component signals are all known precisely, with the exception of the natural dose D_1. As with the luminescence correction method, the decay of each 'dose' component due to the effect of repeated preheating and reading is computed independently. This includes the 'decay' of the natural dose which is the dose when the sample is first measured D_1 – which is usually unknown and is the equivalent dose to be determined from the measurements. An estimated value, D_e can be used to correct the data. The estimated value can be improved by using an iterative procedure to repeatedly calculate new D_e-values. After each iteration the new data set, calculated using the previous D_e estimate, is plotted and fitted using a standard curve fitting procedure. This results in a new estimate of D_e for the sample which is fed back into the equation 4.5 to create a new data set that can be fitted once again. Starting from an initial estimate for D_e of zero, the value quickly converges to give what is taken to be the correct D_e. Since the response of quartz to green stimulation is not linear, it is appropriate to consider the dose correction procedure. The nonlinearity of response is more marked for the heated quartz, so the dose correction procedure was applied to the single aliquot measurements on heated quartz, for which D_1=0, with the result shown in fig. 4.7.

4.2.4 Comparison of single and multiple aliquot growth curves

For both the bleached quartz and the heated quartz, conventional multiple aliquot measurements of the luminescence growth with beta dose are required, to serve as the

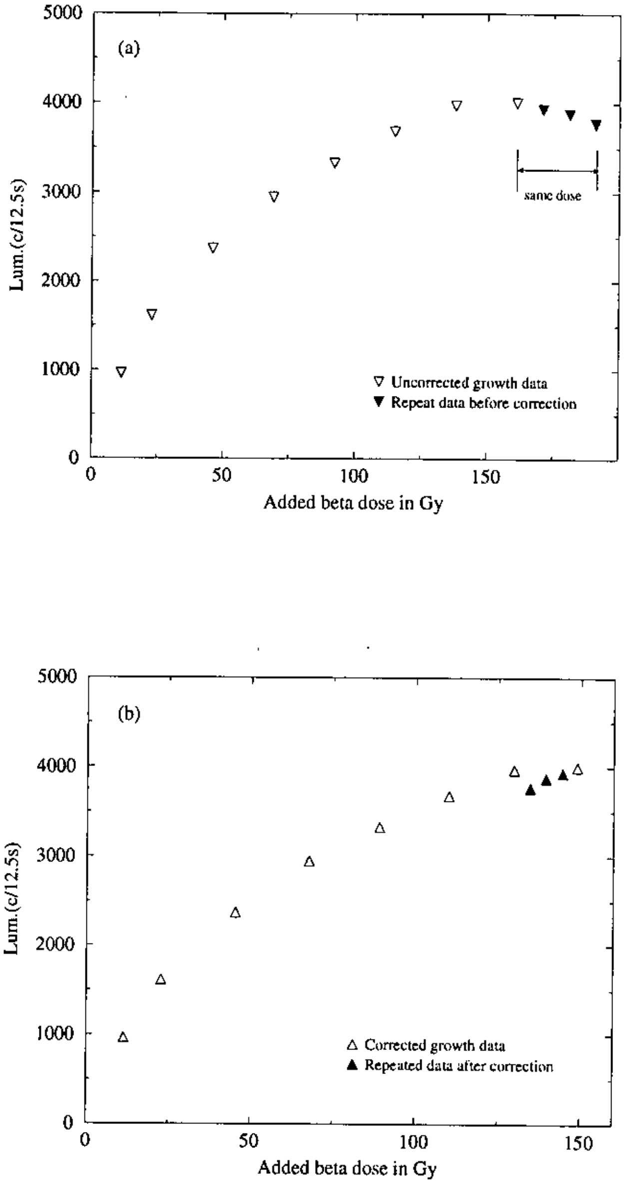


Figure 4.7. The single aliquot additive dose method for heated quartz corrected by the dose correction method; (a)uncorrected data and (b)corrected data.

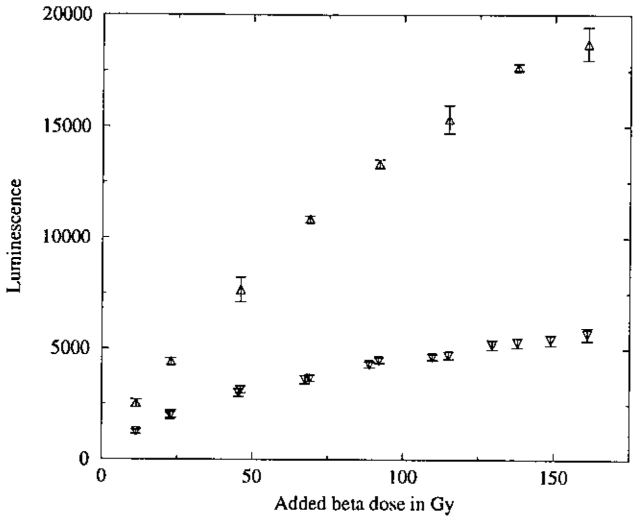


Figure 4.8. The multiple aliquot measurements for bleached(△) and heated(▽) quartz.

standard of comparison against which to judge the success of the corrected single aliquot growth curves. The following multiple aliquot procedure was used. After measuring the background, the beta dose was given, the sample preheated for 1minute at 220°C and then the luminescence measured. This was repeated for three samples for each dose and for eight doses ranging from 12Gy to 167Gy matching the doses in the single aliquot measurements in figs. 4.5 and 4.6. The samples were then normalized to generate a growth curve showing the dependence of luminescence on dose. In normalizing, in order to avoid any predose effect[96] each sample had a second beta dose added after reading so that the first dose plus the second dose equalled the maximum beta dose applied to any of the set of samples to be normalized. The samples were then bleached in a Honle SOL-2 solar simulator for 1hr. Each sample was then given an equal beta dose, preheated, measured and normalized. The resulting multiple aliquot growth curves are shown in fig. 4.8. Each point is the mean of measurements on three aliquots with the error bars indicating the spread.

For the heated quartz, normalized multiple aliquot measurements were also made at another seven doses(3 aliquots per dose) to match the 'effective dose' values resulting from the dose correction of the single aliquot measurements in fig. 4.7(b).

The course adopted in order to compare the growth curve resulting from corrected single aliquot measurements with that from conventional multiple aliquot measurements is to take the ratio of the responses determined by the two methods at each value of dose. If the response takes precisely the same form in both methods of measurement, the ratio of the single aliquot number of counts to the multiple aliquot number of counts for each beta dose should be a constant independent of dose. Alternatively, one can say that this 'single : multiple' ratio should be independent of the number of times the single aliquot has been used. Consider briefly how the single : multiple ratio would depend on the number of times the single aliquot has been used, if the single aliquot correction is wrong. The first measurement made on the single aliquot requires no correction for re-use, the second use of the aliquot requires a small correction and correction increases with re-use(figs. 4.5, 4.6 and 4.7(b)). If the correction procedure underestimates the required correction, the first measurement would be correct and the underestimate should increase with re-use of the aliquot so that the single : multiple ratio would fall with increasing re-use of the aliquot. Use of the single aliquot method for equivalent dose determination would then give excessively high equivalent dose values. Conversely, if the procedure used overestimates the single aliquot correction, the single : multiple ratio would increase with re-use of the aliquot and then an equivalent dose value would be too small.

Measurements on five single aliquots of bleached quartz were made and corrected by the 1^{st}, the 2^{nd} luminescence correction method and the least squares fitting correction method(figs. 4.9(a), 4.10(a) and 4.11(a)). They were compared with the multiple aliquot measurements on bleached quartz(fig. 4.8) to give the single : multiple ratios in fig. 4.13. Each aliquot gives a ratio which is constant within the accuracy. To quantify this observation, a least squares linear fit was made to the ratios for each aliquot and the percentage change in the ratio per re-use of the aliquot determined.

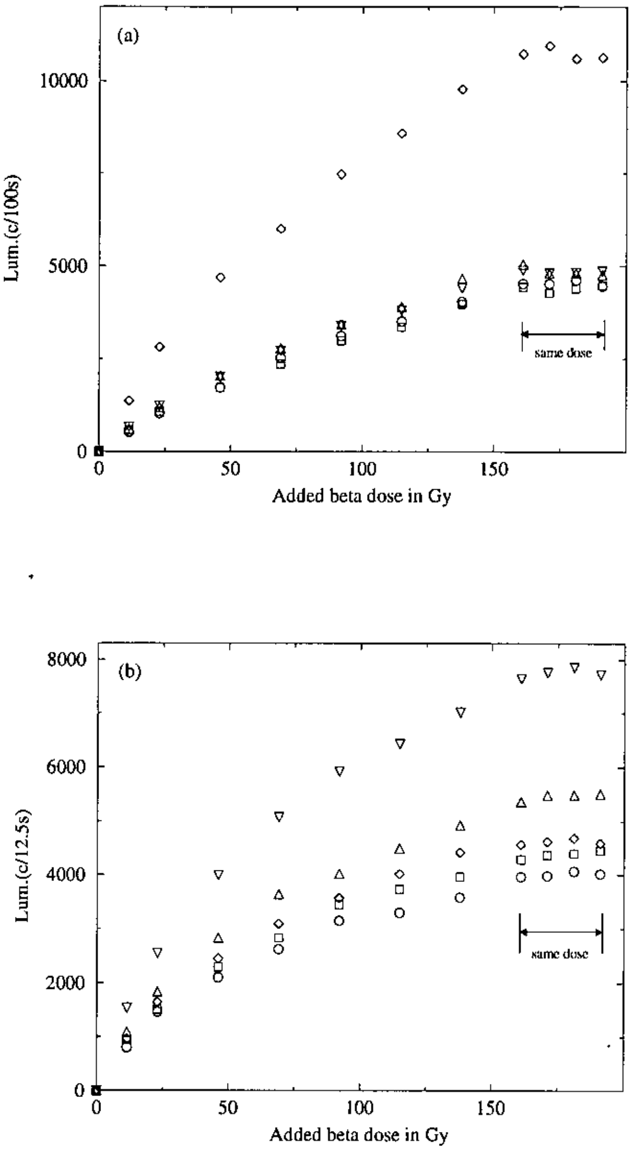
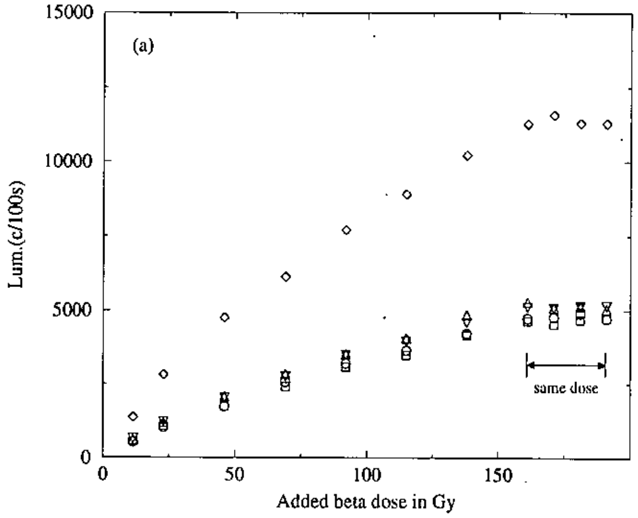


Figure 4.9. Five single aliquot measurements, corrected by the the 1^{st} luminescence correction method, of the dose dependence of green luminescence from quartz previously bleached by daylight(a) and heated quartz(b).



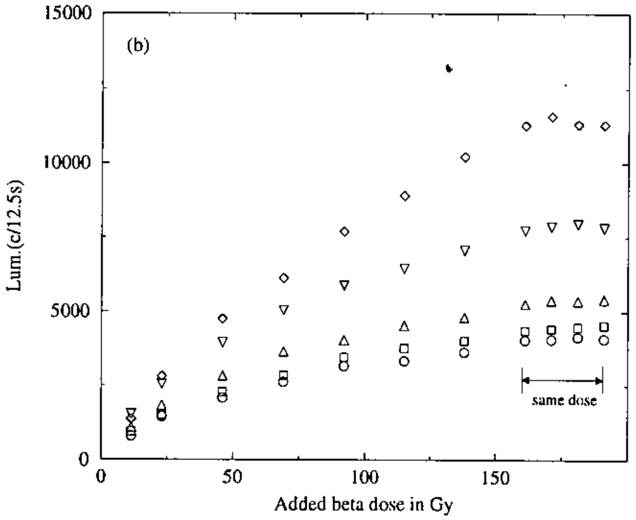


Figure 4.10. Five single aliquot measurements, corrected by the 2^{nd} luminescence correction method, of the dose dependence of green luminescence from quartz previously bleached by daylight(a) and heated quartz(b).

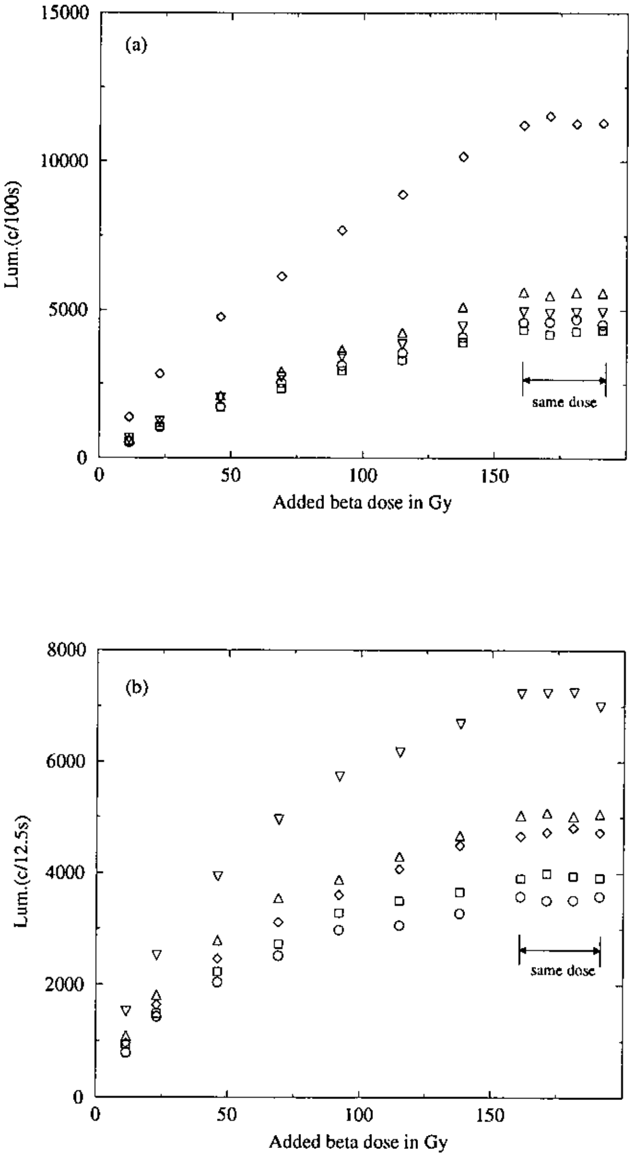


Figure 4.11. Five single aliquot measurements, corrected by the least squares fitting correction method, of the dose dependence of green luminescence from quartz previously bleached by daylight(a) and heated quartz(b).

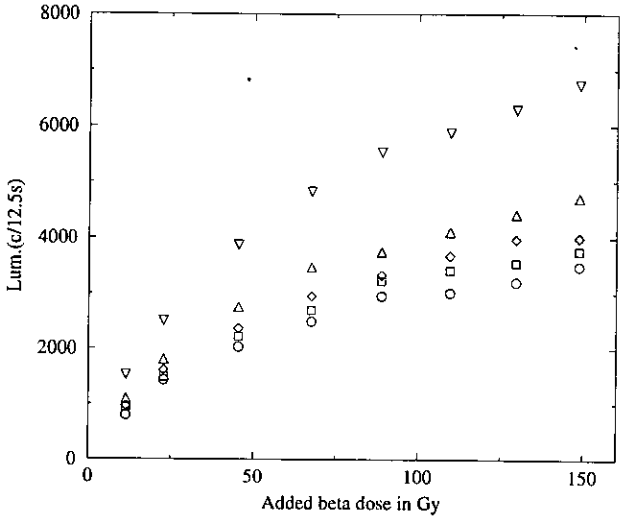


Figure 4.12. Five single aliquot measurements, corrected by the dose correction method, of the dose dependence of green luminescence from heated quartz.

The mean percentage changes in single : multiple ratio per re-use of the aliquot are given in table 4.1.

As was surmised from fig. 4.5, there is little to choose between the correction procedures and table 1 shows that they are equally successful. Also, measurements on five single aliquots of heated quartz were made and corrected by the 1^{st}, the 2^{nd} luminescence method, least squares fitting correction method and dose correction method(figs. 4.9(b), 4.10(b), 4.11(b) and 4.12). Similar to the previous way, single : multiple ratios were used to test the correction procedures applied to five single aliquots of heated quartz(fig. 4.14) with the results quoted in table 4.1. All of the correction methods can be accepted as successful. Note that each ratio shown in figs. 4.13 and 4.14 simply refers to a different single aliquot measurement without any particular meaning.

4.2.5 Discussion

So far as application of the single aliquot method to the dating of sediments is concerned, it is the tests on the bleached quartz that are relevant. For this material the

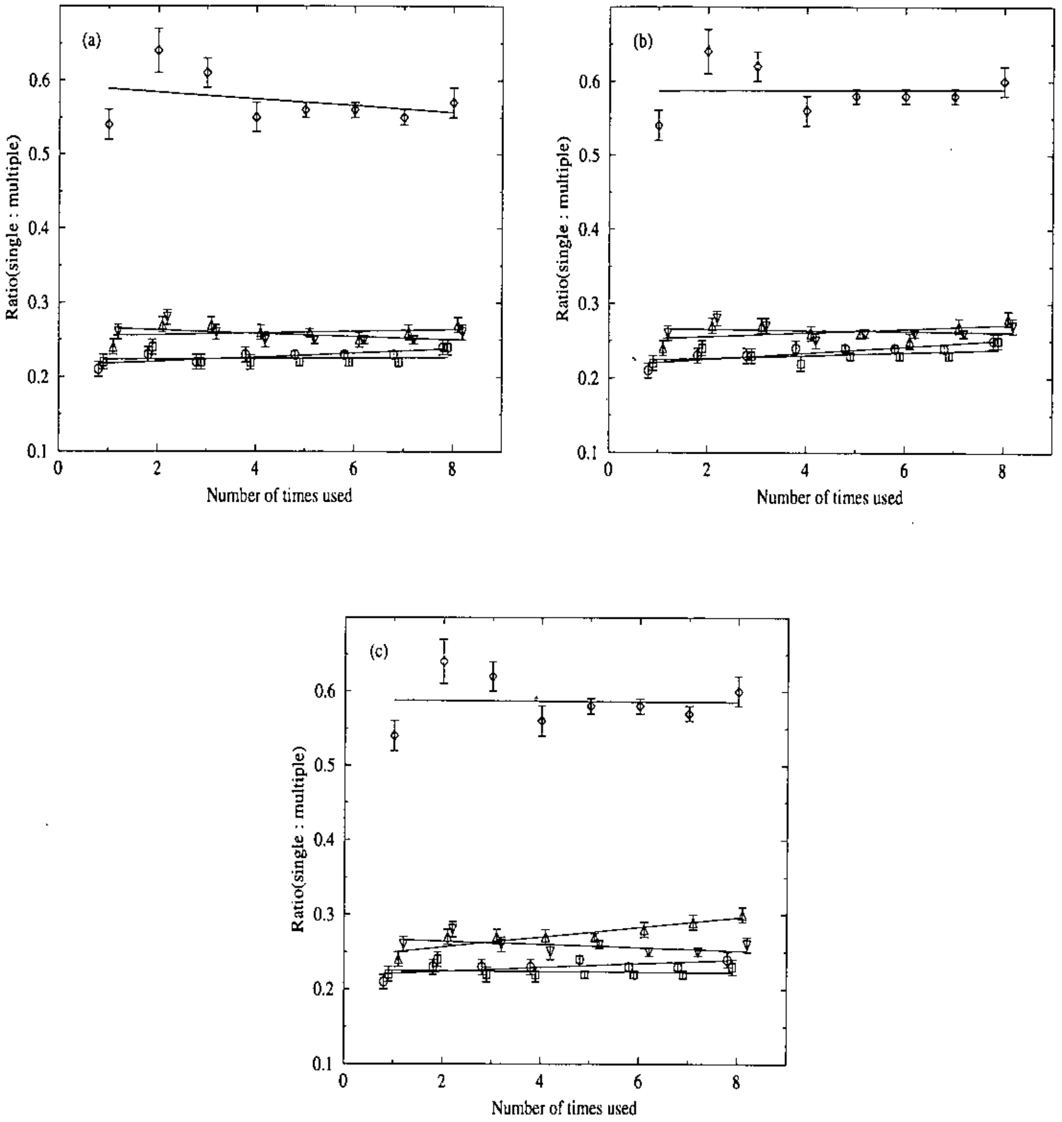


Figure 4.13. Ratio of single to multiple aliquot counts plotted against the number of dose, preheat and green light cycles for the single aliquot measurements in the case of quartz bleached by daylight before use and corrected by the 1^{st} luminescence correction method(a), the 2^{nd} luminescence correction method(b) and the least squares fitting procedure(c). Each symbol refers to a different single aliquot. The error bars arise from the scatter in the multiple aliquot measurements. Least squares linear fits to the data points are drawn.

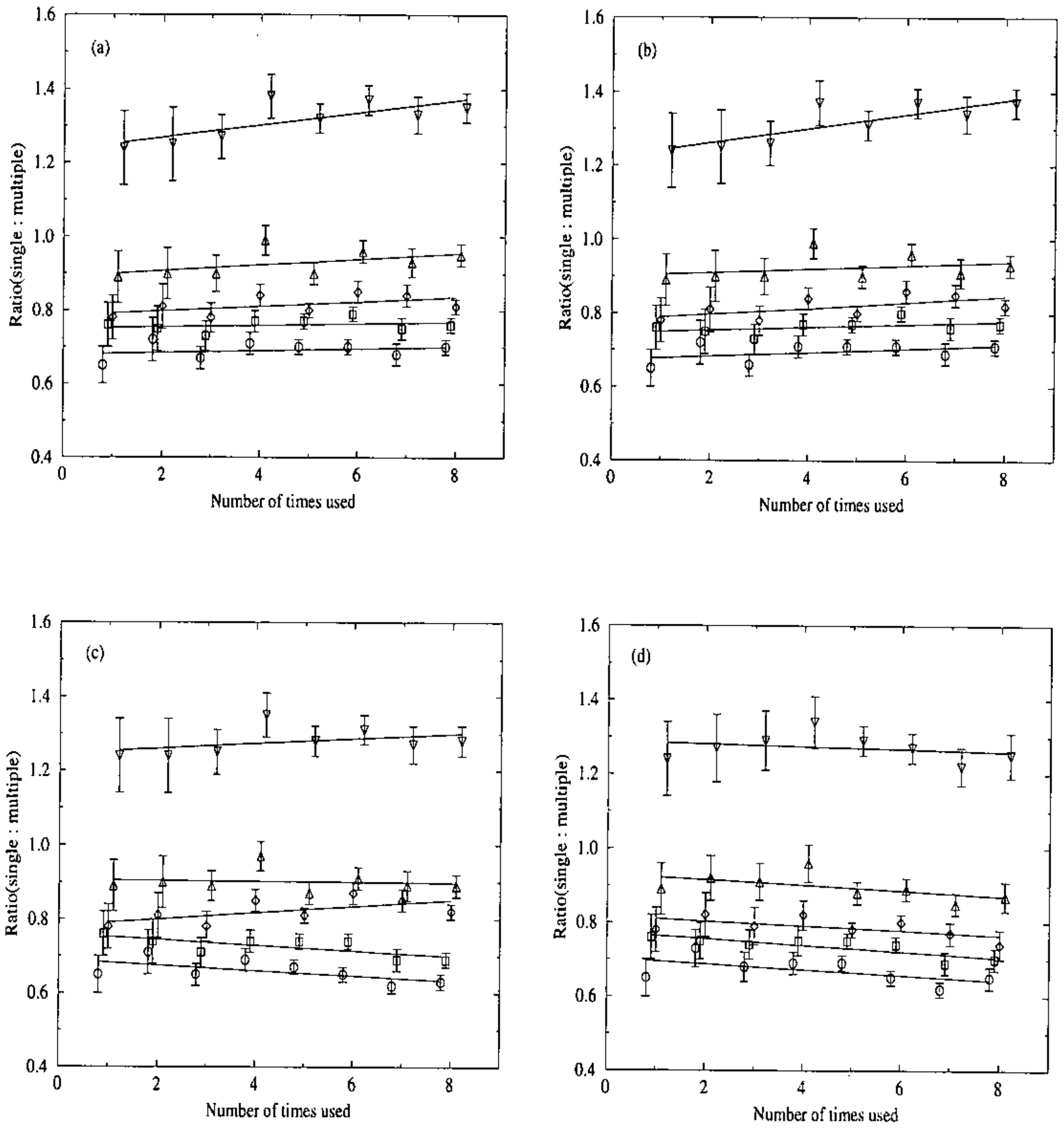


Figure 4.14. Ratio of single to multiple aliquot counts plotted against the number of dose, preheat and green light cycles for the single aliquot measurements in the case of quartz drained by heating at 500°C for 1min. before use and corrected by the 1^{st} luminescence correction method(a), the 2^{nd} luminescence correction method(b), the least squares fitting procedure(c) and dose correction method(d). Each symbol refers to a different single aliquot. The error bars arise from the scatter in the multiple aliquot measurements. Least squares linear fits to the data points are drawn.

Table 4.1. The mean percentage change in the single to multiple ratio per re-use of the aliquot(as defined in the text) for single aliquot correction methods

sample	all BDH quartz						
preheating	all 220°C/1min						
bleaching	daylight			heating(500°C/5min)			
cor. method	1^{st} *LC	2^{nd} LC	*LSQ	1^{st} LC	2^{nd} LC	LSQ	*DC
% change	0.1±0.6	0.7±0.5	0.6±1.5	0.7±0.4	0.9±0.4	-0.1±0.6	-0.8±0.3

*LC : Luminescence correction, *LSQ : Least square fitting correction, *DC : Dose correction.

decay ratios(the decay curve of figs. 4.2 or fig. 4.4(a)) are dose independent and all three correction methods tested produced a similar dose response(fig. 4.5) which was in each case consistent with the response determined by a conventional multiple aliquot method(table 4.1). That the 1^{st} luminescence correction method works for the green stimulation of quartz but not for the infrared stimulation of feldspar[25] is due to the exponential decay of luminescence from the quartz aliquot with re-use(fig. 4.4(a)) which is quite different from the form of decay for feldspar[93]. The 1^{st} luminescence correction method compensates for the loss of signal by using the ratio of second to first measurement of luminescence in a sequence such as shown in figs. 4.2 and 4.3, but since for an exponential decay each point on the decay curve should be in the same ratio to the immediately preceding point, there may be some advantage in accuracy if the value of this ratio is averaged over several decay readings, as is in effect done in the other correction methods which use several points on the decay curve. The proposed least squares fitting method of correction gives corrected values consistent with those determined by use of correction data measured using a separate aliquot. This alternative correction method has the advantage that, since the correction is determined from measurements on the same aliquot that is being corrected, there can be no error due to difference in mineralogy between the aliquot used for equivalent dose determination and a separate aliquot used to determine the decay ratio. Further, it is more convenient to be able to make all necessary measurements on only one aliquot. Entirely similar remarks can be made regarding the tests on heated quartz, relevant to the dating of pottery, except to consider the indication in figs. 4.3 and 4.4(b) that the decay data which form the basis of single aliquot correction may be slightly dose dependent. The single aliquot measurements which were corrected using the higher dose decay data to the values shown in figs. 4.6 and 4.7(b), are in agreement with the multiple aliquot measurements(table 4.1). The lower dose decay data gives less satisfactory correction. This is no doubt because the correction, as can be seen in figs. 4.6 and 4.7(b), is very small at low doses and becomes more significant at higher doses. The least squares fitting method will tend to produce a decay ratio appropriate to the highest dose in the data. The dose response of heated quartz is clearly nonlinear and so, on the basis of work done on the infrared stimulation of feldspar[26], it would be expected that the dose correction method applied to the single aliquot data(as in fig. 4.7(b)) should give better agreement with the multiple aliquot response(fig. 4.8). The results in table 4.1 do not support this expectation. Indeed if any one method is to be preferred for heated quartz, from the figures in table 4.1 it would be the least squares fitting method, although with due allowance for the uncertainties in the measurements there is little to choose between the methods considered.

4.3 Tests using the 16 new Nichia green light emitting diodes

In the above section, it is shown that the single aliquot measurements after the correction can reproduce a similar form of dose response to the multiple aliquot measurement. Further measurements were made for verifying whether this fact is independent of preheating. The preheating adopted for multiple aliquot measurement was for 5minutes at 220°C which has been generally used in dating analysis, while two preheatings, 1minute at 220°C and 5minutes at 220°C, were chosen for the single aliquot measurements.

4.3.1 Equipment and samples

All single and multiple aliquot measurements were made using the same automated system[23] but now equipped with the 16 new Nichia green light emitting diodes for stimulation. The samples were prepared in the same way as described in the previous section(4.2.1).

4.3.2 Methodology

After measuring the background a beta dose was given to make an additive growth. One set of the samples was preheated for 1minute at 220°C and another set of samples for 5minutes at 220°C before each measurement. The measurement time of exposure to light from the green LEDs was chosen to be 1s for both the bleached and the heated quartz because of the greater intensity from the new Nichia LEDs. The sequence of measurements followed was the same as the previously used procedure except for using two different preheatings, as exemplified in figs. 4.18 and 4.19. Three further measurement cycles of preheating and reading of luminescence without adding any beta dose were also performed to test the correction methods.

4.3.3 Investigation of the decay curve

Figures 4.15(b) and (c) show the decay of the signal due to repeated preheating and reading for aliquots dosed to 48Gy, 119Gy and 238Gy for quartz bleached by daylight prior to dosing. Figure 4.15(b) represents a preheating of 1minute at 220°C and fig. 4.15(c) a preheating of 5minutes at 220°C. In order to investigate how much the signal decreases due to exposure to light only without the preheating, the decay curve due to only the reading was also included in fig. 4.15(a). Figures 4.16(b) and (c) concern quartz heated to 500°C for 5minutes before use and show the decay of luminescence due to repeated preheating and reading for aliquots dosed to 48Gy, 119Gy and 238Gy. As for the bleached quartz, the decay curve for the heated quartz due to only the reading was included in fig. 4.16(a).

In figs. 4.15 and 4.16, three aliquots were measured for each dose. Each point is the mean of the three measurements and error bars indicate the spread in the measurements. The decay curves for the bleached and heated quartz are independent of initial dose. For heated quartz, this contrasts with the measurements done with the original LED's(fig. 4.3) which indicated a slight dependence of decay rate on initial dose. Considering the greater intensity of the new Nichia LEDs, the slight dose dependence shown(fig. 4.3) in the previous decay ratio may be the scatter from each measurement.

A second important aspect of the comparison of the decay curve for the bleached quartz(fig. 4.15) and for the heated quartz(fig. 4.16) is that the luminescence signal from the heated quartz decays more slowly with repeated preheating and reading than does the signal from the bleached quartz, particularly significant in measurements using a preheating of 1minute at 220°C. This mainly results from the preheating rather than the reading since the decay curve for only the reading without the preheating does not show any difference between the bleached quartz and heated quartz. The loss of luminescence signal for each re-use of bleached quartz in measurements using a preheating of 1minute at 220°C is about 16% compared with about 8% for heated

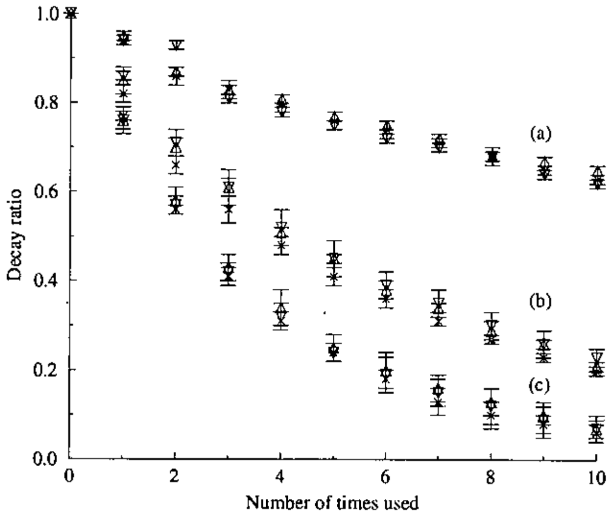


Figure 4.15. The decay in luminescence signal due to successive reading ((a) exposure green light only) and successive two different preheatings((b) 1minute at 220°C and (c) 5minutes at 220°C) and reading sequences relative to the first measurement for quartz bleached by daylight dosed to each of 48Gy(△), 119Gy(▽) and 238Gy(×).

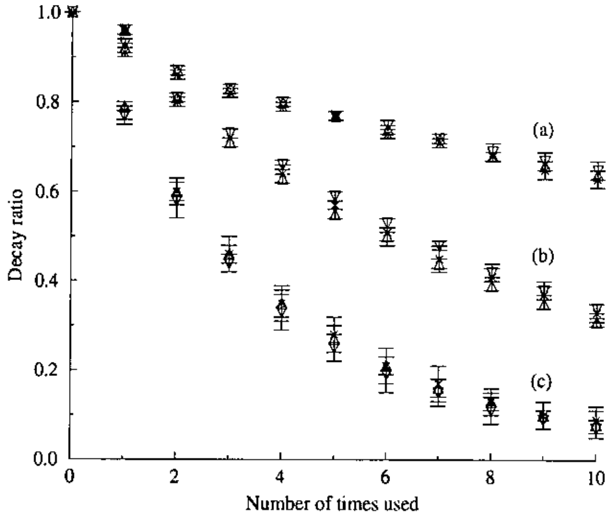
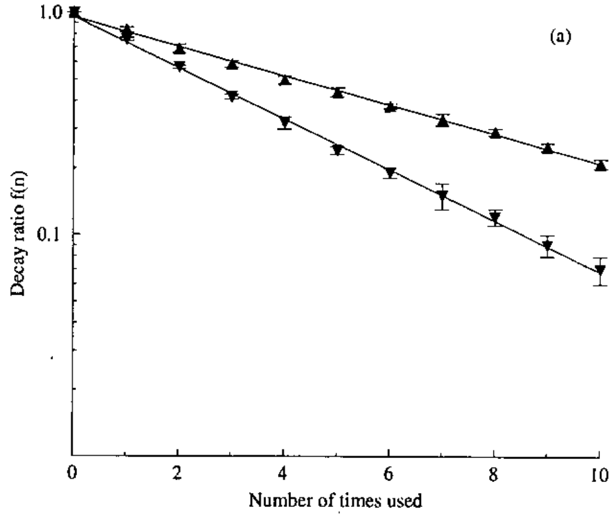


Figure 4.16. The decay in luminescence signal due to successive reading ((a) exposure green light only) and successive two different preheatings((b) 1minute at 220°C and (c) 5minutes at 220°C) and reading sequences relative to the first measurement for heated quartz dosed to each of 48Gy(△), 119Gy(▽) and 238Gy(×).



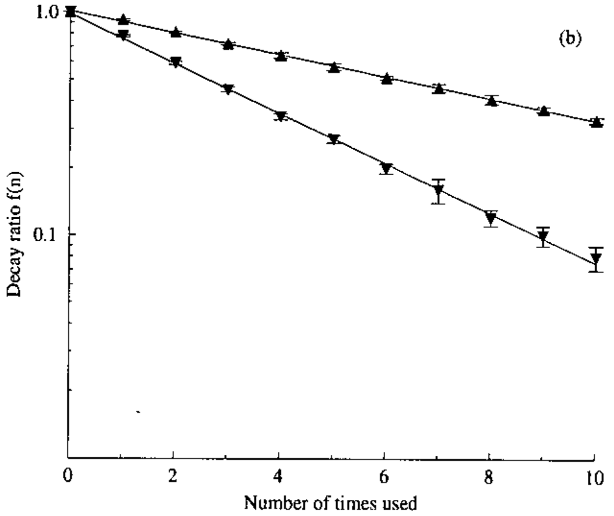


Figure 4.17. (a)The decay data of fig. 4.15(b) and (c), for bleached quartz, exemplifying the relationship $f(n) = \exp[-c(n-1)]$, for the fraction of initial signal $f(n)$ in terms of the number of times n that the aliquot is used. (b)Similar relationships for the heated quartz data of fig. 4.16(b) and (c).

quartz, independent of initial dose. The reason for this is not clear.

A plot of the decay from figs. 4.15 and 4.16 with a logarithmic axis for the fraction of signal was investigated. Figure 4.17 shows the correction factors to be well represented by an exponential decay.

4.3.4 Comparison of the correction methods

Three correction procedures are considered, all as discussed in the previous section(4.2.3). They are the 1^{st}, 2^{nd} luminescence correction methods of Duller[25] and the iterative least squares fitting procedure of Galloway[93](figs. 4.18 and 4.19). The dose correction method of Duller[26] was excluded because in previous tests the two luminescence correction methods and the least squares fitting procedure for quartz were successful in spite of showing a nonlinear response with dose.

For the 1^{st} luminescence correction method, F=0.84 for the measurements using a preheating of the 1minute at 220°C and F=0.76 for the measurements using a preheating of 5minutes at 220°C were used for the bleached quartz, while F=0.92 and F=0.78 respectively for the heated quartz.

As shown in figs. 4.18 and 4.19, the results from the different correction methods were indistinguishable. The small differences between points corrected by the different correction methods can be attributed to scatter in the measurements of the decay curves in figs. 4.15(b),(c) and figs. 4.16(b),(c).

4.3.5 Comparison of single and multiple aliquot growth curves

For both the bleached quartz and the heated quartz, multiple aliquot measurements of the luminescence growth with beta dose were made(fig. 4.20) to serve as the standard of comparison against which to judge the success of the corrected single aliquot growth curves. The multiple aliquot procedure used was illustrated in the previous section(4.2.4), but the sample was preheated for 5 minutes at 220^{0}C, as generally used in the dating process. Contrary to the multiple aliquot measurements using a preheating

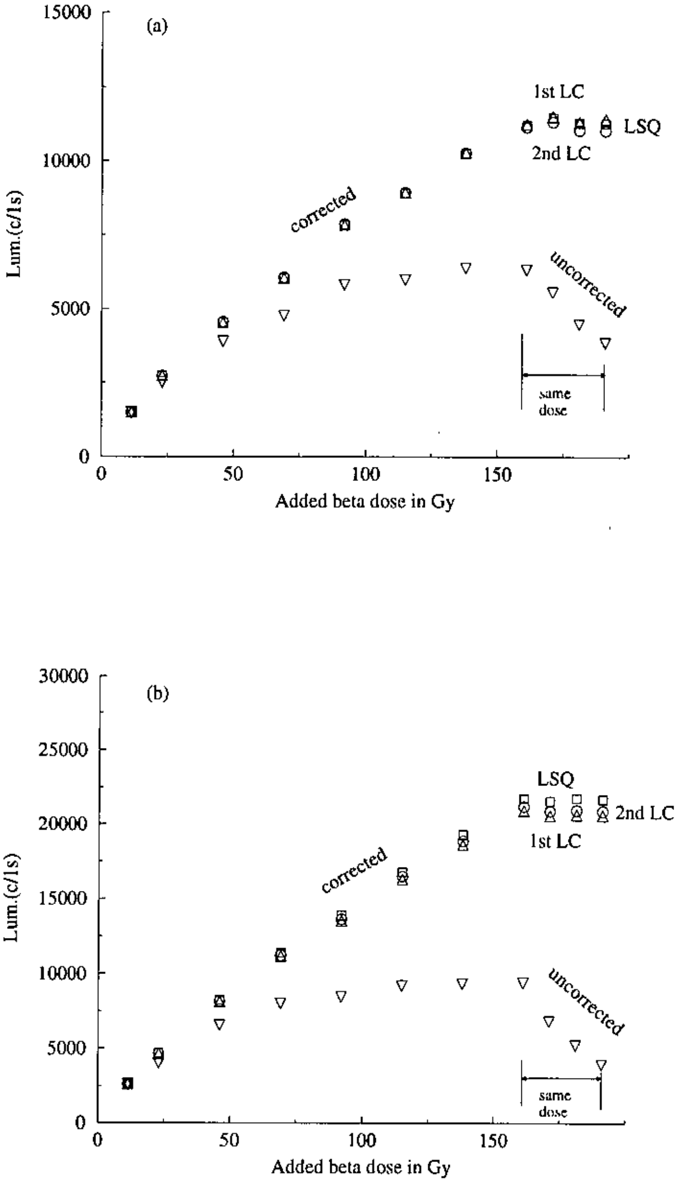


Figure 4.18. An example of single aliquot measurements for quartz bleached by daylight which were corrected by the 1^{st} luminescence correction method(△), 2^{nd} luminescence correction method(o), the least squares fitting procedure(□) along with uncorrected data(▽). Preheating was for 1min. at 220^0C(a) and for 5min. at 220^0C(b).

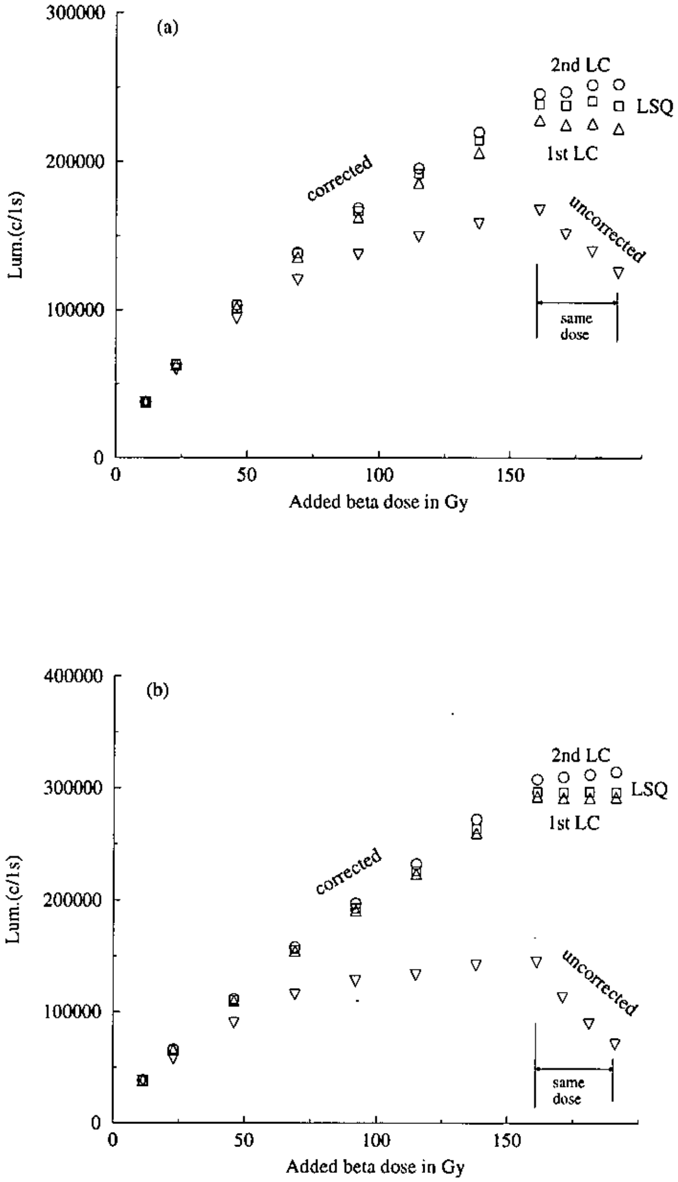


Figure 4.19. An example of single aliquot measurements for heated quartz which were corrected by the 1^{st} luminescence correction(△), 2^{nd} luminescence correction method(○), the least squares fitting procedure(□) along with uncorrected data(▽). Preheating was for 1min. at 220^{0}C(a) and for 5min. at 220^{0}C(b).

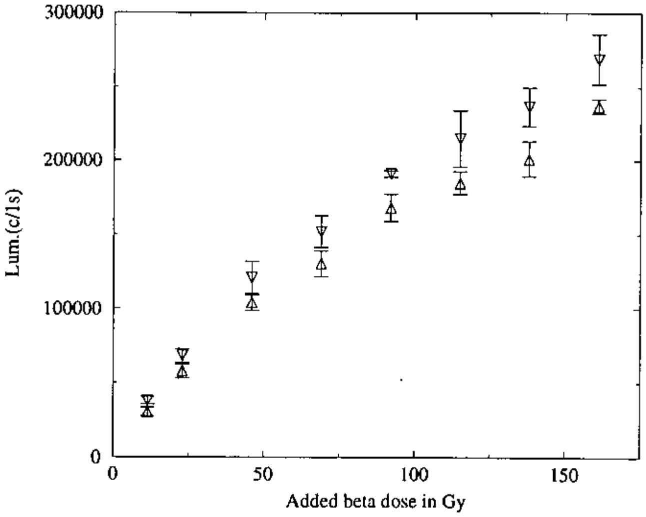


Figure 4.20. The multiple aliquot measurements for bleached(△) and heated(▽) quartz. The intensity of the luminescence for bleached quartz was multiplied by a factor of ten. Preheating before measurement was 5 min. at 220^{0}C.

of 1minute at 220^{0}C(fig. 4.8), the measurements for 5minutes showed a similar form of dose response for the bleached and the heated quartz, except for greater sensitivity of the heated quartz(fig. 4.20).

Measurements of dose response on five single aliquots of bleached quartz using the two different preheatings were made and corrected by the 1^{st}, the 2^{nd} luminescence method and the least squares fitting correction method(figs. 4.21, 4.23 and 4.25). They were compared with the multiple aliquot measurements on bleached quartz by plotting single : multiple ratios(figs. 4.27 and 4.28). A least squares linear fit was made to the ratios for each aliquot and the percentage change in the ratio per re-use of the aliquot determined. The mean percentage changes in single : multiple ratio per re-use of the aliquot are given in table 4.2. Of the two different preheating times considered, the shorter preheating time gave a better accuracy. The reason is presumably because the correction factor of the measurement using shorter preheating time is less for each step.

Similar to the previous way, measurements on five single aliquots of heated quartz using the two different preheatings were made and corrected by the 1^{st}, the 2^{nd} luminescence method and least squares fitting correction method(figs. 4.22, 4.24 and 4.26). Also, single : multiple ratios were used to test the correction procedures applied to the five single aliquots of heated quartz(figs. 4.29 and 4.30) with the results quoted in table 4.2. Similar to the bleached quartz, the shorter preheating time gave a better accuracy. However, it should be emphasized that this effect is more noticeable in the heated quartz, as can be seen in fig. 4.30 and in table 4.2. Although one should consider the spread in the multiple aliquot measurements(fig. 4.20), an increase in sensitivity is shown in all cases and so may well reflect a genuine effect. Note that each ratio shown in figs. 4.27 $\sim$ 4.30 simply refers to a different single aliquot measurement without any particular meaning.

4.3.6 Discussion

The single aliquot measurements were tested with the new green Nichia LEDs using two different preheatings. For both the bleached and heated quartz the decay ratios were independent of initial dose and the three correction methods considered produced a similar dose response regardless of which of the two different preheating times was used. However, the single aliquot measurements using the shorter preheating time were in better agreement with the multiple aliquot measurements(table 4.2), particularly for the heated quartz. Mejdahl and Botter-Jensen[63] noted that in dating heated archaeological quartz the single aliquot measurements using a preheating of 220^{0}C for 40 seconds gave better dating results than that of 260^{0}C for 40 seconds.

The question of appropriate preheating for single aliquot measurements is discussed further in chapter 5.

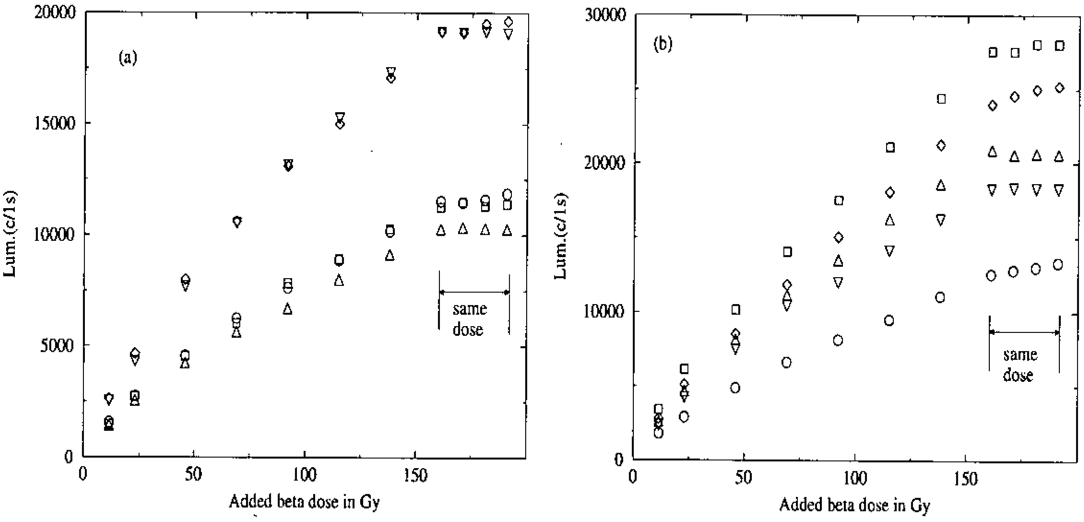


Figure 4.21. Five single aliquot measurements, corrected by the the 1st luminescence correction method, of the dose dependence of green luminescence from quartz previously bleached by daylight quartz. Preheating was for 1min. at 220°C(a) and for 5min. at 220°C(b)

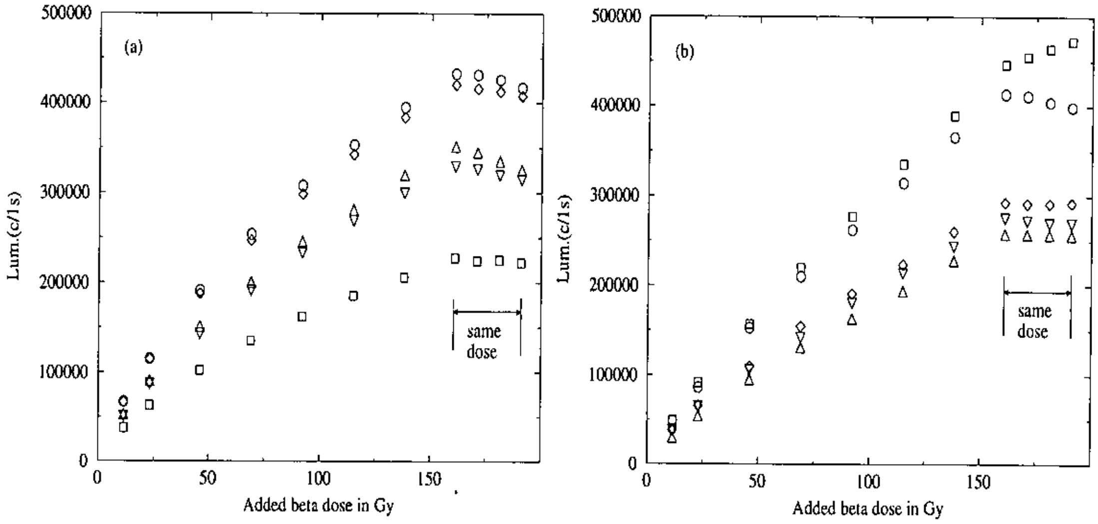


Figure 4.22. Five single aliquot measurements, corrected by the 1st luminescence correction method, of the dose dependence of green luminescence from quartz previously heated quartz. Preheating was for 1min. at 220°C(a) and for 5min. at 220°C(b)

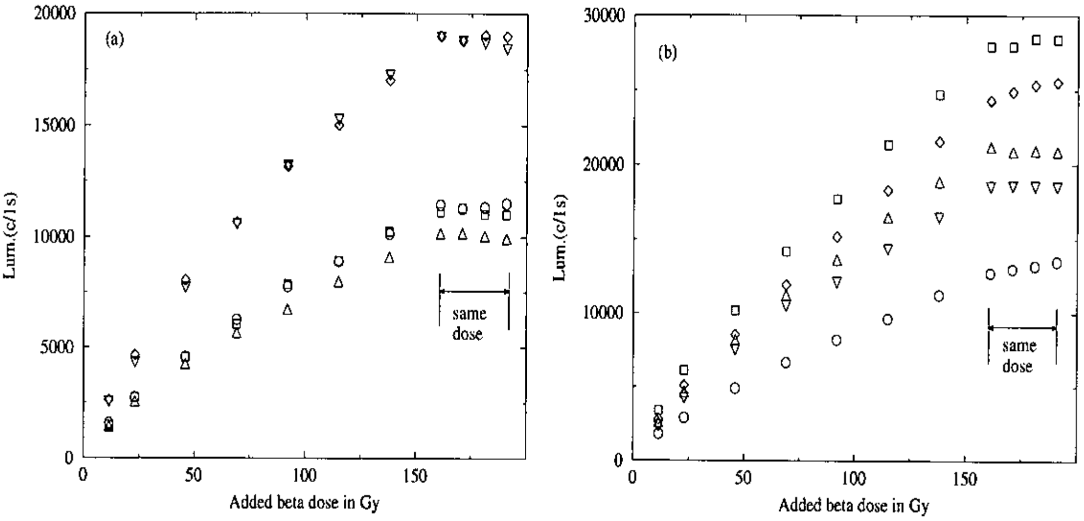


Figure 4.23. Five single aliquot measurements, corrected by the 2^{nd} luminescence correction method, of the dose dependence of green luminescence from quartz previously bleached by daylight quartz. Preheating was for 1min. at 220^{0}C(a) and for 5min. at 220^{0}C(b)

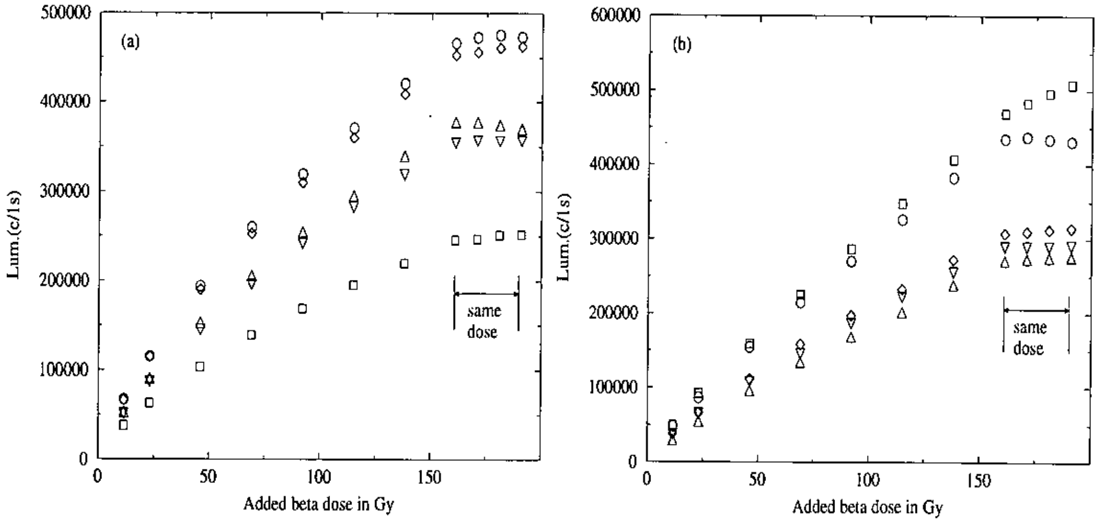


Figure 4.24. Five single aliquot measurements, corrected by the 2^{nd} luminescence correction method, of the dose dependence of green luminescence from quartz previously heated quartz. Preheating was for 1min. at 220^{0}C(a) and for 5min. at 220^{0}C(b)

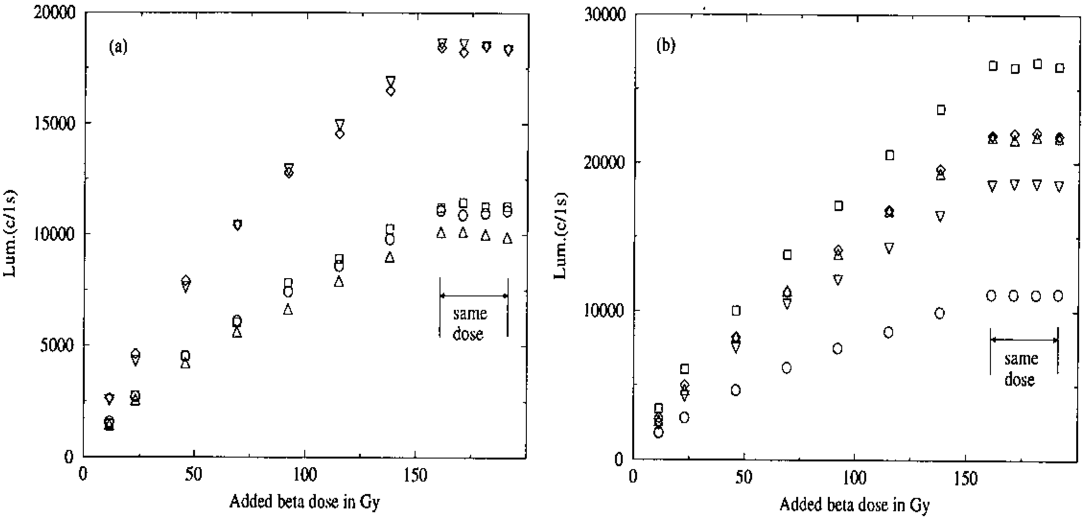


Figure 4.25. Five single aliquot measurements, corrected by the least squares fitting correction method, of the dose dependence of green luminescence from quartz previously bleached by daylight quartz. Preheating was for 1min. at 220^{0}C(a) and for 5min. at 220^{0}C(b)

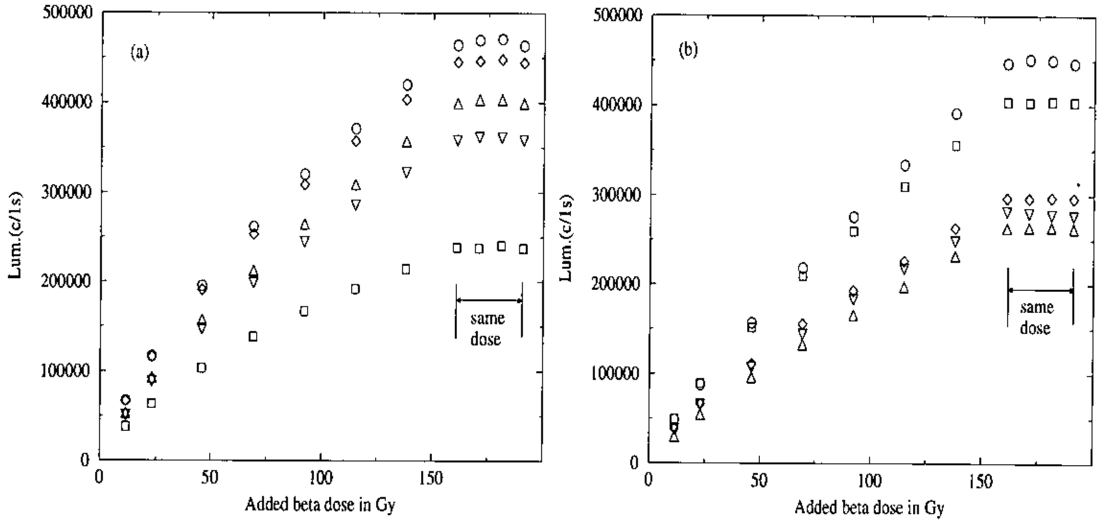


Figure 4.26. Five single aliquot measurements, corrected by the least squares fitting correction method, of the dose dependence of green luminescence from quartz previously heated quartz. Preheating was for 1min. at 220^{0}C(a) and for 5min. at 220^{0}C(b)

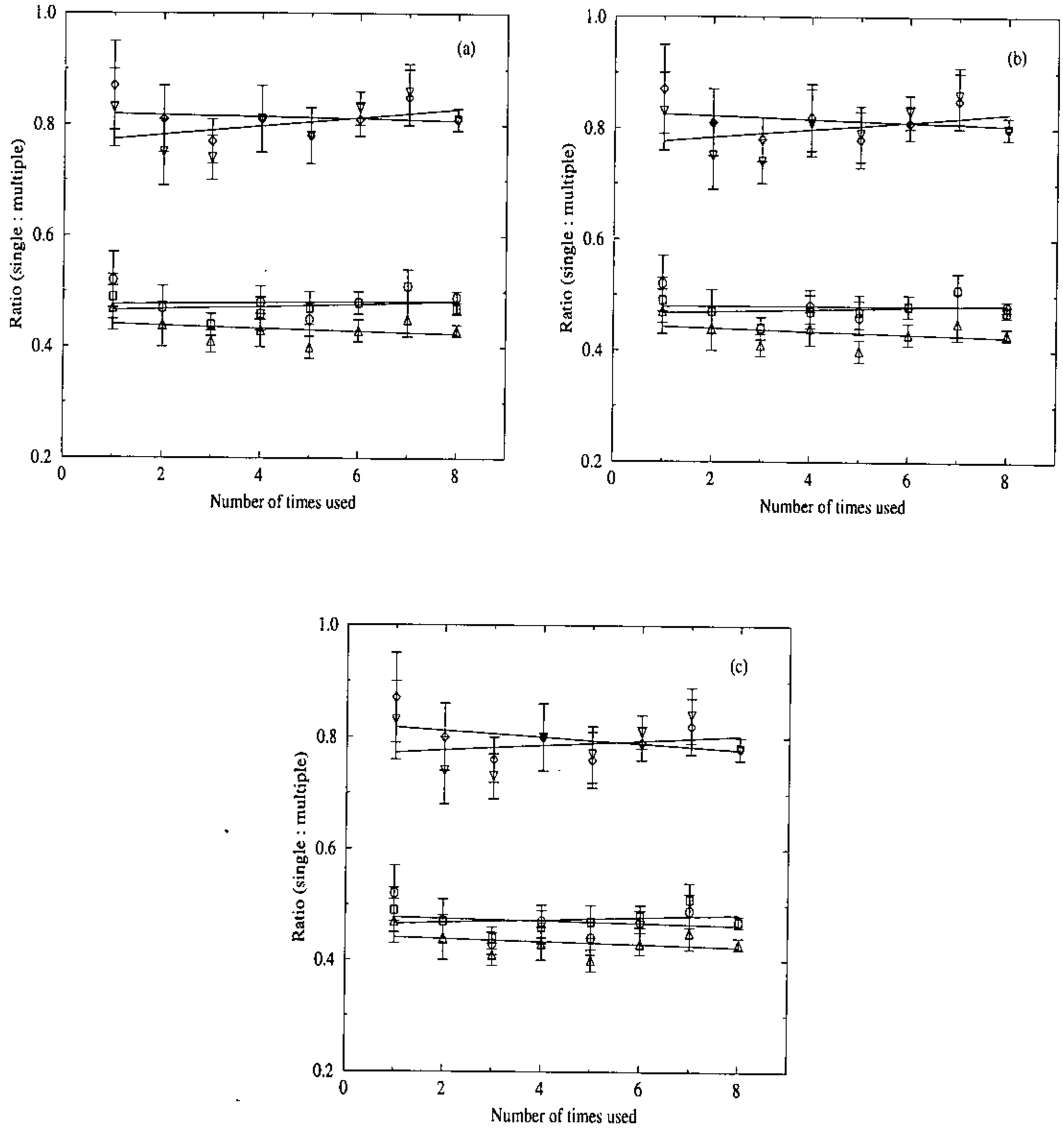


Figure 4.27. Ratio of single to multiple aliquot counts plotted against the number of dose, preheat and green light cycles for the single aliquot measurements in the case of quartz bleached by daylight before use and corrected by the 1^{st} luminescence correction method(a), the 2^{nd} luminescence correction method(b) and the least squares fitting procedure(c). Each symbol refers to a different single aliquot. The error bars arise from the scatter in the multiple aliquot measurements. Least squares linear fits to the data points are drawn. Preheating for the single aliquot measurements was for 1min. at 220^{0}C.

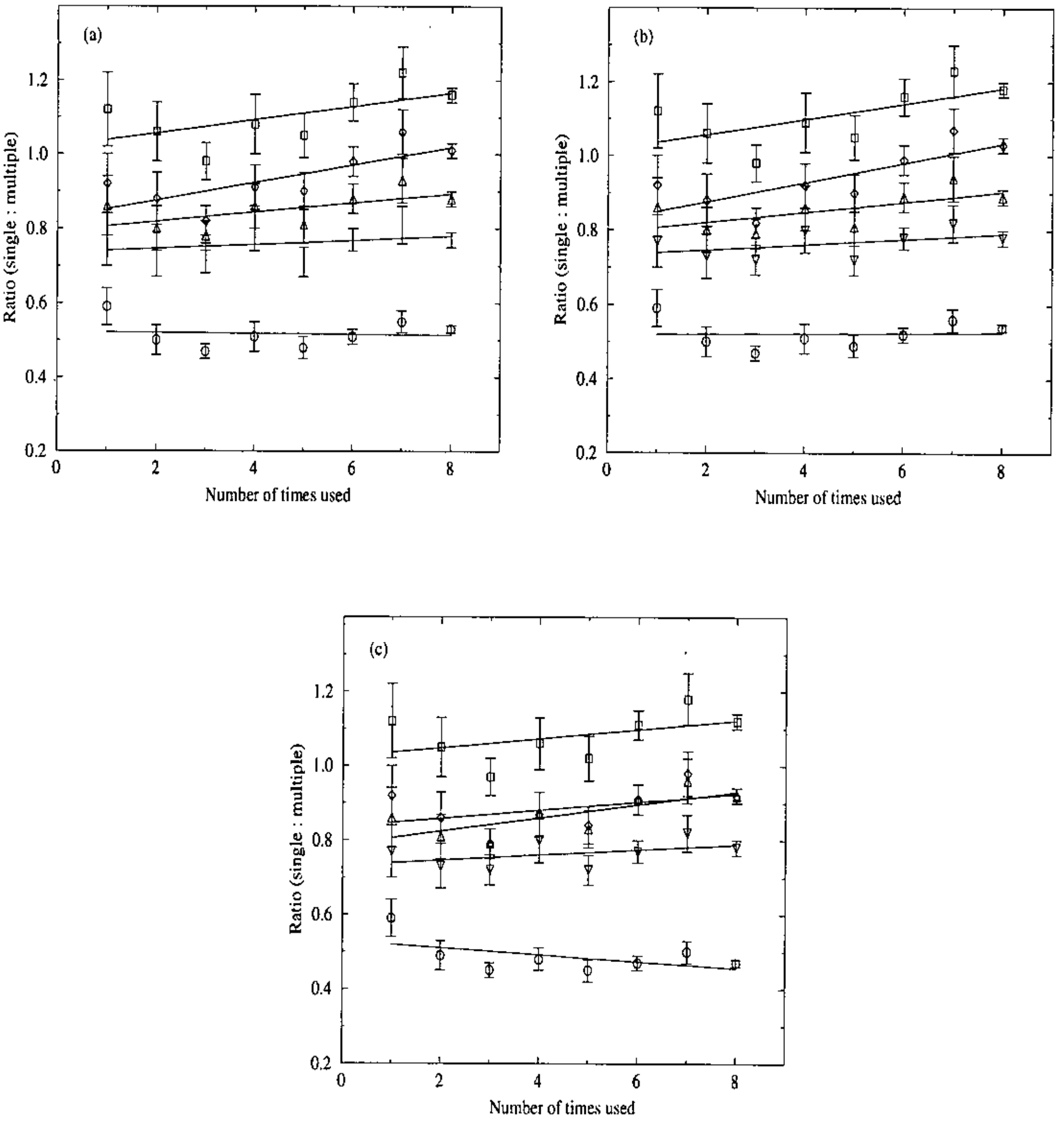


Figure 4.28. Ratio of single to multiple aliquot counts plotted against the number of dose, preheat and green light cycles for the single aliquot measurements in the case of quartz bleached by daylight before use and corrected by the 1st luminescence correction method(a), the 2nd luminescence correction method(b) and the least squares fitting procedure(c). Each symbol refers to a different single aliquot. The error bars arise from the scatter in the multiple aliquot measurements. Least squares linear fits to the data points are drawn. Preheating for the single aliquot measurements was for 5min. at 220^{0}C.

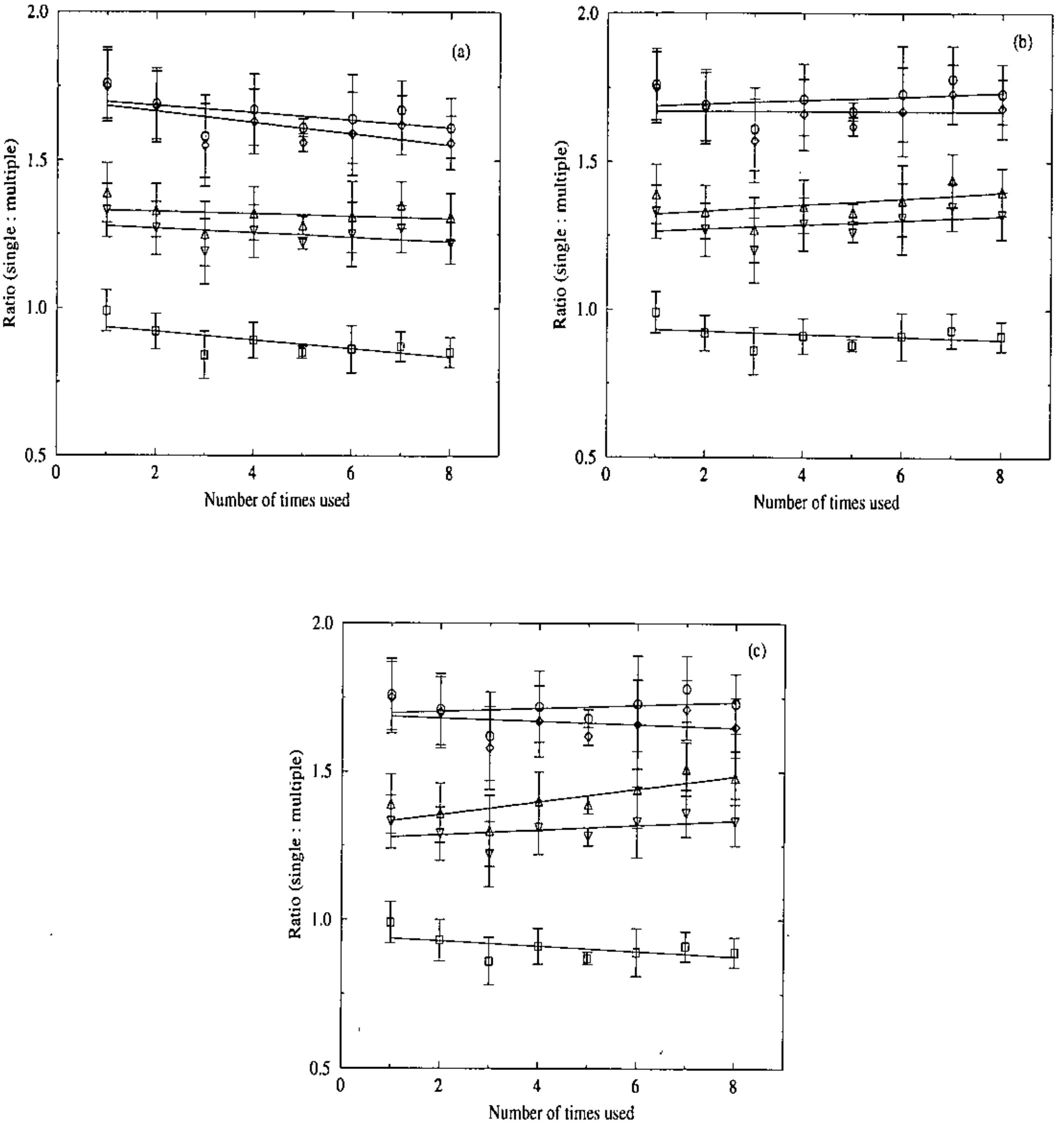


Figure 4.29. Ratio of single to multiple aliquot counts plotted against the number of dose, preheat and green light cycles for the single aliquot measurements in the case of heated quartz before use and corrected by the 1^{st} luminescence correction method(a), the 2^{nd} luminescence correction method(b) and the least squares fitting procedure(c). Each symbol refers to a different single aliquot. The error bars arise from the scatter in the multiple aliquot measurements. Least squares linear fits to the data points are drawn. Preheating for the single aliquot measurements was for 1min. at 220^{0}C.

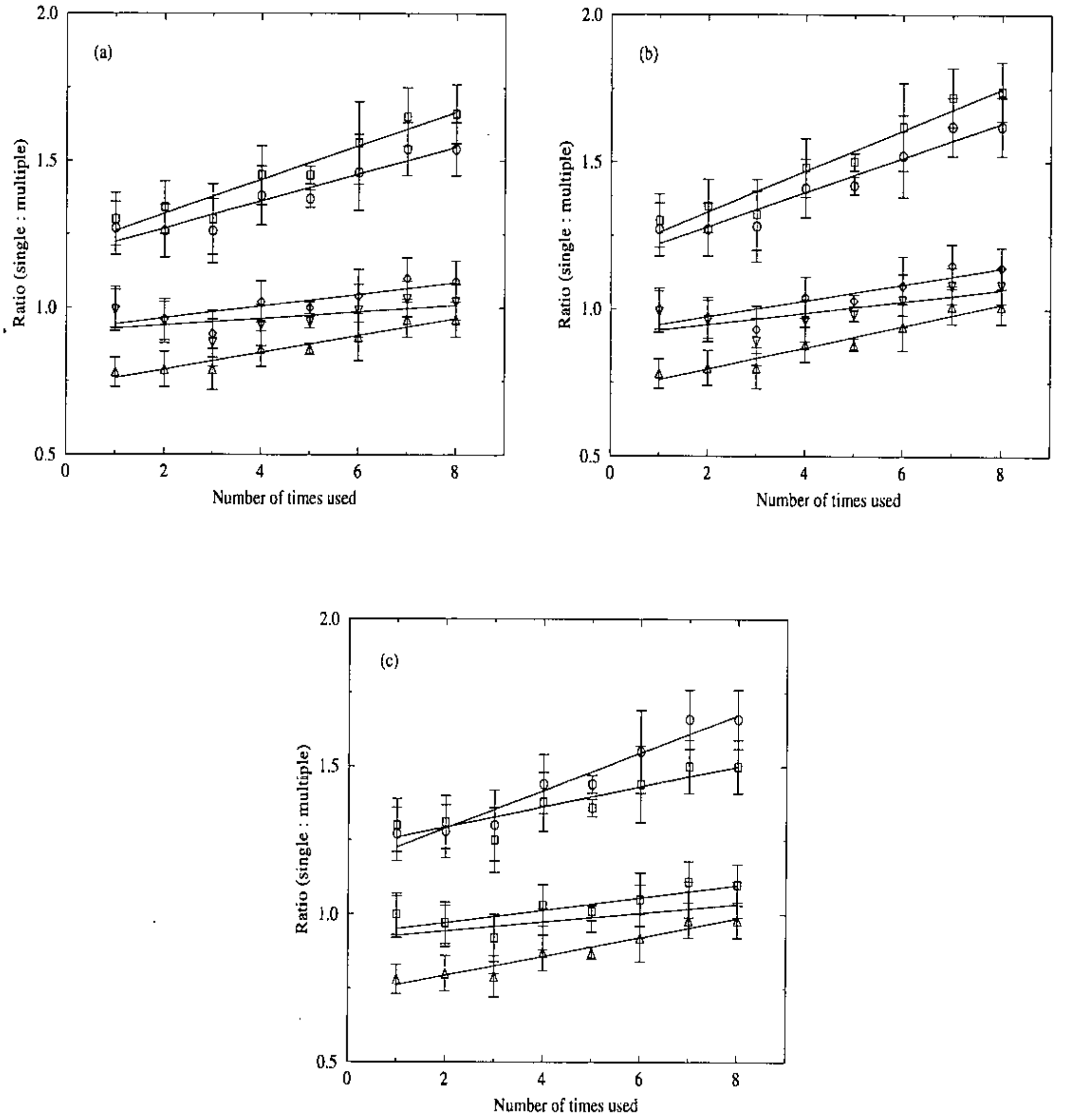


Figure 4.30. Ratio of single to multiple aliquot counts plotted against the number of dose, preheat and green light cycles for the single aliquot measurements in the case of heated quartz before use and corrected by the 1^{st} luminescence correction method(a), the 2^{nd} luminescence correction method(b) and the least squares fitting procedure(c). Each symbol refers to a different single aliquot. The error bars arise from the scatter in the multiple aliquot measurements. Least squares linear fits to the data points are drawn. Preheating for the single aliquot measurements was for 5min. at 220^0C.

Table 4.2. The mean percentage change in the single to multiple ratio per re-use of the aliquot for single aliquot correction methods using new green LEDs.

sample	BDH quartz					
preheating	220°C/1min (220°C/5min)					
bleaching	daylight			heating(500°C/5min)		
cor. method	1st *LC	2nd LC	*LSQ	1st LC	2nd LC	LSQ
% change	0.4±0.1 (1.3±1.1)	0.3±0.2 (1.6±1)	-0.1±0.3 (0.8±1.7)	-0.8±0.4 (3.2±1.3)	0.3±0.2 (4.2±1.4)	0.3±0.7 (3.3±1.4)

*LC : Luminescence correction, *LSQ : Least square fitting correction.

4.4 Conclusion

A comparative study has been carried out of single aliquot and multiple aliquot measurements with bleached and heated quartz using green light for stimulation of the luminescence signal. From the tests described so far, the single aliquot additive dose method applied to quartz offers good agreement with standard multiple aliquot measurements, allowing for the uncertainty due to scatter in the multiple aliquot measurements. However, it should be emphasized that of the two different preheating times investigated for the single aliquot measurements the shorter preheating time gave a much better accuracy, presumably because the correction factor is less, and also the growth data resulting from the corrected single aliquot measurements compared better with that from the normalized conventional multiple aliquot measurements. There was no evidence to favour any particular one of the single aliquot correction methods used. The results are encouraging for single aliquot additive dose dating using green light stimulated luminescence from quartz, whether initially zeroed by light or by heating.

Chapter 5

Equivalent dose determination

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5.1 Introduction

In chapter 4, it was shown that the single aliquot additive dose method applied to quartz, whether initially zeroed by daylight or by heating, can generate the same luminescence response as a function of dose as was determined by the conventional multiple aliquot method. In particular, a shorter duration of preheating gave a better result. While these results are encouraging, there is still a need for further tests to determine whether a similar single aliquot technique is successful in the case of quartz having a natural dose.

This chapter concerns the comparison of equivalent dose values determined using the single aliquot additive dose method with those determined using the conventional multiple aliquot method for quartz from sediment and heated material. The comparison of the results provide another reasonable validation of the single aliquot additive dose method analyzed by various correction procedures. Before the comparison of the equivalent dose values, a fundamental requirement of the single aliquot method has been investigated; whether the signal induced by the dose artificially added to the natural dose decays in the same way due to repeated preheating and reading as the natural signal.

Work on equivalent dose measurement using a single aliquot of quartz from sediment has recently been reported by Murray et al.[97].

5.2 Equipment and samples

All single and multiple aliquot measurements were carried out using an automated system[23] equipped with the 16 new Nichia green light emitting diodes for stimulation, described in chapter 2.

Four quartz samples from sediments were collected, named as SH1, SH2, GF120 and GF140 and four quartz samples from heated materials obtained, named as THEOP1, THEOP2, THEOP3(from pottery) and BS(from burnt soil). No independent age information was available for these samples. They were selected purely for the comparison of equivalent dose values determined using the single aliquot additive dose method with those determined using the conventional multiple aliquot method for quartz from sediment and heated material. The quartz samples of the $\sim 125\mu m$ fraction were separated following the procedures described in chapter 3.

5.3 Investigations of the decay curve

The decay curves for bleached and heated quartz given a laboratory dose were discussed in chapter 4. The concern now is with the decay characteristics of quartz which has a natural dose.

The first investigation was made using natural quartz samples from both sedimentary and heated material without adding any artificial dose. Fig. 5.1(a) concerns quartz sample SH1 from a sediment. Thirteen aliquots of the sample were prepared and divided into three groups.

The first group(five aliquots) was used to examine the decay behaviour for a sequence of ten cycles of only repeat measuring the luminescence for 1s at room temperature(fig. 5.1(a)).

The second group(five aliquots) was used to investigate the decay behaviour for a similar sequence as performed with the first group but with a preheating(220^0C/1min.). Considering the scatter, there is no noticeable difference in the decay ratios between the first group and the second group(fig. 5.1(a)). It suggests that the preheating used(220^0C/1min.) does not significantly reduce a stable signal.

The final group(three aliquots) looked at the decay behaviour by the same sequence and condition as done in the second group except for using a longer preheating(220^0C/5min.). Fig. 5.1(a) shows that, contrary to the shorter preheating(220^0C/1min.), the longer preheating(220^0C/5min.) reduces the stable signal significantly.

The large scatter in the decay curves(fig. 5.1(a)) may come from counting statistics because of the initially low luminescence signal.

Fig. 5.1(b) concerns quartz sample THEOP2 from pottery. Nine aliquots of the sample were prepared and divided into three groups(three aliquots in each group) in the same way as done above. In contrast to the behaviour of quartz sample SH1 from sediment, the luminescence signal was very sensitive to preheating(i.e. compared with the first group without giving preheating, the difference of the decay ratio of the second group and the third group between sample SH1 and THEOP2 was noticeable if allowance has been made in the scatter between measurements.). In addition, the scatter in each group of the sample THEOP2 was considerably less. It implies that the counting statistics in quartz sample THEOP2 from pottery is not as significant as in quartz sample SH1 from sediment, presumably because of initially high luminescence signal.

Each point in fig. 5.1 is the mean of the measurements and the error bars indicate the spread in the measurements.

The second investigation looked at the validity of the assumption of the single

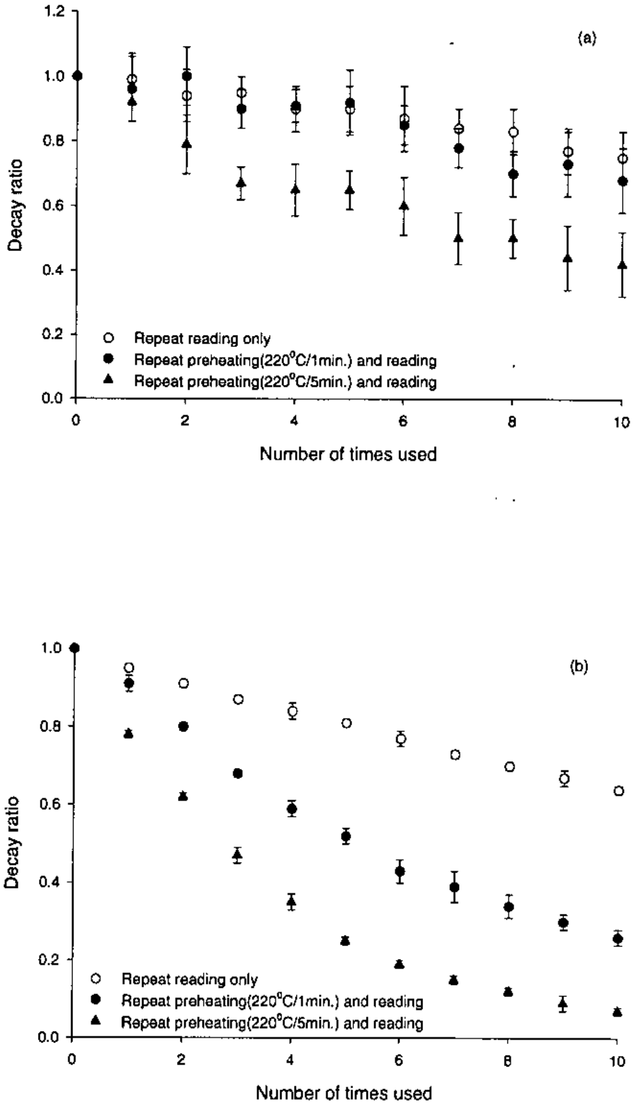


Figure 5.1. Natural dose decay curves for sample SH1(a) from sediment and (b)THEOP2 from pottery.

aliquot additive dose method described by Duller[25], namely whether luminescence signals induced by different artificial doses decay independently of initially given dose during repeated preheating and reading. This result was compared with the decay ratio of the natural dose. Fig. 5.2(a) concerns quartz sample SH1 from sediment and shows the decay of the signal due to repeated preheating(220^0C/1min.) and reading for aliquots given beta doses of 23Gy, 69Gy and 115Gy in addition to the natural dose along with the decay curve for the natural dose alone. The doses artificially added are equivalent to approximately two, five and eight times the natural dose, $\sim$ 13.5Gy(table 5.1). Three aliquots were measured for each dose(In the case of the natural dose, five aliquots were used). While the decay curves for the dosed samples are independent of initially given dose, they differ slightly from the decay of the natural dose. However, accepting the scatter of decay ratios the drawing of any conclusion is not definitive. In order to confirm this result, a similar sequence using a longer preheating time(220^0C/5min.) was made for aliquots beta dosed to 23Gy and 115Gy in addition to the natural dose and for aliquots with the natural dose alone. For aliquots dosed in addition to the natural dose, a similar result was obtained(the decay ratios do not depend on initially given dose), but the difference of the decay ratio between the natural and the natural plus artificial dose was noticeable, compared with the result using the shorter preheating.

Similar results were obtained from the sediment sample SH2. Measurements were made on quartz sample GF140 from sediment in a similar manner as above, illustrated in fig. 5.2(b). The aliquots were given beta doses of 115Gy and 230Gy in addition to the natural dose. These added doses correspond to half of the natural dose and the natural dose($\sim$ 230Gy, table 5.1) respectively. While the tendency of the decay characteristics is similar to those of sample SH1, the sample GF140 decays more slowly. For example, for aliquots dosed to 115Gy in addition to the natural dose the final decay ratio for the longer preheating(220^0C/5min.) was 0.18±0.04 for sample SH1 and 0.32±0.06 for sample GF140. No difference was found between the samples GF140 and GF120.

Each point in fig. 5.2 is the mean of the measurements and the error bars indicate the spread in the measurements.

In recent work Murray et al.[97] also found a weak dependence of decay constant between natural dose and natural dose plus artificial dose; for the 200^0C/10s preheating the natural dose samples decay more rapidly than the laboratory dosed samples while for the 280^0C/10s preheating the natural dose samples decay more slowly than the laboratory dosed samples. Although a direct comparison of their result with my result is difficult because of different measuring condition(particularly, they measured the luminescence for 0.1s at 110^0C) and the scatter in the decay curves, one may conclude that the decay curves for samples artificially dosed in addition to the natural dose are not remarkably dependent on initially given dose irrespective of preheating condition. However, the decay curves for the natural dose samples differ from the decay curves for samples artificially dosed in addition to the natural dose. The difference depends on preheating conditions. With extending of preheating time(or with increasing of preheating temperature), the natural dose sample decays more slowly than the sample dosed in addition to the natural dose.

Fig. 5.3(a) concerns quartz sample BS from burnt soil and shows the decay of luminescence due to repeated preheating(using two preheatings the same as applied to samples from sediments, 220^0C/1min. and 220^0C/5min.) and reading for aliquots beta dosed to 69Gy in addition to the natural dose and for the natural dose alone. Contrary to the quartz samples from sediments investigated in this study, the decay curve shows no difference between natural dose and natural plus artificial dose for both preheatings introduced.

Similar measurements were made on quartz THEOP2 from pottery and the result was similar to those from the sample BS, as can be seen in fig. 5.3(b), except that the sample THEOP2 decays more rapidly. Each point in fig. 5.3 is the mean of three measurements and the error bars indicate the spread in the measurements. The decay ratios from samples THEOP1 and THEOP3 were not different from those obtained from sample THEOP2.

The final investigation involved whether the shape of the decay curves(figs. 5.2 and 5.3) defines a functional form suitable for the alternative least squares fitting correction method[93] of the single aliquot measurement. Plotting of the decay from figs. 5.2 and 5.3 with logarithmic axis for the fraction of signal, figs. 5.4 and 5.5 show the correction factors to be well represented by an exponential decay.

5.4 Equivalent dose determination by single aliquot additive dose method

After measurement of the natural signal, the sequence of beta dosing, preheating and measuring was repeated for five beta doses to construct a growth curve using a single aliquot. The dose range chosen for samples SH1, SH2, BS, THEOP1, THEOP2 and THEOP3 was from 0 to 58Gy and 0 to 345Gy was selected for samples GF120 and GF140 because of a low luminescence intensity after beta dosing. Two preheatings were introduced; One was 1minute at 220^0C and the other 5 minutes at 220^0C, as investigated in section 5.3. The measurement time of exposure to light from the green LEDs was chosen to be 1s for all quartz.

Since the decay ratios of sediment samples having only a natural dose differ from those of the samples dosed in addition to the natural dose, particularly significant in measurements using longer preheating, a question arises which decay ratio should be applied to correction of the single aliquot measurement. With the sediment sample SH1 two corrections based on the same single aliquot measurement were made; one was corrected by the decay ratio of the natural dose alone and the other was corrected by the average of the decay ratio of the dosed aliquots. With the two single aliquot measurement corrected by the above way, three further measurement cycles of preheating and reading of luminescence without adding any beta dose, which was used by Duller[25] as a test of single aliquot method(chapter 4), were tested. As shown in fig.

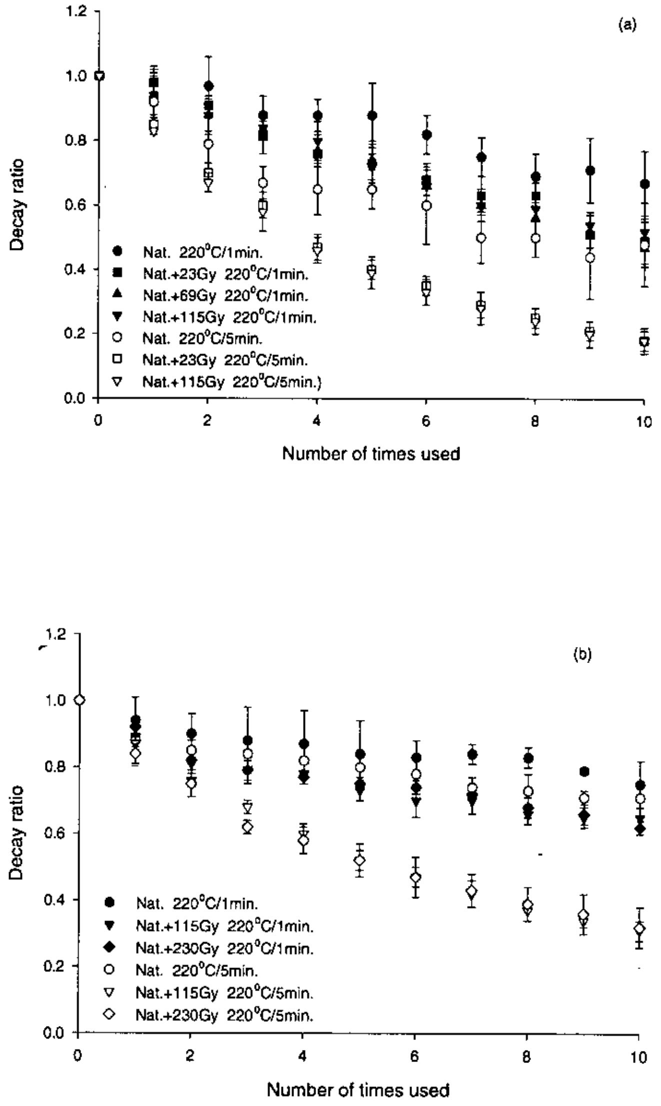


Figure 5.2. The decay in luminescence signal due to successive preheating and measurement sequences relative to the first measurement for quartz sample SH1(a) and GF140(b) from sediment.

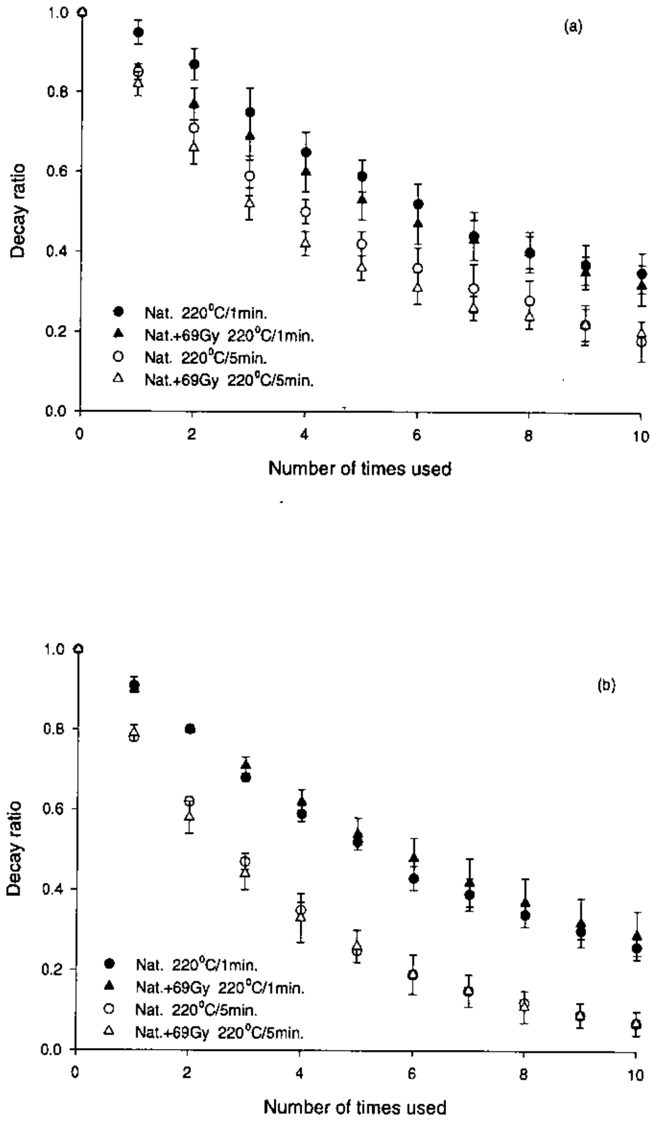
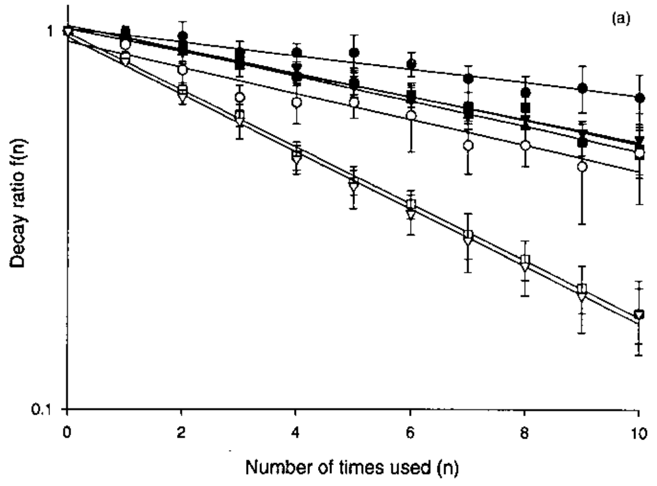


Figure 5.3. The decay in luminescence signal due to successive preheating and measurement sequences relative to the first measurement for quartz sample BS from burnt soil(a) and THEOP2 from pottery(b).



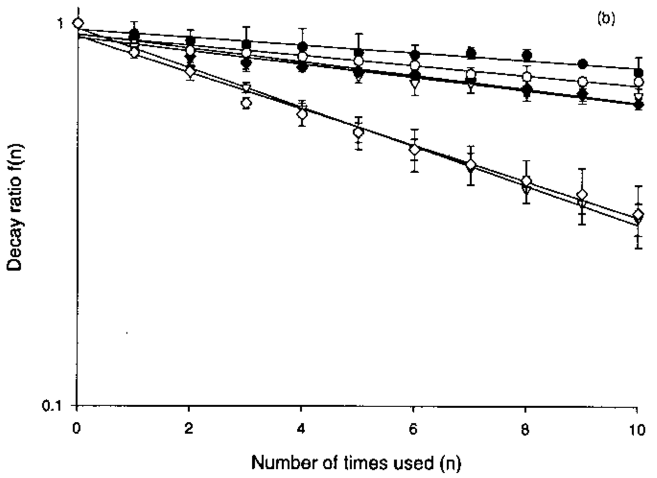


Figure 5.4. The decay data of fig. 5.2, for quartz sample SH1(a) and GF140(b), exemplifying the relationship $f(n) = \exp[-c(n-1)]$, for the fraction of initial signal $f(n)$ in terms of the number of times n that the aliquot is used. The symbols have the same meanings as in fig. 5.2.

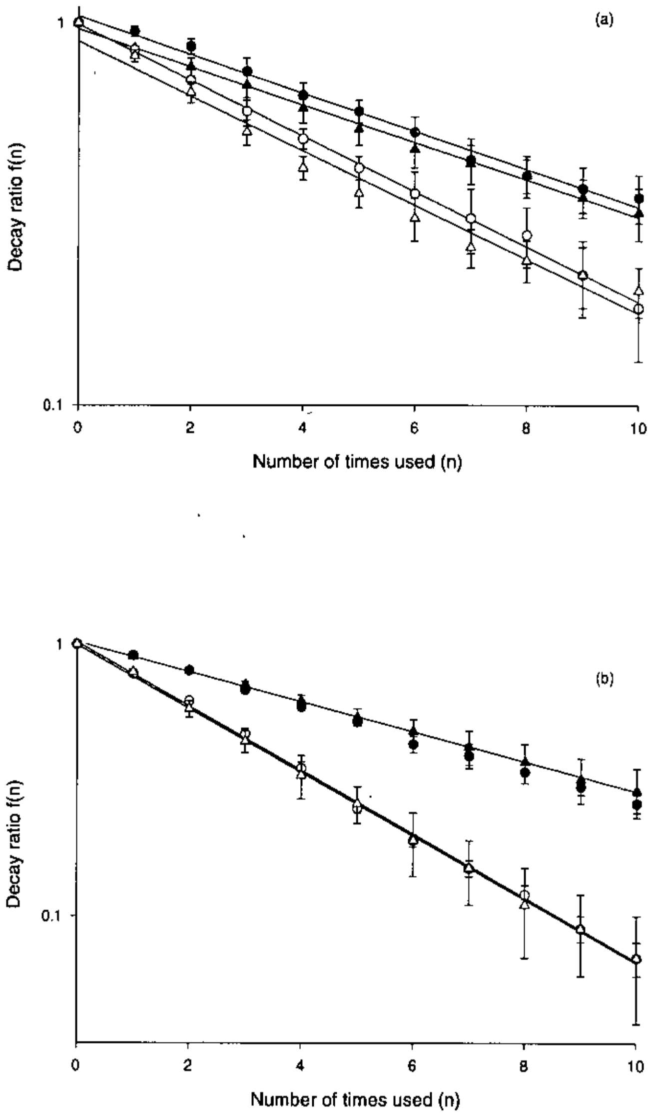


Figure 5.5. The decay data of fig. 5.3, for quartz sample BS(a) and THEOP2(b), exemplifying the relationship $f(n) = \exp[-c(n-1)]$, for the fraction of initial signal $f(n)$ in terms of the number of times n that the aliquot is used. The symbols have the same meanings as in fig. 5.3.

5.6 the single aliquot measurement corrected by the average of the decay ratio of the dosed aliquots gave a better result irrespective of preheating condition. For a practical purpose, the equivalent dose values were determined with each growth curve corrected by different decay ratios and compared. Although the growth curve of the single aliquot measurement corrected by the average of the decay ratio of the dosed aliquots shows a less curved shape(fig. 5.6), similar equivalent dose values were obtained if one considers the error limits. For example, the equivalent dose values determined by the single aliquot measurement corrected by the decay ratio of the natural dose alone and by the average of the decay ratio of the dosed aliquots were 12.6±1.7Gy and 13.2±1.6Gy for a preheating of 220^0C/1min., and for a preheating of 220^0C/5min. 14±1.4Gy and 14.4±1.5Gy. 10 aliquots were used for the comparison of equivalent dose values for both preheatings. For these reasons, the average of the decay ratio of the dosed aliquots was used for correction of the single aliquot measurement.

Measurements on a single aliquot of each quartz sample were made and corrected by the 1^{st}, 2^{nd} luminescence correction method and the least squares fitting correction method. Before the equivalent dose determination, three further measurement cycles of preheating and reading of luminescence without adding any beta dose were performed for the least squares fitting correction method and for checking the validity of the correction methods. Figs. 5.7 - 5.14 are examples, randomly chosen, of the single aliquot measurements for each sample corrected by the different correction methods. As shown in figs. 5.7 - 5.14, the results from the different correction methods were indistinguishable. The small differences between points corrected by the different correction methods can be attributed to scatter in the measurements of the decay curves. However, the dose response curves using a shorter preheating time for samples SH1, SH2, THEOP1, THEOP2 and THEOP3 show a different relationship between luminescence and dose from those for using a longer preheating time. The former are clearly non-linear which is in good agreement with multiple aliquot measurements(figs. 5.23 and 5.24), whereas the latter show an approximately linear response to added

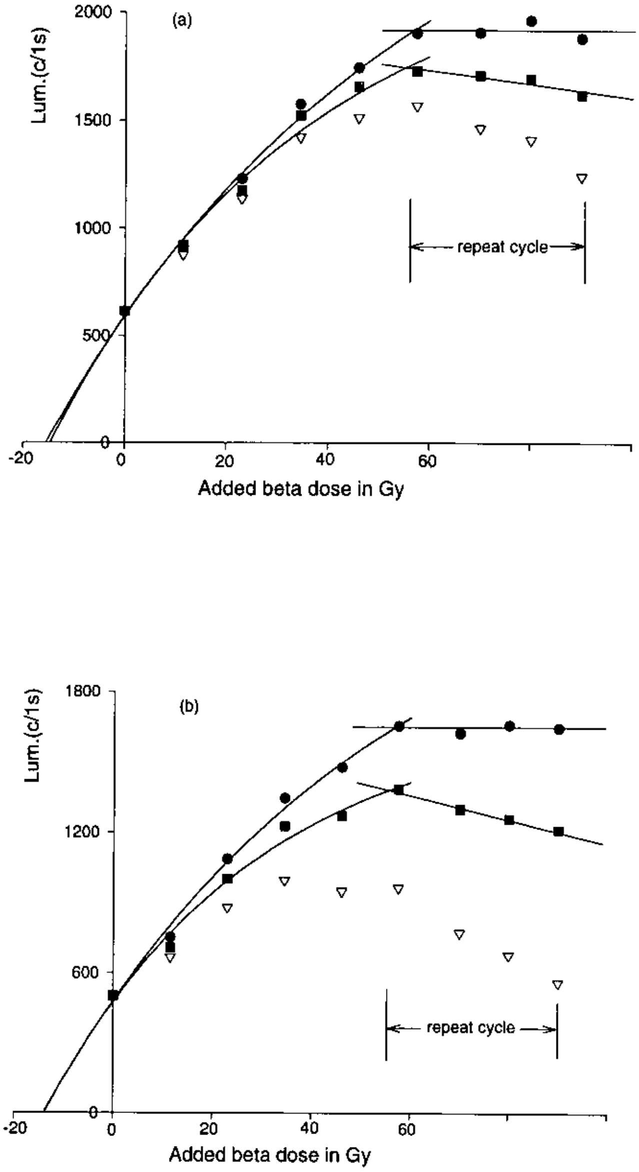


Figure 5.6. An example of the single aliquot growth curves corrected by the decay ratio of the natural dose alone(solid square) and by the average of the decay ratio of the dosed aliquots(solid circle) along with the uncorrected single aliquot measurement(open triangledown) for sample SH1, (a) for 220^0C/1min. preheating and (b) for 220^0C/5min. preheating. A single saturating exponential function was applied for determination of the equivalent dose.

beta dose. This could be connected with trapped charge population. As the single aliquot measurements are made, the trapped charge population within the sample after any given dose becomes progressively lower with increasing preheating time(or temperature). This results in more charge being trapped for the next additional dose in the sequence of single aliquot measurement. Consequently, the growth curve of the single aliquot measurement using longer(higher) preheating becomes steeper and less curved after correction. This confirms the test results for single aliquot measurement described in chapter 4(i.e. The single aliquot measurements using shorter preheating time were in better agreement with the multiple aliquot measurement. In particular, for heated quartz all single : multiple ratios showed an increasing tendency when the longer preheating was applied to the single aliquot measurement). The effect will only be significant for samples whose growth curve is not linear. For instance, in the case of the sample BS which shows a linear luminescence response to dose in the multiple aliquot measurement(fig. 5.24(a)), the corrected growth curves of the single aliquot measurements are quite similar to each other(i.e. linear response) irrespective of the different preheating times(fig. 5.11). For the samples GF120 and GF140 the difference between the growth curves for single aliquot measurement using different preheating times is not noticeable(figs. 5.9 and 5.10) although the growth curves of the multiple aliquot measurement are nonlinear(fig. 5.24(b) and (c)). This can be explained since the decay ratios using the longer preheating for these two samples are higher than the decay ratios of samples SH1, SH2, THEOP1, THEOP2 and THEOP3(figs. 5.2 and 5.5(b)), so that the probability for more charge being trapped, even if longer(higher) preheating is used, is small. However, the uncertainty from counting statistics should be considered because of the low luminescence signal despite the large additional dose.

Similar results can be found in work by Murray et al.[97]. In their measurement using lower preheating(200^0C/10s), the shape of the single aliquot growth curve is quite consistent with that of multiple aliquot measurement. However, when using higher preheating(280^0C/10s) the growth curve of single aliquot measurement shows a clearly linear response while non-linear shape of growth curve can be seen in the same dosage range of the multiple aliquot measurement.

The equivalent doses were assessed by extrapolation of the growth curve based on the corrected single aliquot data. Three correction methods mentioned earlier were applied to the same uncorrected data and the corrected data for all samples were fitted with a single saturating exponential function, as exemplified figs. 5.15 - 5.22. The results of the equivalent dose determined are summarised in table 5.1.

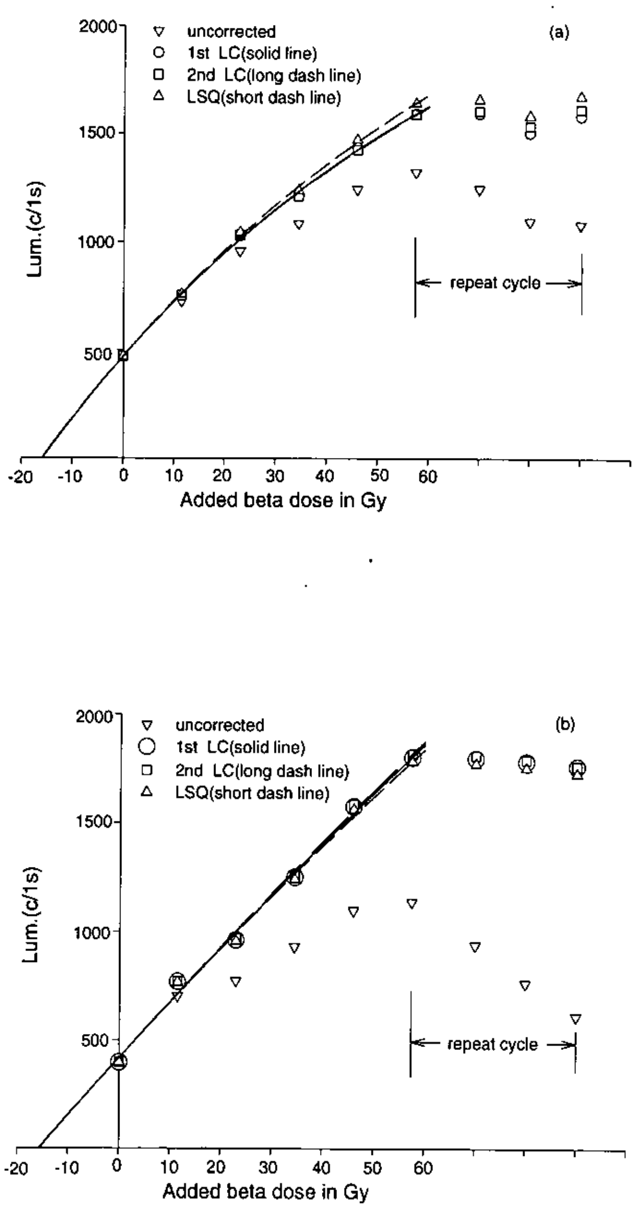


Figure 5.7. An example of single aliquot measurements for quartz sample SH1 which were corrected by the 1^{st} luminescence correction method(o), the 2^{nd} luminescence correction method(□), the least squares fitting procedure(△) along with uncorrected data(▽). Preheating was for 1min. at 220^0C(a) and for 5min. at 220^0C(b).

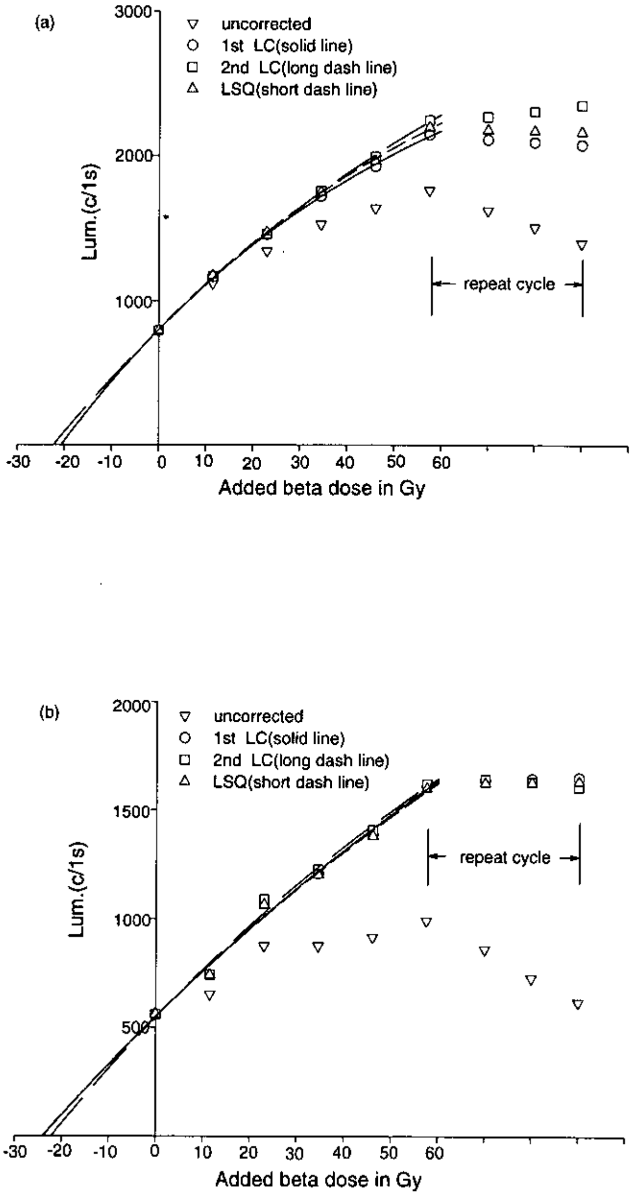


Figure 5.8. An example of single aliquot measurements for quartz sample SH2 which were corrected by the 1^{st} luminescence correction method(○), the 2^{nd} luminescence correction method(□), the least squares fitting procedure(△) along with uncorrected data(▽). Preheating was for 1min. at 220^0C(a) and for 5min. at 220^0C(b).

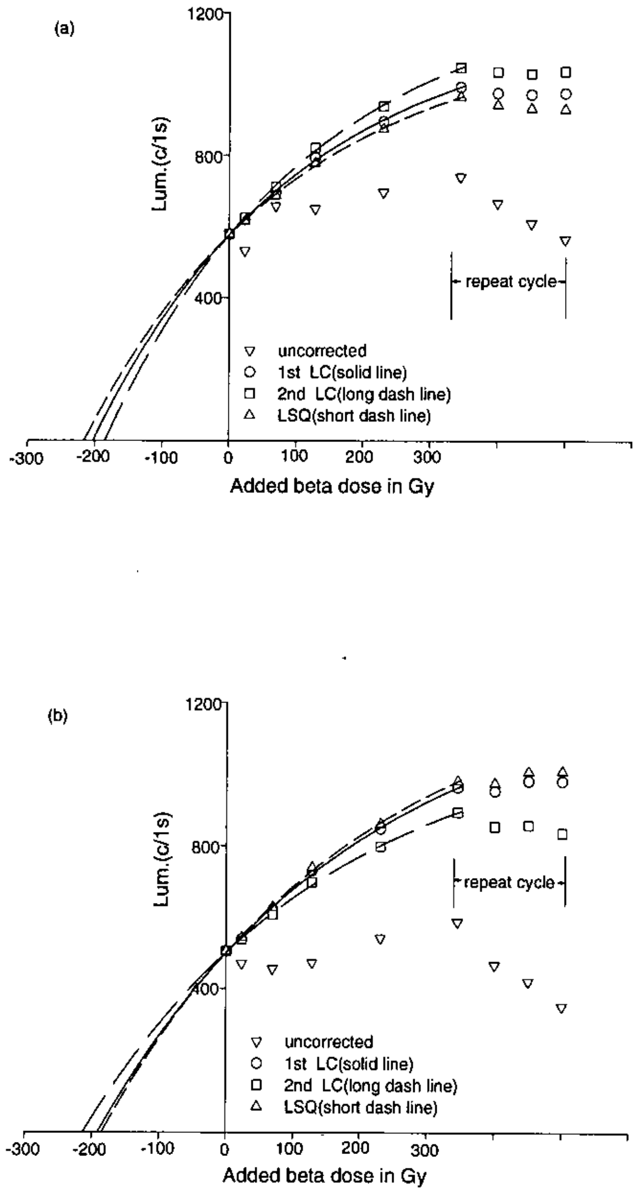


Figure 5.9. An example of single aliquot measurements for quartz sample GF120 which were corrected by the 1^{st} luminescence correction method(o), the 2^{nd} luminescence correction method(□), the least squares fitting procedure(△) along with uncorrected data(▽). Preheating was for 1min. at 220^0C(a) and for 5min. at 220^0C(b).

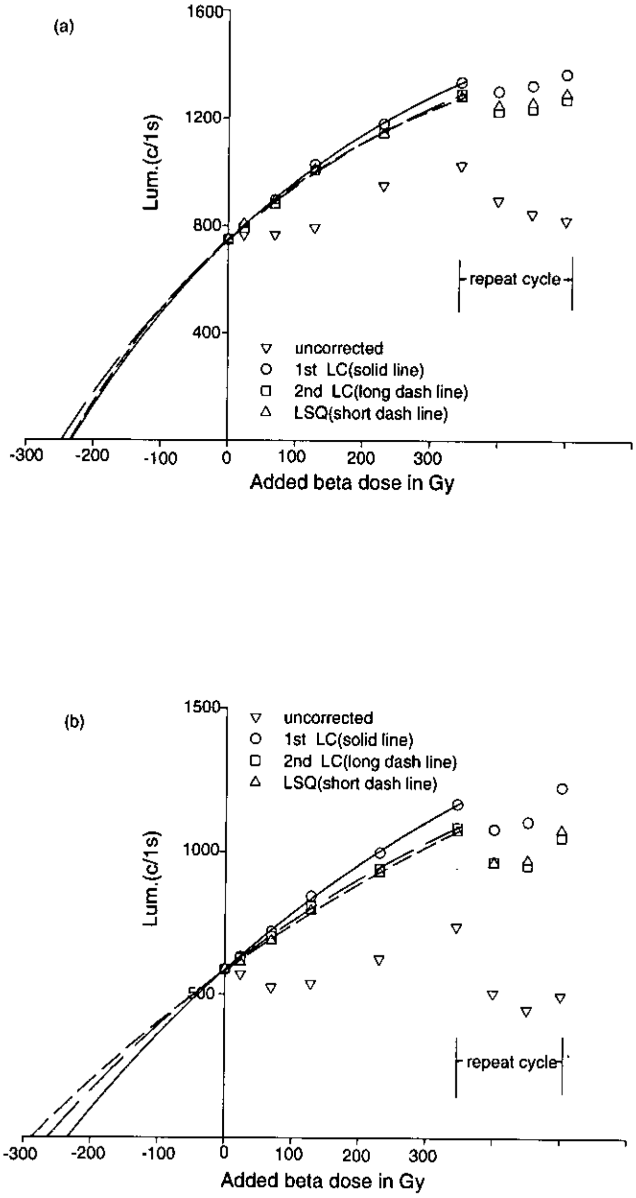


Figure 5.10. An example of single aliquot measurements for quartz sample GF140 which were corrected by the 1^{st} luminescence correction method(○), the 2^{nd} luminescence correction method(□), the least squares fitting procedure(△) along with uncorrected data(▽). Preheating was for 1min. at 220^0C(a) and for 5min. at 220^0C(b).

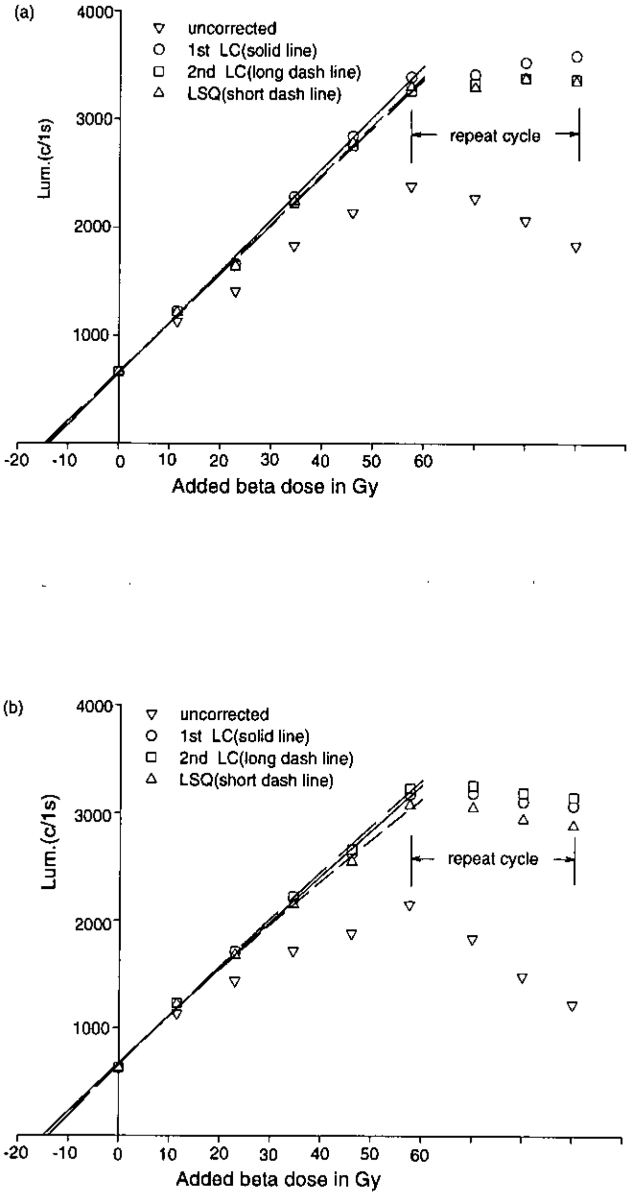


Figure 5.11. An example of single aliquot measurements for quartz sample BS which were corrected by the 1^{st} luminescence correction method(o), the 2^{nd} luminescence correction method(□), the least squares fitting procedure(△) along with uncorrected data(▽). Preheating was for 1min. at 220^0C(a) and for 5min. at 220^0C(b).

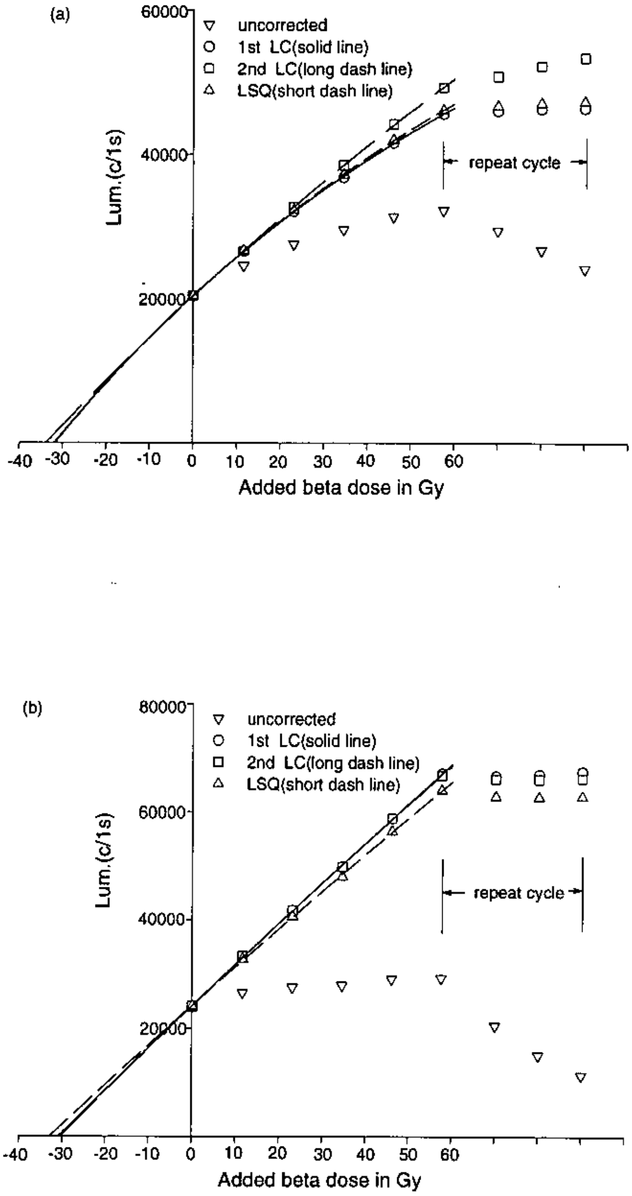


Figure 5.12. An example of single aliquot measurements for quartz sample THEOP1 which were corrected by the 1^{st} luminescence correction method(o), the 2^{nd} luminescence correction method(□), the least squares fitting procedure(△) along with uncorrected data(▽). Preheating was for 1min. at 220^0C(a) and for 5min. at 220^0C(b).

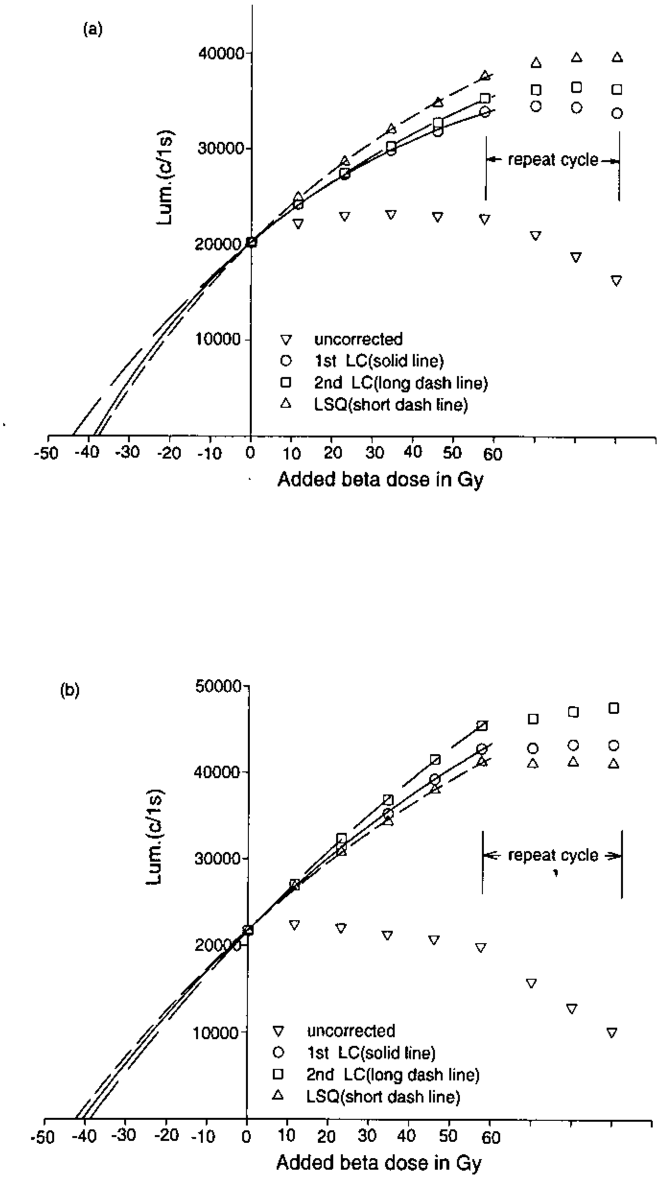


Figure 5.13. An example of single aliquot measurements for quartz sample THEOP2 which were corrected by the 1^{st} luminescence correction method(o), the 2^{nd} luminescence correction method(□), the least squares fitting procedure(△) along with uncorrected data(▽). Preheating was for 1min. at 220^0C(a) and for 5min. at 220^0C(b).

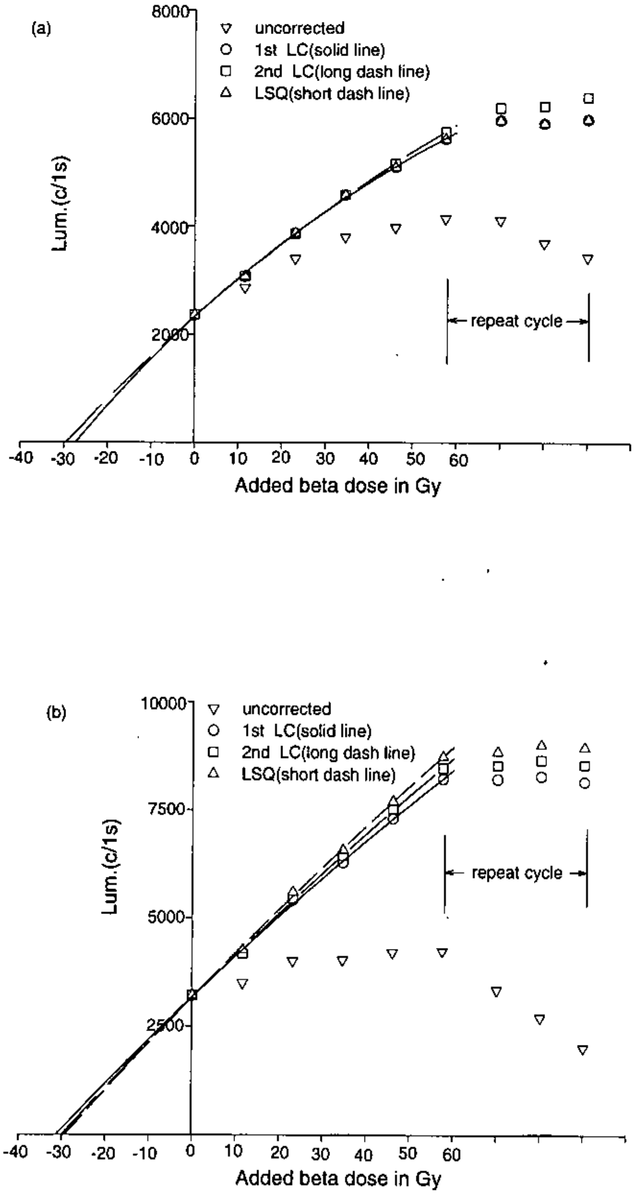


Figure 5.14. An example of single aliquot measurements for quartz sample THEOP3 which were corrected by the 1^{st} luminescence correction method(○), the 2^{nd} luminescence correction method(□), the least squares fitting procedure(△) along with uncorrected data(▽). Preheating was for 1min. at 220^0C(a) and for 5min. at 220^0C(b).

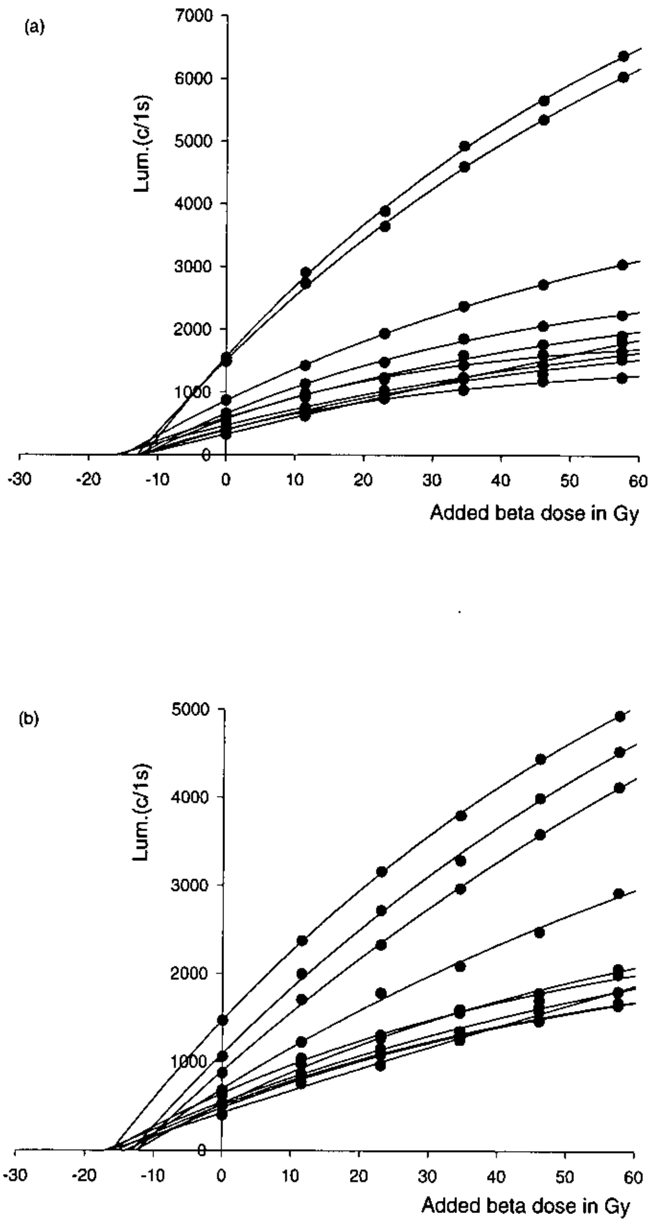


Figure 5.15. An example of equivalent dose determination based on single aliquot measurements for quartz sample SH1 which were corrected by the 1^{st} luminescence correction method. Preheating was for 1min. at 220^0C(a) and for 5min. at 220^0C(b). Ten single aliquots were used for each preheating.

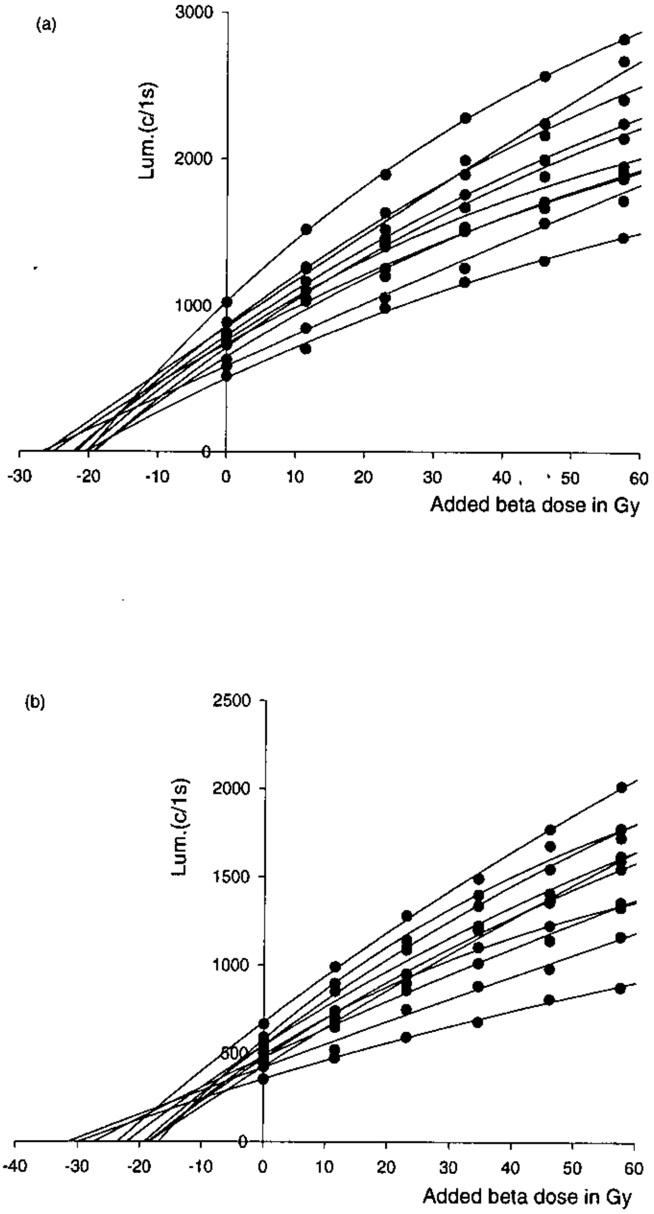


Figure 5.16. An example of equivalent dose determination based on single aliquot measurements for quartz sample SH2 which were corrected by the 2^{nd} luminescence correction method. Preheating was for 1min. at 220^0C(a) and for 5min. at 220^0C(b). Ten single aliquots were used for each preheating.

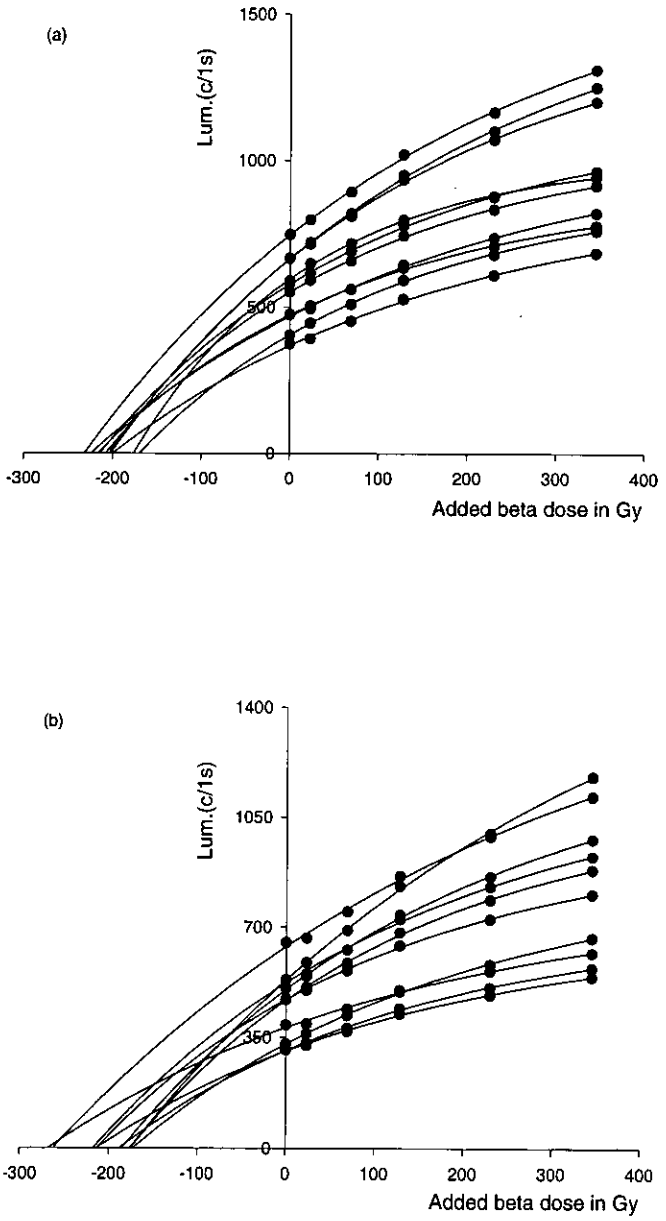


Figure 5.17. An example of equivalent dose determination based on single aliquot measurements for quartz sample GF120 which were corrected by the least squares fitting procedure. Preheating was for 1min. at 220°C(a) and for 5min. at 220°C(b). Ten single aliquots were used for each preheating.

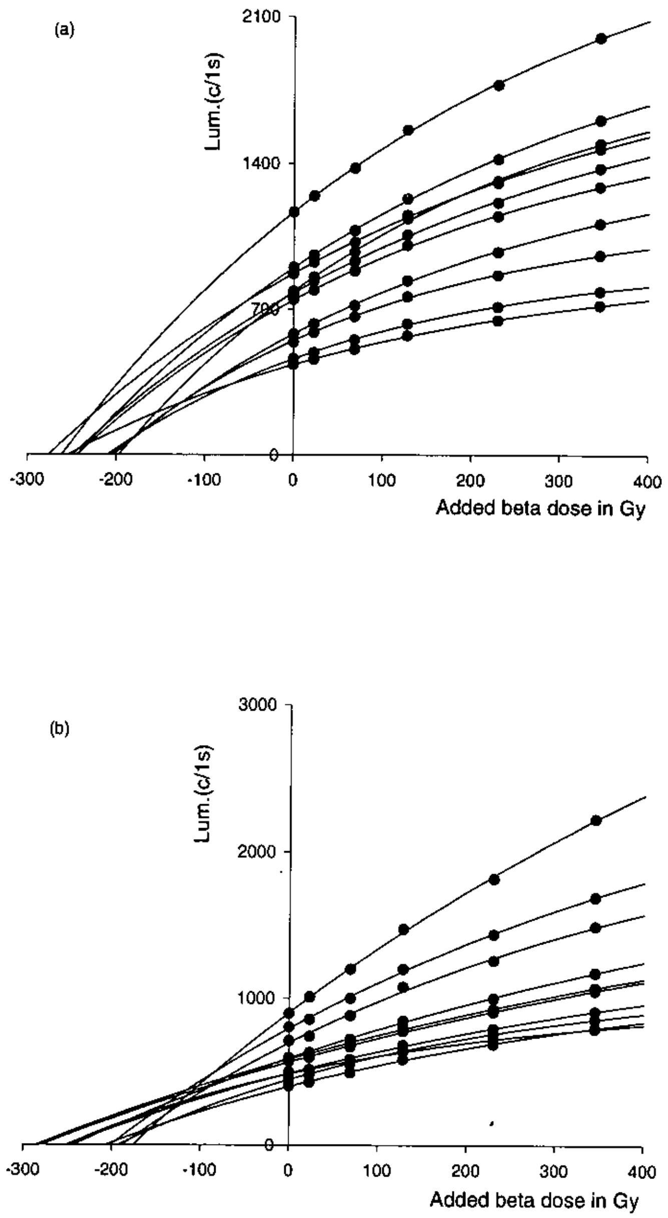


Figure 5.18. An example of equivalent dose determination based on single aliquot measurements for quartz sample GF140 which were corrected by the least squares fitting procedure. Preheating was for 1min. at 220^{0}C(a) and for 5min. at 220^{0}C(b). Ten single aliquots were used for each preheating.

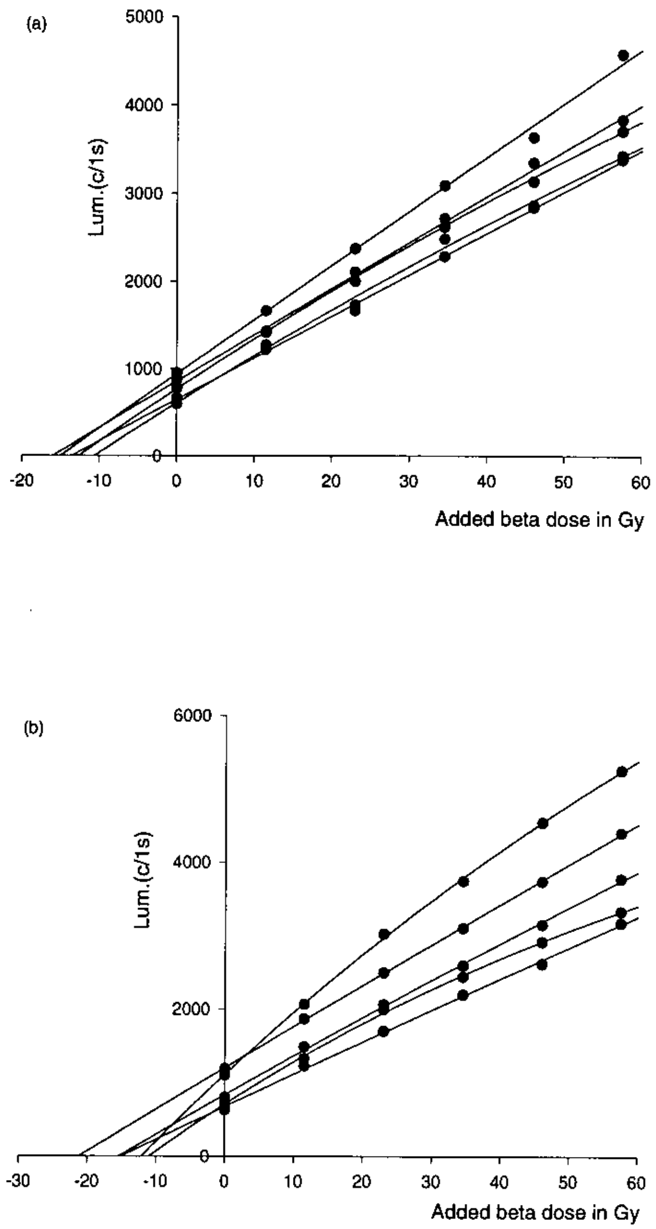


Figure 5.19. An example of equivalent dose determination based on single aliquot measurements for quartz sample BS which were corrected by the 1^{st} luminescence correction method. Preheating was for 1min. at 220^0C(a) and for 5min. at 220^0C(b). Five single aliquots were used for each preheating.

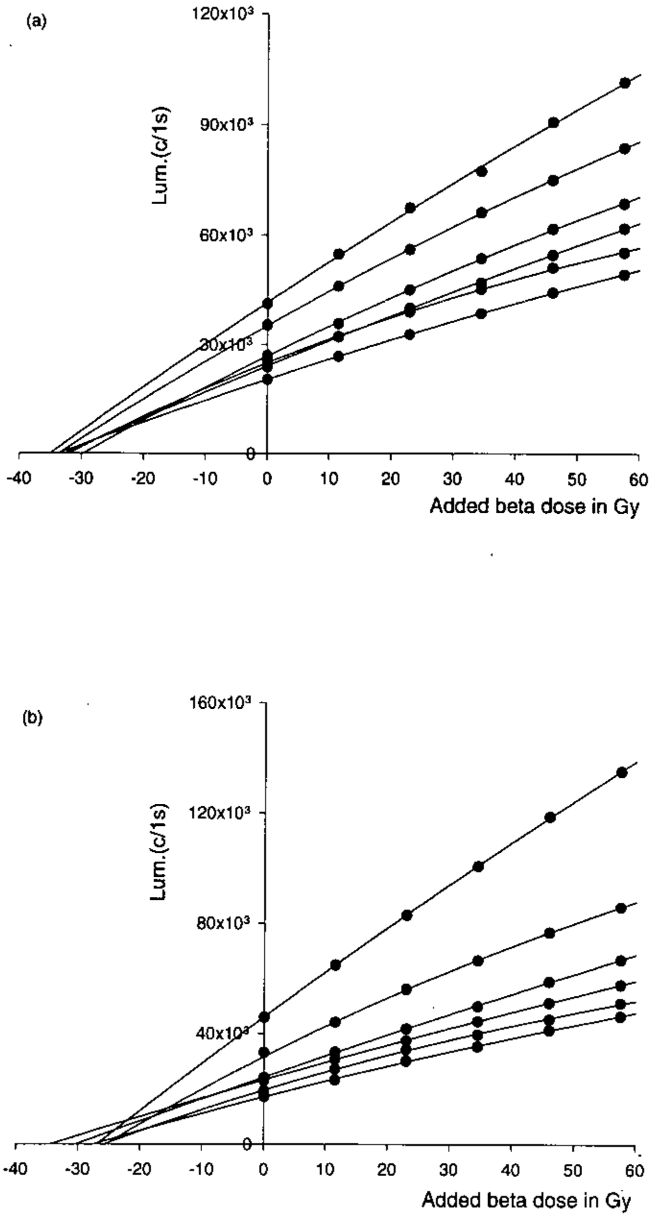


Figure 5.20. An example of equivalent dose determination based on single aliquot measurements for quartz sample THEOP1 which were corrected by the 2^{nd} luminescence correction method. Preheating was for 1min. at 220⁰C(a) and for 5min. at 220⁰C(b). Six single aliquots were used for each preheating.

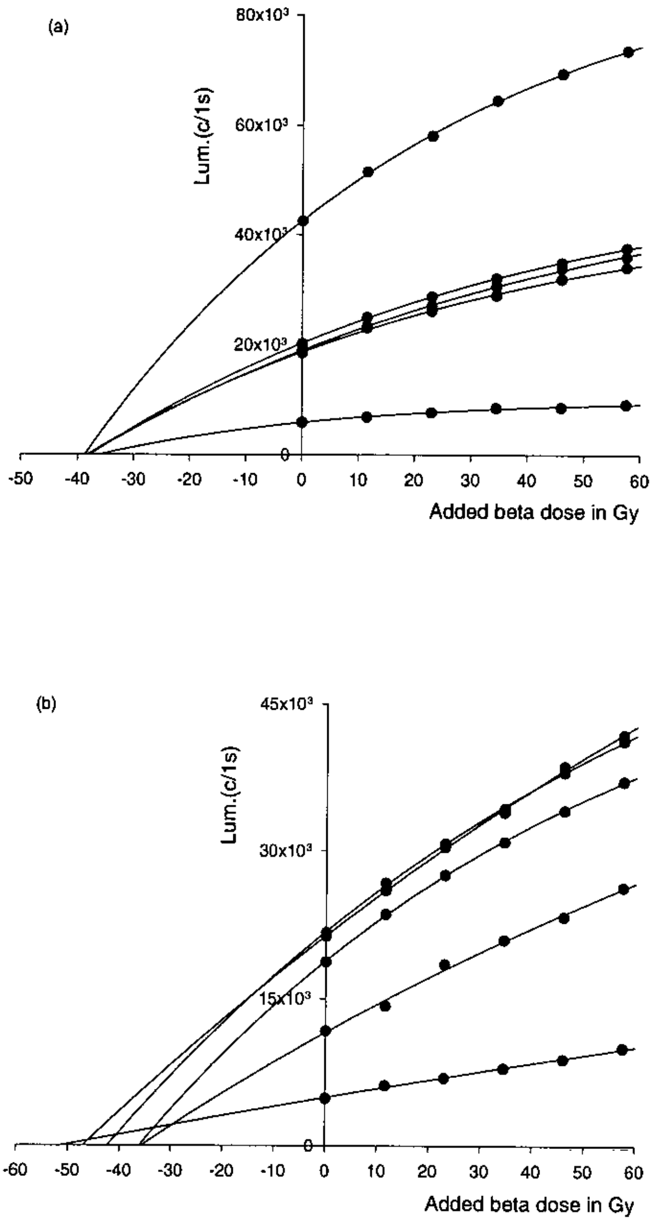


Figure 5.21. An example of equivalent dose determination based on single aliquot measurements for quartz sample THEOP2 which were corrected by the least squares fitting procedure. Preheating was for 1min. at 220^{0}C(a) and for 5min. at 220^{0}C(b). Five single aliquots were used for each preheating.

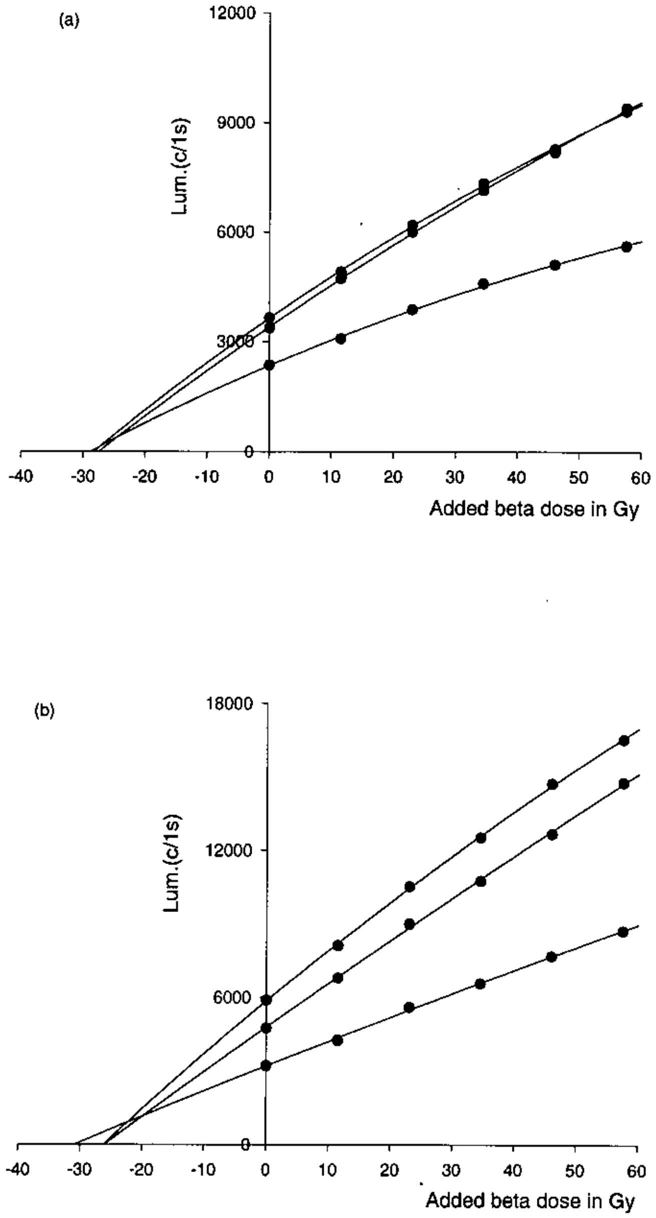


Figure 5.22. An example of equivalent dose determination based on single aliquot measurements for quartz sample THEOP3 which were corrected by the least squares fitting procedure. Preheating was for 1min. at 220^{0}C(a) and for 5min. at 220^{0}C(b). Three single aliquots were used for each preheating.

5.5 Equivalent dose determination by multiple aliquot additive dose method

With the same materials mentioned above, the equivalent doses were determined by multiple aliquot measurement in order to compare with those determined by single aliquot measurement. The standard procedure of the multiple aliquot additive dose method was adopted and the measurements were normalised by dose normalisation, as described in chapter 3. A preheating of 5 minutes at 220^0C for all measurements was chosen, along with 1s green light exposure time. The dosage range and dose step distribution in the growth curve were matched to the single aliquot measurement in order to avoid uncertainties associated with the extrapolation of the equivalent dose value. Three aliquots for each dose point were used for samples SH1, SH2, BS, THEOP1 and THEOP2, whereas five aliquots were used for samples GF120 and GF140 because of larger scatter between measurements. In the case of sample THEOP3 the multiple aliquot measurement was impossible since the amount of sample was limited, illustrating another advantage of the single aliquot measurement. The resulting multiple aliquot measurement growth curves are shown in figs. 5.23 and 5.24 and the equivalent dose determined for each sample is listed in table 5.1. A single saturating exponential function was applied for determination of the equivalent dose.

5.6 Discussion

The equivalent dose values were determined by the single aliquot additive dose method for natural quartz samples from sedimentary and heated material. In investigations of decay characteristics, all samples examined decayed exponentially with successive preheating and reading. Such exponential decay leads to the alternative least squares fitting correction method having an advantage over other correction methods(for example, besides a simplicity for correction the equivalent dose determination is possible

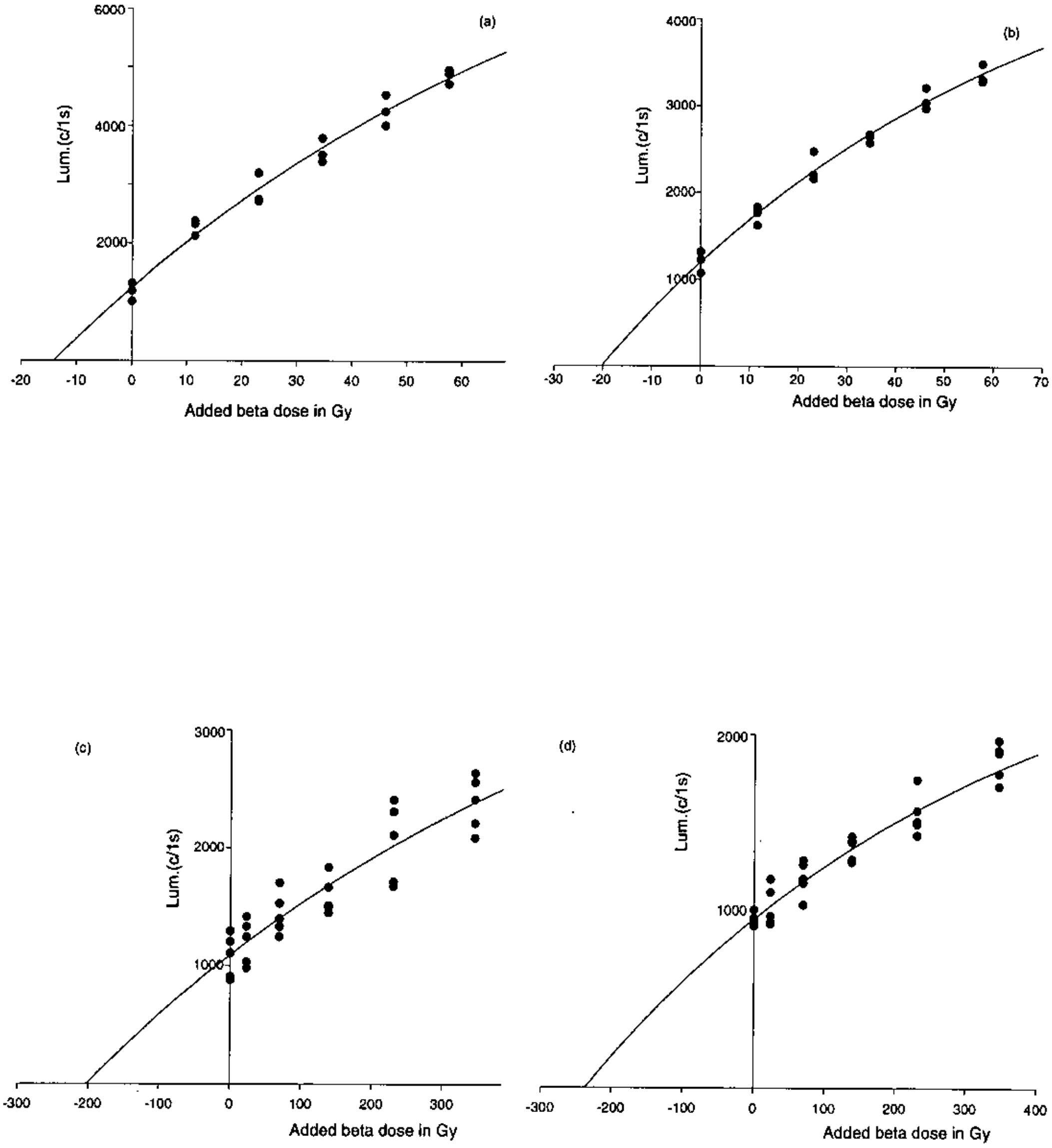


Figure 5.23. Multiple aliquot additive growth curve for quartz sample from sediment; SH1(a), SH2(b), GF120(c) and GF140(d). Three aliquots for each dose point were used for samples SH1 and SH2 and five aliquots for sample GF120 and GF140. Preheating was for 5min. at 220^{0}C for all samples.

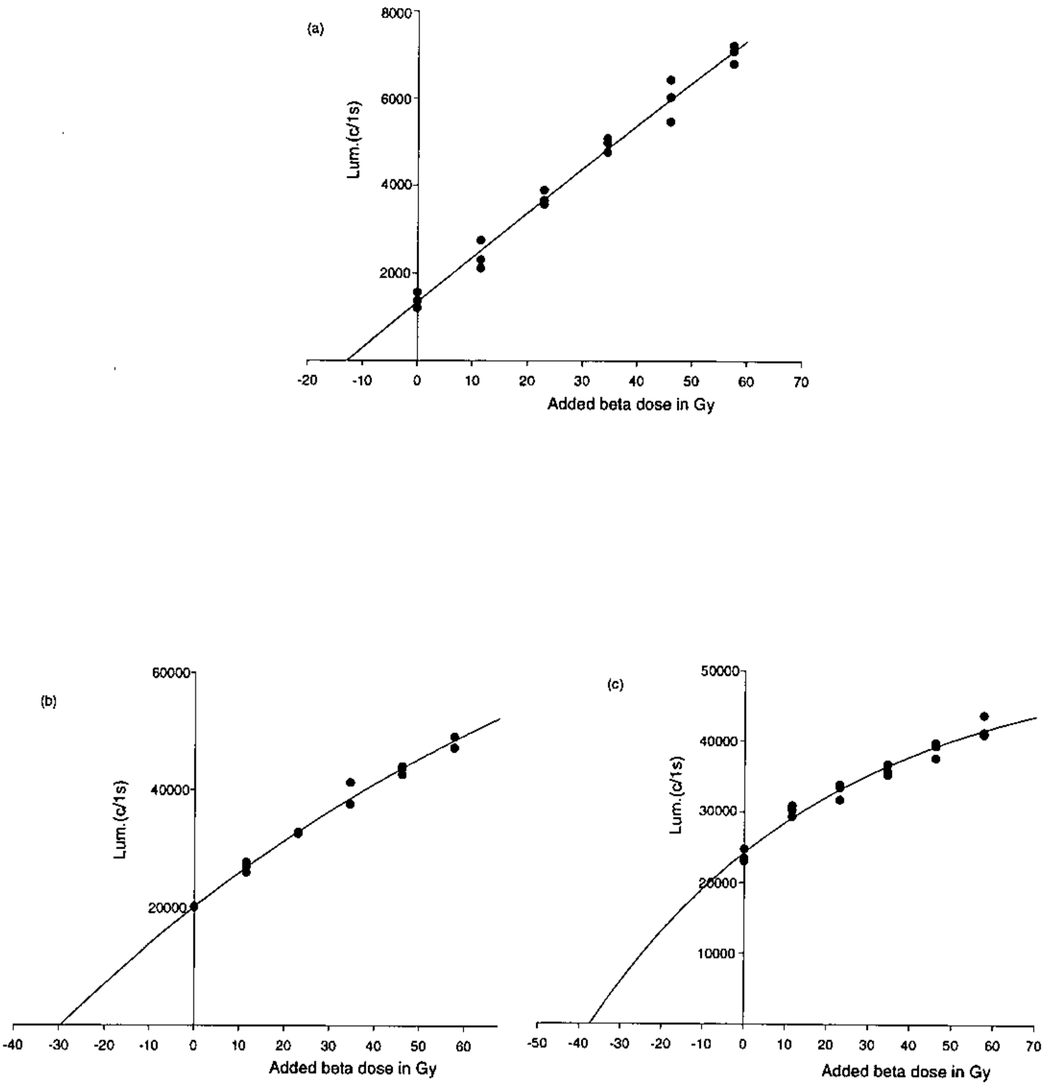


Figure 5.24. Multiple aliquot additive growth curve for quartz samples from heated material; BS(a), THEOP1(b) and THEOP2(c). Three aliquots for each dose point were used and preheating was for 5min. at 220^{0}C for all samples.

Table 5.1. Comparison between equivalent dose(Gy) estimates from multiple and single aliquot measurement.

	Single aliquot additive dose method				Multiple aliquot additive dose method	
preheating	220°C/1min (220°C/5min)				220°C/5min	
cor. method	1st *LC	2nd LC	*LSQ	n		m
BS1	13.6±1.9	14±2.2	14.3±1.7	5	12.8±1.9	18
	(14.6±2.8)	(14.8±3.4)	(14.7±3.3)	5		
Theop/1	31.5±2.4	32.8±1.7	30.7±2.8	6	29.7±1.7	18
	(29.8±2.9)	(28.4±3.1)	(31.2±3.6)	6		
Theop/2	37.9±1.2	39.3±1.6	37.6±0.9	5	37.3±3.6	18
	(42.6±7.5)	(40.2±6.7)	(42.4±6)	5		
Theop/3	28±0.7	30.5±1.1	28.1±0.6	3	n.d.	
	(27.1±2.9)	(26.5±2.9)	(27.7±2.3)	3		
SH1	13.3±1.4	13.2±1.6	13.3±1.5	10	14±2.9	18
	(14.7±1.6)	(14.4±1.5)	(14.7±1.6)	10		
SH2	20.8±3.1	22.1±2.7	20.8±2.8	10	20.2±2.3	18
	(24.4±5.8)	(22.6±5)	(24.4±5.6)	10		
GF120	214±19	193±17	205±18	10	203±40	30
	(197±15)	(215±19)	(207±33)	10		
GF140	222±27	225±28	234±27	10	237±41	30
	(198±23)	(217±30)	(227±37)	10		

1) *LC : Luminescence correction, *LSQ : Least square fitting correction. 2) n : the number of single aliquot measurements averaged. 3) m : the number of aliquots used in multiple aliquot measurement. 4) n.d. : not determined.

for only one aliquot.). Concordant results from the three correction methods reflect on this fact(table 5.1). While the decay ratios of heated materials show a good agreement between the natural and the natural plus artificial dose, the decay ratios for the natural dose samples from sediment differ from those for samples artificially dosed in addition to the natural dose. However, the equivalent dose values determined by the single aliquot measurement corrected using two different decay ratios did not give any noticeable difference(5.6), so that the decay ratios of the sediment samples were, for practical purposes, also essentially independent of dose.

Accepting the error limit calculated from the equivalent doses, the equivalent dose values determined by the single aliquot method are in reasonable agreement for the two durations of preheating despite different shapes of growth curve. However, overall the equivalent dose value determined using the shorter preheating gave better accuracy. This supports the result of tests on the single aliquot method done in chapter 4. The discrepancy of the single aliquot growth shape between different durations of preheating, as explained in earlier section 4.3, is connected with the trapped charge population after repeated preheating and reading in a nonlinear growth portion. For a similar reason, Duller[26] suggests the dose correction method as suitable for correction of a single aliquot growth curve showing a nonlinear response. In studying with feldspar, he found that the single aliquot measurement corrected by luminescence correction gave an underestimate of the equivalent dose value if the relationship between the trapped charge concentration and dose was not constant. In this study, the single aliquot growth curves using longer preheating obviously appeared less curved than those using shorter preheating, which showed a similar form with multiple aliquot measurement, but no noticeable difference between equivalent dose value can be found in table 5.1. The reason could be the growth curve not being strongly curved. If any noticeable difference between equivalent dose due to nonlinear response happens it should be apparent for the samples GF120 and GF140 which give the largest equivalent dose among the samples investigated in this study. Although the counting statistics should be considered, table 5.1 does not reflect this view.

5.7 Conclusion

The equivalent dose values determined by the single aliquot additive dose method were in good agreement for the three correction methods considered.

The equivalent dose values determined by the single aliquot additive dose method were consistent with results obtained using the standard multiple aliquot method. However it should be emphasized that the growth shape of the corrected single aliquot measurement using a shorter preheating(220^0C/1min.) was shown to be in far better agreement with that of the standard multiple aliquot method. Also, the equivalent dose values obtained by the single aliquot additive dose method using the shorter preheating(220^0C/1min.) gave a better accuracy.

Although there is still a need for further study for the equivalent dose determination with different shape of growth curve, it was concluded that the single aliquot additive dose method for equivalent dose determination can be used as a good replacement for the standard multiple aliquot procedure.

Chapter 6

Single aliquot dating of ceramics

6.1 Introduction

In previous chapters, the single and multiple aliquot methods gave the same dependence of luminescence on dose(chapter 4) and showed no significant disagreement between equivalent dose determined(chapter 5), although a short preheating(i.e. 220^0C/1min.) for the single aliquot measurement was recommended. Further, an alternative correction method(see section 4.2.3) was satisfactory for correction of single aliquot measurement for all quartz investigated in this study.

While the main project of the thesis concerns whether the single aliquot additive dose method introduced by Duller[25] for feldspar stimulated by infrared is successful also in the case of quartz stimulated by green light, few ceramic samples were available to date.

Concerning a dating application of the single aliquot additive dose method to the stimulation of quartz by green light, Liritzis et al.[95] reported on two ceramic shreds for which consistent ages were determined by single aliquot measurement(3030±370 BC and 660±200 BC) and thermoluminescence procedure(3000±250 BC and 1180±500 BC, respectively).

Naturally, most dating by optical stimulation has been applied to sediment, the field which inspired the development of the technique. Closer to the dating of a ceramic, Botter-Jensen and Duller[49] determined the age of a burnt stone by multiple aliquot additive dose measurements on extracted quartz stimulated by green light and obtained an age very close to the age determined by thermoluminescence. Later, Mejdahl and Botter-Jensen[63] reported that ages obtained by SARA(single aliquot regeneration and added dose) technique on quartz from two archaeological samples(ceramic and brick) stimulated by green light were found to be in satisfactory agreement with independent age estimates. Two successful laboratory simulations of pottery equivalent dose determination by multiple aliquot additive dose green light stimulation of quartz were reported by Galloway[55]. Results from the similar simulation performed in chapter 3 also encourage application of the optically stimulated luminescence technique to archaeological samples.

The dating of ceramics by the single aliquot additive dose green light stimulation of quartz is discussed further in this chapter in relation to sherds from boreholes sunk in the north-western Peloponnese, Greece.

6.2 The experimental equipment and samples

All single aliquot measurements were made using the automated system equipped with the 16 original green light emitting diodes along with the 16 new Nichia green light emitting diodes for stimulation described in chapter 2.

The samples came from bore holes sunk in a search for the lost city of Helike. Helike was the most important city of ancient Achaia, in northwestern Peloponnese. It was founded in Mycenean times, and Homer refers both to the city and the area. It was destroyed by a catastrophic earthquake on a winter night in 373 BC. The land on which the city was built sank into the Corinthian Gulf and its inhabitants were completely annihilated by the disaster. Literary sources suggest that remains of the submerged city were visible under sea water at least until the Byzantine period[98]. They were subsequently buried under river-borne sediments. The approximate location of Helike has long been known but its exact site has yet to be found. Most previous efforts to locate Helike(1950-1974) concentrated on the sea bed[99][100]. Since 1991 several bore holes(up to 45m depth) were drilled at selected sites in the plain between the deltas of the rivers Selinous and Kerynites. This was the area where Pausanias, in the second century AD, placed a village called Helike, at a distance of 40 stadia from Aegion, and described it as the site of the famous lost classical city. Most of the pieces of ceramic from the bore holes were so small($\sim$ 1-2cm) that the quantity of extracted quartz was insufficient for traditional multiple aliquot luminescence dating measurements. Consequently only a single aliquot approach was possible and so single aliquot additive dose measurement and related tests with green light stimulation were undertaken. Five pieces of pottery, named as HQ1, HQ1A, HQ2, HK1 and HQ4, were dated in this way. The resulting relationship between age and depth at which the piece of ceramic was found is compared with the age-depth relationship for the same samples previous dated in other ways(fig. 6.6).

Sample preparation followed the standard procedures, as described in chapter 3.

6.3 Single aliquot measurement and correction procedure

The single aliquot additive dose measurement described in chapter 5 was applied to the quartz samples extracted from five ceramics from the Helike bore holes. The sequence was : preheat and read natural signal; add beta dose, preheat and read; add further beta dose, preheat and read; continue in this way, adding dose, preheating and reading until the desired number of additive dose measurements have been made; preheat and read again several times without adding further beta dose. The dose range to construct a growth curve for equivalent dose determination was chosen from 0 to 30Gy with every additional beta dose of 5Gy. The least squares fitting correction procedure[93] was used for compensation of loss of luminescence signal due to repeated re-use of the same aliquot because of significant simplicity. The essential test for the correction method was made, namely decay curve for the correction should be exponential. Fig. 6.1 is an example for the samples HQ1A and HQ2 and shows the correction factors to be well represented by an exponential decay. For the other samples HK1, HQ1 and HQ4, an exponential decay also showed.

The duration of exposure to green light for luminescence stimulation was 12.5s for the original green light emitting diode system and 1s for the new Nichia green light emitting diode system(chapter 2). The latter system provided far better statistical precision in the measurements. For example, the equivalent dose values determined for the sample HK1 were 6.0±3.0Gy for the original green light emitting diode system[101] and 5.4±1.3Gy for the new Nichia green light emitting diode system. In addition, for sample HQ4 the equivalent dose value was 8.0±0.3Gy for measurement with the new Nichia green light emitting diode system, while with the original green light emitting diode system the sample seemed not to respond to optical stimulation. In fig. 6.2, the difference of luminescence output measured with the same sample(HQ1) using the two systems is a good illustration of the superiority of the new Nichia green light emitting diode system. In the case of samples HQ1A and HQ2, the limited amount of sample material available made possible only measurements by the original green light emitting diode system(because some of the measurements precede the development of the new Nichia green light emitting diode system), so that there was little opportunity to try to improve on the first attempts. However, a reasonable agreement in equivalent dose values of the samples HQ1 and HK1 was obtained for the both systems(table 6.5).

Examples of additive dose growth curves for equivalent dose determination are shown in Figs. 6.2 - 6.4. In the case of the sample HQ1 there was sufficient material to determine of equivalent dose with both the old green light emitting diode system and the new Nichia green light emitting diode system. Fig. 6.2 refers to sample HQ1 using the two green light emitting diode systems. Sample HQ1, like samples HQ1A and HQ2, shows a saturating dose response. Figs. 6.3 and 6.4 show the data for samples HQ2,

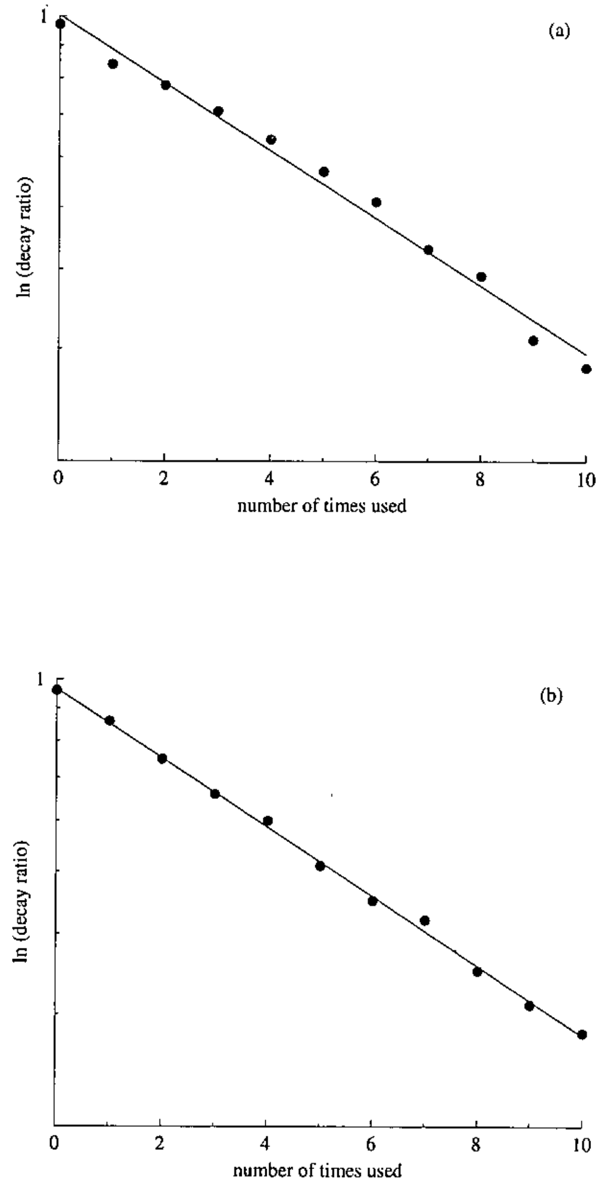


Figure 6.1. Two decay curves for quartz showing exponential decay: (a) for sample HQ1A and (b) sample HQ2. Preheating was at 220^{0}C for 1min. and 12.5s measuring time was used. The samples were dosed to 46Gy.

Table 6.1. A comparison of the equivalent dose values(Gy) determined using two fitting functions.

	samples			
fitting function	HQ1	HQ1A	HQ2	HQ4
sin. sat. exp. fit.*	9.9±0.6	8.2±0.2	7.4±0.3	8.0±0.3
sin. sat. exp. lin. fit.*	10.2±0.8	8.4±0.3	7.7±0.4	8.0±0.3

1) sin. sat. exp. fit.* : single saturating exponential fitting and 2) sin. sat. exp. lin. fit.* : single saturating exponential with linear fitting.

HQ1A, HK1 and HQ4. No noticeable difference of the shape of the growth curves with different preheating duration time was found(figs. 6.2, 6.3 and 6.4(b)) .

Of the samples investigated in this study , the sample HK1 shows a supralinear response and seems in this case to be appropriately extrapolated by a linear fit to the points up to 15Gy added dose(fig. 6.4). Except for the sample HK1, two fitting functions described in chapter 3 were used for the equivalent dose estimates in order to confirm the values. One approach was made by the single saturating exponential function and the other by the single saturating exponential with the addition of a linear function(table 6.1). Since the equivalent dose values determined using two fitting functions did not show any difference, simply the equivalent dose values determined by the former function were used for dating analysis.

6.4 Preheating investigation

A series of equivalent dose determinations were made with preheatings of increasing duration for determination of the appropriate preheating condition, as suggested by

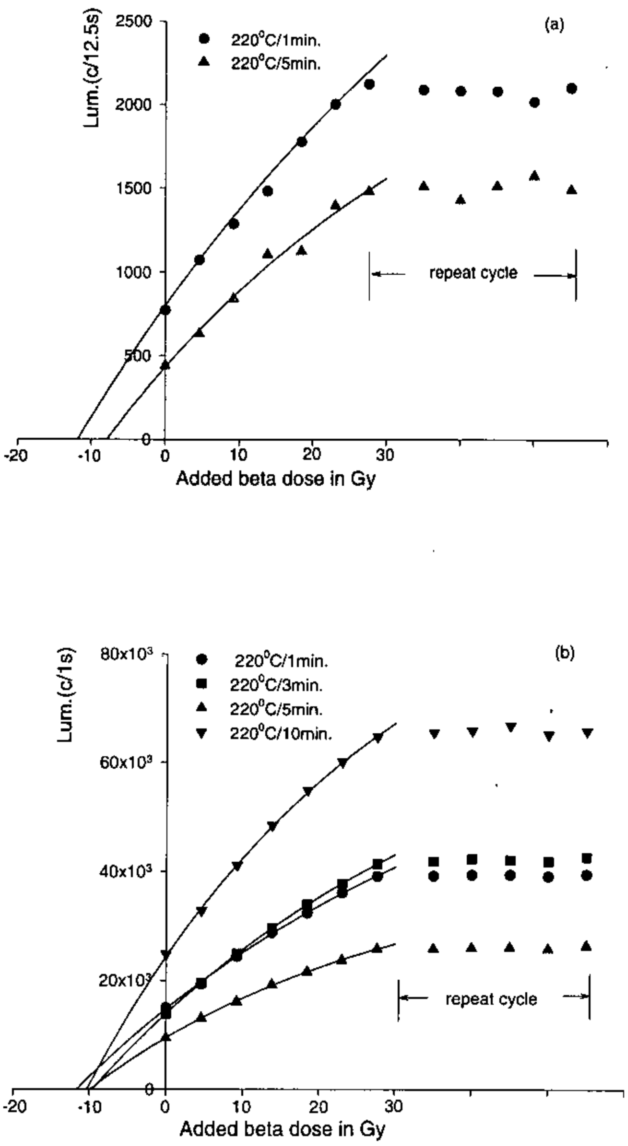


Figure 6.2. An example of single aliquot additive dose data using different preheating duration time and green light emitting diode set for sample HQ1 : (a) for original green light emitting diode set with 12.5s measuring time and (b) for new Nichia green light emitting diode set with 1s measuring time. All single aliquot measurements were corrected by the least squares fitting procedure. A single saturating exponential fit was applied to the data points.

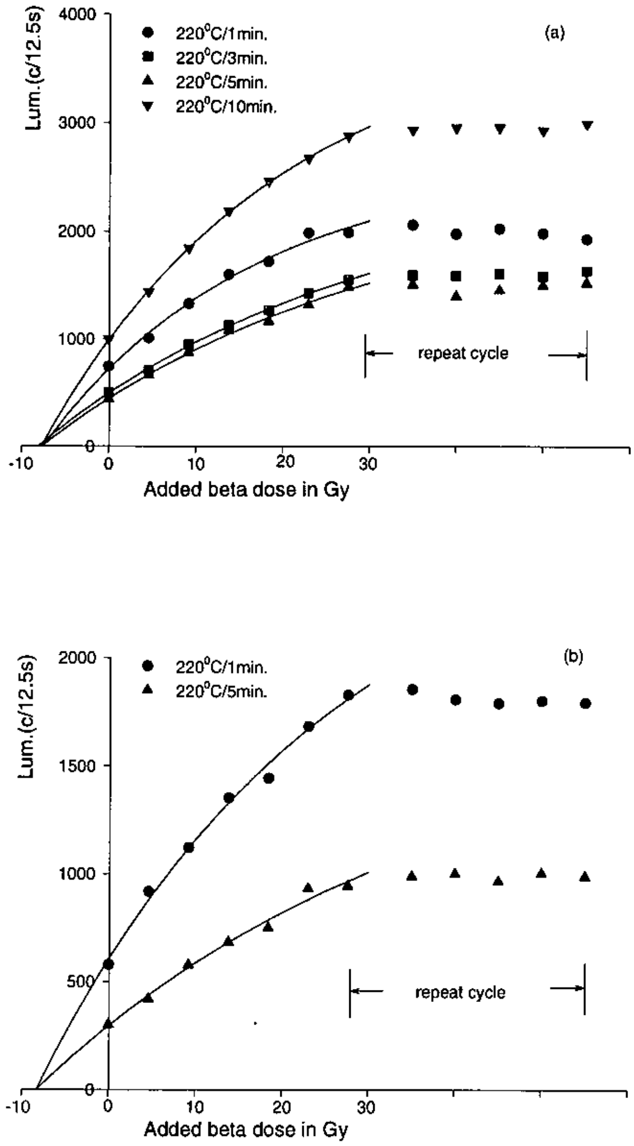


Figure 6.3. An example of single aliquot additive dose data using different preheating duration time for samples which were corrected by the least squares fitting procedure : (a) HQ2 and (b) HQ1A. Original green light emitting diode set was used, along with 12.5s measuring time. A single saturating exponential fit was applied to the data points.

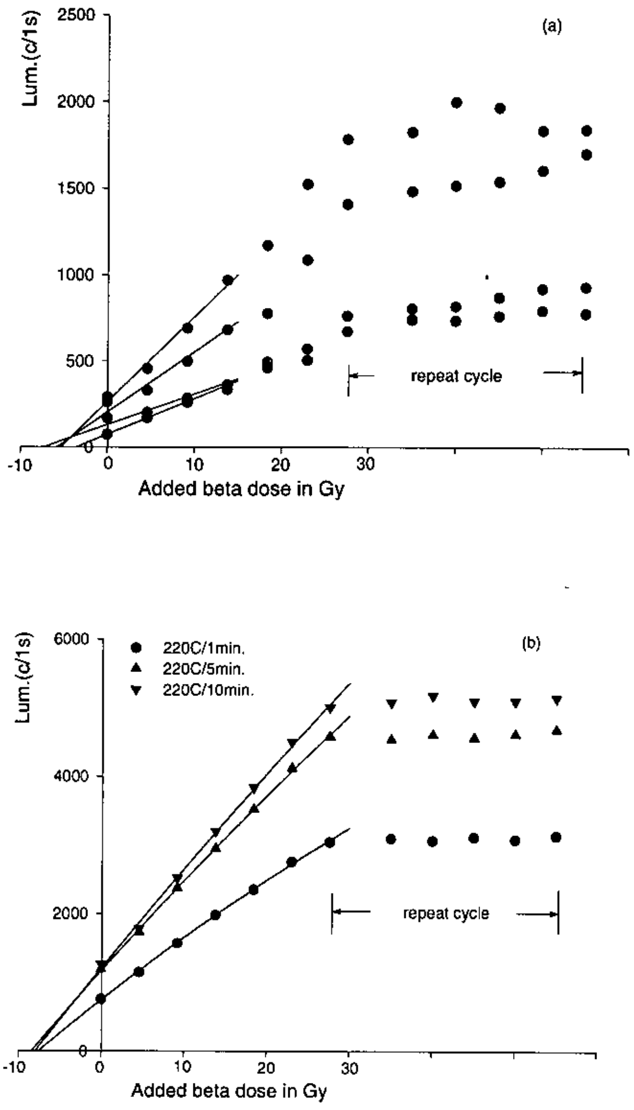


Figure 6.4. An example of single aliquot additive dose data for samples which were corrected by the least squares fitting procedure : (a) HK1 with linear fit and 220^0C/1min. of preheating and (b) HQ4 with a single saturating exponential fit and different preheating duration time. New Nichia green light emitting diode set was used, along with 1s measuring time.

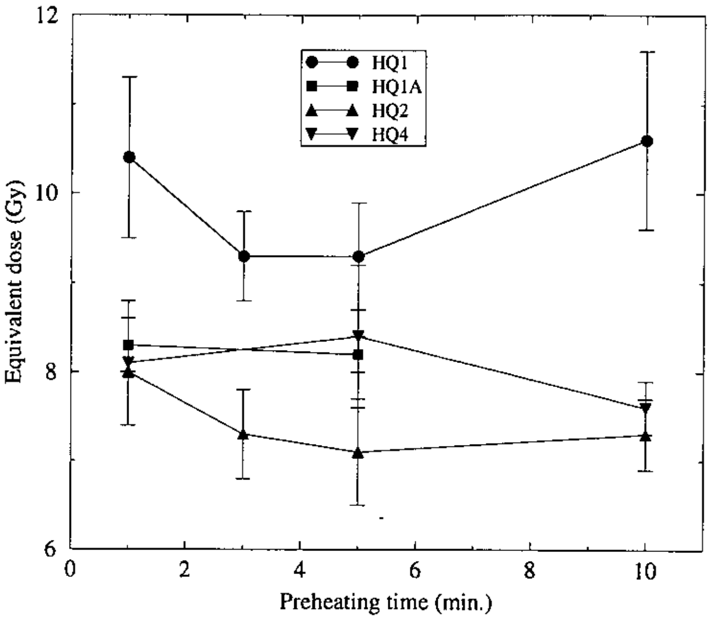


Figure 6.5. Preheat plateaus for Helike samples. Each data point is the average of equivalent dose values determined by independent aliquot along with standard error.

Huntley et al.[10]. On the basis of a preheating temperature of 220^0C, four preheating duration times(1min., 3min., 5min. and 10min.) were applied to the samples HQ1 with 16 aliquots and HQ2 with 12 aliquots, three preheating duration times(1min., 5min. and 10min.) to the sample HQ4 with 9 aliquots and two preheating duration times(1min. and 5min.) to the sample HQ1A with 6 aliquots. The equivalent dose values for the plateau test were determined by the single saturating exponential function. Fig. 6.5 represents the result of variations of equivalent dose value against different preheating duration times. There was no evidence to choose any particular one of the preheating duration times examined. For a better statistical accuracy the average of all equivalent dose values determined irrespective of preheating conditions was used for age calculation.

6.5 Dose rate

In a dating analysis based on luminescence, measurement of the radiation dose rate to which the material of interest has been exposed since its deposition is another essential factor for dating along with the equivalent dose value(eq. 1.1). Four components contribute to the radiation dose rate of the sample of interest. They are alpha, beta, gamma from the radioactive isotopes of uranium, thorium and potassium present in the samples and its immediate environment, and a small component from cosmic rays. Of the four components, the influence of the alpha particles was removed in the commonly used inclusion technique of thermoluminescence dating[60] because the crystal surface was etched away.

While all radiation dose received by sediments can be measured from surrounding materials, in the case of pottery the beta dose mainly comes from radioisotopes within the sample and the gamma dose rate from radioisotopes within surrounding materials.

A variety of approaches have been introduced to obtain an accurate value of dose rate, see Aitken[1] for a detailed description of the principles and measurement techniques used in various methods.

Among the methods, gamma ray spectrometry is one convenient method for determination of the specific activities of the radionuclides present in environmental samples. The process of determining specific activity by gamma ray spectrometry usually involves efficiency calibration of the detector in precisely the same geometrical relationship to the calibrating sources as is used in the measurements on samples of unknown activity. For dating, the measurement of gamma ray spectrometry can be achieved either directly in situ or indirectly by taking to the laboratory a sample of the surrounding materials in which the sample to be dated was buried. Each method has advantages and disadvantages.

The former, usually performed by a sodium iodide(NaI) detector, has the advantages of providing a rapid measurement and detecting of the cosmic radiation dose

Table 6.2. Details of standard samples used for calibration of gamma spectroscopic system(U, Th and K content of standard ores as quoted by the supplier)

Standard material	ppm U	ppm Th	% K	kBq/kg
RGU	400±2			5.00±0.02
BL4	1730±40			21.62±0.50
DL1A	116±3	76±4		1.45±0.04 for U, 0.31±0.02 for Th
RGTH		800±16		3.26±0.06
RGK			44.8±0.3	13.71±0.09
KCL			52.5±0.3	16.03±0.09

with the disadvantage of lack of information on the state of equilibrium over the burial period[1]. In the laboratory a hyper pure germanium(HPGe) detector can be employed with the advantage of enabling information on radioactive disequilibrium of the uranium or thorium decay chains to be obtained because of the far better energy resolution of the detector, but this requires a long measuring time(several days at least).

For gamma dosimetry, the laboratory-based method of dose rate evaluation using a high purity germanium detector(HPGe) was adopted in this study because of a convenient computer program designed by Galloway and difficulty in reaching the relevant location down a borehole.

Since the system used was established for determination of the activity of natural samples by gamma ray spectrometry[102][103], a simple test for calibration with seven standard sources before measurement for dose rate was made in order to confirm the system.

Table 6.3. The percentage difference(N) of calibration for gamma spectroscopic system with standard samples listed in table 6.2.

		Standard material						
	Radioisotope	RGTH	RGK	KCL	RGU	BL4	DL1A	AVG.
^{238}U	^{234}Th				2±3	4±3	4±3	3±3
	^{226}Ra				1±6	0±6	11±6	4±6
	^{214}Pb				3±3	1±3	5±3	3±3
	^{214}Bi				4±3	1±3	4±3	3±3
	^{210}Pb				2±4	3±4	-1±4	1±4
^{232}Th	^{212}Pb	-4±3					6±3	1±3
^{40}K	^{40}K		-5±3	-3±3				-4±3

The test adopted is to take the percentage difference(N) of the known activity(A_{kn}) from the counted activity(A_c),

$$N = \frac{A_c - A_{kn}}{A_{kn}} \times 100 \tag{6.1}$$

If the calibration was perfectly made, the percentage(N) should be zero. Six standard materials for test were used as summarized in table 6.2. The first measurement using standard samples RGB, BL4 and DL1A relates to five members of the ^{238}U series; ^{234}Th(63.3keV), ^{226}Ra(186.2keV), ^{214}Pb(295.3 and 351.9keV), ^{214}Bi(609keV) and ^{210}Pb(46.5keV). The second measurement using standard samples RGTH and DL1A concerns one member of the ^{232}Th series; ^{212}Pb(238.6keV). The final measurement using standard samples RGK and KCL involves ^{40}K(1461keV).

For each radioisotope the percentage difference(N) is detailed in table 6.3. Accepting the error limits no significant problem was detected in the established calibration.

Although the beta dose rate can be indirectly evaluated from determination of potassium content along with estimation of uranium and thorium series content from gamma ray spectrometry[104] it is recommended that each component of the annual dose should be measured individually[1]. The beta dose rate was measured using the calibrated plastic scintillation counter described by Galloway and Liritzis[105], and Galloway[106]. The instrument had just recently been recalibrated[107]. Table 6.4 summarises the beta and gamma dose rate for all quartz samples investigated in this study. A factor of 0.9 was assumed to allow for beta dose attenuation within the grains of quartz together with the etching of the crystal surface[1].

The dose rate within a sample can be affected by its moisture content because of absorption of part of the dose by water. For the samples found below the present water table(Q1 and Q1A) the excavators recommended assuming the presence of 15% water by weight in the ceramics(which mainly influences the beta dose rate), and 30% water in the surrounding soil(which mainly influences the gamma dose rate). For all the

Table 6.4. Result of beta and gamma dose rate(mGy yr^{-1}) for quartz samples from the Helike boreholes.

	samples				
component	HK1	HQ1	HQ1A	HQ2	HQ4
beta dose rate	2.36±0.08	1.97±0.07	1.68±0.06	1.79±0.07	1.67±0.08
gamma dose rate	0.64±0.02	0.65±0.02	0.65±0.02	0.74±0.03	0.49±0.02

other samples(HK1, HQ2 and HQ4), which were found above the present water table, corresponding values of 5% and 10%, respectively were assumed. Finally, a cosmic ray contribution was taken as 0.15 mGy yr^{-1} for the samples HQ1, HQ1A, HQ2 and Hk1 and 0.10 mGy yr^{-1} for the sample HQ4 because of greater depth.

The dose rate in table 6.5 refers to the annual dose rate corrected for water content using the formula of Zimmerman[39], and includes beta dose attenuation.

6.6 Age determination

With the age equation(eq. 1.1), the ages of the five pieces of sherd from Helike were determined. The ages determined for the sherds were plotted against depth in fig. 6.6 and showed a plausible roughly linear increase in age with depth. Also plotted is one thermoluminescence age(pers. com. Michael) which is entirely consistent with the ages from the green light stimulation of the quartz single aliquot. One age determined by radiocarbon dating[108] is also plotted in fig. 6.6.

Table 6.5. Summary of the single aliquot additive dose green light stimulated luminescence measurements on quartz samples from the Helike boreholes.

Sample	Grain size (μm)	Equivalent dose (Gy)	Number of aliquots used	Dose rate (mGy yr^{-1})	Age (years)	Sample depth (m)
HK1	60-106	5.4±1.3$^{(a)}$ 6.0±3.0$^{(c)}$ 4.0±1.0$^{(d)}$	4	2.9±0.1	1860±450 1800±320$^{(e)}$	1.40$^{(b)}$
HQ2	70-150	7.4±0.3$^{(f)}$	12	2.7±0.1	2740±230	5.70
HQ1	70-150	9.9±0.6$^{(a)}$ 11.0±0.4$^{(f)}$	16 4	2.8±0.1	3540±250	6.58
HQ1A	70-150	8.2±0.2$^{(f)}$	6	2.5±0.1	3280±150	6.58
HQ4$^{(g)}$	70-150	8.0±0.3$^{(a)}$	9	2.1±0.1	3810±230 4705±285$^{(h)}$	9.20

(*a*) : By new Nichia green light emitting diodes system.
(*b*) : 1^{st}-4^{th} century Roman remains found at this level.
(*c*) : By original green light emitting diodes system[101].
(*d*) : By infrared stimulation of feldspar from HK1[101].
(*e*) : Thermoluminescence determination by Michael, personal communication.
(*f*) : By original green light emitting diodes system in this study.
(*g*) : No measurable luminescence by original green light emitting diodes system.
(*h*) : ^{14}C dating[108].

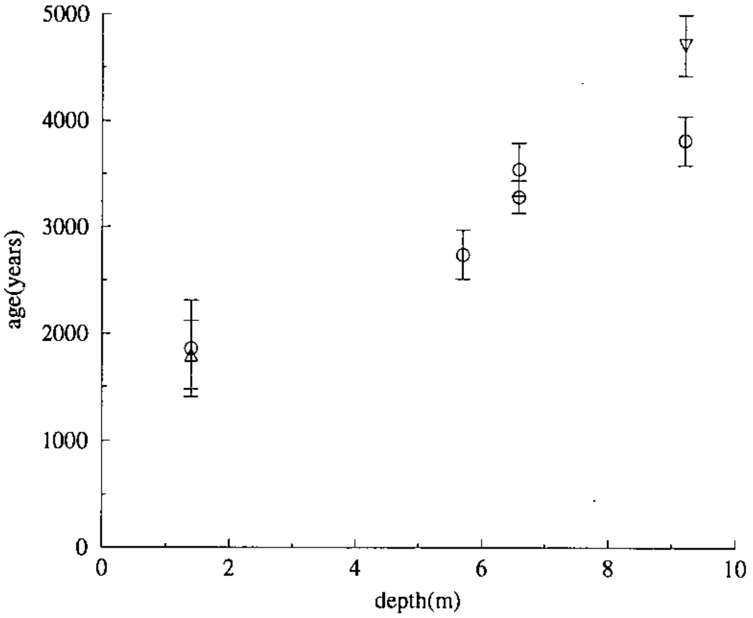


Figure 6.6. The relationship between age and depth over the area in which boreholes were sunk. Circles(○) refer to ages deduced from single aliquot green light stimulation of luminescence of quartz from pieces of ceramic; the upward pointing triangle(△) to thermoluminescence age; the downward pointing triangle(▽) to ^{14}C dating.

6.7 Conclusion

The additive dose single aliquot method of determining equivalent dose, with correction for re-use of the aliquot, can be successfully applied to the luminescence stimulated from quartz by green light for the purpose of dating. The single aliquot method can enable ages to be found when insufficient sample material is available for multiple aliquot optical or thermoluminescence dating. The decay factors, required for correction purposes, show an exponential dependence on the number of times of re-use of the aliquot.

The additive dose method with green light stimulation of a single aliquot of quartz should contribute significantly to future dating work.

Chapter 7

Conclusions

The first phase of this thesis concerned the development of an original green light emitting diode arrangement. The new assembly equipped with the new Nichia green light emitting diodes was shown to be of comparable sensitivity to the traditionally used argon ion laser system[109]. Hence, the developed system is the most compact and economical system for green light stimulation of luminescence and so should provide a most convenient tool for luminescence dating with quartz.

The next work for improving of the new system could be to replace the Nichia green light emitting diodes with the Nichia blue light emitting diodes, along with an appropriate filter choice, because the production of optically stimulated luminescence from quartz increases as the stimulation wavelength is reduced.

The second phase of this thesis focused on whether the single aliquot procedure described by Duller[25] could be successful in the case of quartz, initially zeroed by daylight or by heating, stimulated by green light. Comparative investigations have been carried out of the single and the multiple aliquot measurements. As a result, it is concluded that the 1^{st} luminescence correction method works for the green stimulation of quartz but not for the infrared stimulation of feldspar[25] due to the exponential decay of luminescence from the quartz aliquot with re-use, which is quite different from the form of decay for feldspar[93].

The proposed least squares fitting method of correction gives corrected values consistent with those determined by use of correction data measured using a separate aliquot, implying that since the correction is determined from measurements on the same aliquot that is being corrected, there can be not only no error due to difference in mineralogy between the aliquot used for equivalent dose determination and a separate aliquot used to determine the decay ratio, but also the equivalent dose value can be determined from only one aliquot.

The single aliquot method could reproduce the same form of relationship between luminescence and radiation dose as a multiple aliquot technique.

The equivalent dose values of natural quartz samples from sediments and heated materials determined by the single aliquot additive dose method offered good agreement with results obtained using the conventional multiple aliquot technique, while the growth shapes of the single aliquot method using a shorter preheating were more consistent with those of the multiple aliquot technique, providing better accuracy of the equivalent dose values determined.

Although the dependence of the shape of growth curve on preheating conditions remains as a further study, the single aliquot additive dose method applied to quartz for equivalent dose determination can be used as a good replacement for the conventional multiple aliquot technique. One aspect, worthy of further study, is whether there is any sensitivity change due to repeated preheating. This could possibly be monitored by use of a small test dose and measurement of the 110^0C thermoluminescence as an indicator of OSL sensitivity, as used in reference [16].

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Appendix A

Appendix

Three papers were published during PhD degree.

- Concerning the normalization of additive dose optically stimulated luminescence data from quartz. *Ancient TL*, 14:1-5, 1996.
- A substantially improved green-light-emitting diode system for luminescence stimulation. *Meas. Sci. Technol.*, 8:267-271, 1997.
- Single aliquot dating of ceramics by green light stimulation of luminescence from quartz. *Nucl. Instr. and Meth. in Phys. Res. B*, 132:457-467, 1997.

Concerning the normalization of additive dose optically stimulated luminescence data from quartz

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Abstract: *Since 'natural normalization' is not possible for low dose samples, several 'second dose' normalization procedures are compared. The use of light and of heat for bleaching before the second dose is considered. Attention is paid to any indication of second dose sensitivity being dependent on the magnitude of the first dose.*

Introduction

Since the introduction of optically stimulated luminescence dating by Huntley et al. (1985) some aspects of the technique have been developed analogously to established aspects of thermoluminescence dating procedures while others are unique to optical stimulation. The concern here is with one particular aspect of additive dose optically stimulated luminescence dating, namely sample to sample normalization when stimulating quartz of low natural dose with green light. 'Natural normalization', that is the use of the luminescence intensity resulting from a brief exposure of each sample to stimulating light prior to the addition of any laboratory dose, provides a very attractive approach to compensating for sample to sample variations (Stokes, 1992) and indeed natural normalisation has been much used with the infrared stimulation of feldspar (Wintle, 1993; Ollerhead et al., 1994). However the accuracy achievable from natural normalization must become less as the natural dose approaches zero and the method cannot be applied to investigations of the dose response properties of bleached material. In these circumstances normalization must be by an appropriate second measurement on the sample and Stokes (1992), using an argon ion laser for stimulation of young quartz, reduced the luminescence to about 1% of the initial value and then applied a dose of 5 Gy to each sample for normalisation. Variations on second dose normalization are compared below, involving the use of light or heat for bleaching before the second dose and looking for any indication of second dose sensitivity being dependent on the magnitude of the first dose.

The samples and measurement system

The quartz samples were prepared from BDH "acid washed sand" which was treated with concentrated HF for one hour. The purity of the quartz after this treatment was tested by verifying, for some randomly selected samples, that no luminescence was stimulated by exposure to infra red radiation. Any such signal would have indicated the presence of feldspar, the most probable contaminant. Some of the quartz was bleached by exposure to daylight for at least one week and some by heating for 5 minutes at 500°C before further use. Samples for measurement were deposited on silicone grease in the central portion of thin stainless steel discs 12 mm in diameter. Dosing was by exposure to a calibrated 90Sr beta source. A 16 green LED system with peak emission at 565 nm wavelength was used for stimulation (Galloway, 1992, 1993) while a carefully chosen filter combination of HA3, BG39, UG11, 7-59 and 7-60 filters, with a peak transmission at 365 nm wavelength, preceded the photomultiplier (EMI type 9635QA) which counted the luminescence photons. The multi-sample system described by Galloway (1991) was used for the measurements.

Method of measurement

First of all for each sample the background due to scattered light and photomultiplier noise was measured. A beta dose was then given, the sample preheated for 1 minute at 220°C to remove any unstable signal component and the luminescence measured. This was repeated for three samples for each dose and for eight doses ranging from 12.5 Gy to 175 Gy and the samples were then normalized to generate a growth curve showing the dependence of luminescence on dose. A separate set of 24 samples was processed in this way for each of the normalization procedures considered.

Normalization required that the samples be bleached prior to application of the normalizing beta dose and bleaching was either by placing the samples in a Honle SOL-2 "solar simulator" for 1 hour or by heating the samples to 450°C for 1 minute. The sensitivity to the normalizing beta dose might depend on the dose to which the samples had been exposed before bleaching, as can occur in the case of thermoluminescence, Aitken (1985). To allow for this possibility the normalized dose response was compared for samples which had a second beta dose added to bring all to the same total dose before bleaching, with samples which had not; this was applied in both the SOL-2 and the heat bleaching procedures. In addition to these four normalization methods, one further procedure was investigated, based on a "single aliquot" approach developed for infra red stimulation of feldspar (Duller, 1991, 1992) and tested to a limited extent with green stimulation of quartz (Galloway, 1994). In this variant, each sample had a second beta dose added so that the sum of the two beta doses equalled the maximum beta dose applied to any of the set of samples to be normalized. The sample was then preheated, read and compensation applied in the single aliquot manner for loss of signal due to the first preheating and reading.

The normalized dose response measurements

a) Quartz bleached by daylight

Dose response curves for quartz initially bleached by daylight and normalized by four of the procedures outlined above are shown in fig. 1. It is immediately clear that one of the methods of normalization, involving heating of the samples to 450°C before applying the normalizing dose, is not successful in reducing the scatter in the data. The two procedures which involved giving all samples an equal dose before normalization, one with bleaching by the SOL-2 and the other developed from the single aliquot approach, show an essentially identical dose response with little scatter in the normalised data. The procedure in which the samples were not given equal doses before bleaching and normalization gives a response which shows little scatter but falls below the others. This could be due to the sensitivity after bleaching increasing with previous dose. That preheating can cause thermal sensitization analogously to the thermoluminescence pre-dose effect has been observed by Godfrey-Smith (1994). The data in fig. 1 were measured with a 100 s exposure time to the green LEDs. The more encouraging normalization procedures, that is excluding the one involving 450°C heating as a bleach, were investigated further using green light measurement times of 50 s and 12.5 s with the results shown in figs. 2 and 3. These measurements confirm that the two procedures which involved giving all samples an equal dose before normalization show an essentially identical dose response with little scatter in the normalised data, while the procedure in which the samples were not given equal doses before bleaching and normalization gives a response which falls below the others.

However extending the investigation to higher doses at which saturation becomes more significant, fig. 4, shows that normalization based on measurements corrected in the single aliquot manner is no longer satisfactory; the simple correction procedure is strictly applicable only when the luminescence response to dose is linear (Duller, 1994).

b) Quartz bleached by heating at 500°C

The tests on quartz initially bleached by daylight should be relevant to sediment dating so for completeness similar tests were carried out on quartz which had all luminescence removed by heating which should be relevant to the dating of pottery. The response curves for five different normalization procedures are shown in fig. 5 and in terms of scatter in the normalized luminescence values there is nothing to choose between the procedures. Four out of the five procedures give consistent results and only the procedure in which the samples were not given equal doses before bleaching by the SOL-2 and normalization gives a response which differs by falling below the others. This procedure showed the same tendency in the tests on daylight bleached quartz in figs. 1, 2 and 3. The initially heated quartz behaved differently from the initially daylight bleached quartz discussed in section (a) above when heating to 450°C was used as a bleach prior to application of the normalizing beta dose, in that entirely acceptable normalization resulted (compare fig. 5 and fig. 1). Further, when 450°C heating was used as a bleach the normalization was not dependent on whether the samples had received the same dose before normalization, in contrast to the situation when the SOL-2 was used for bleaching.

It is interesting to note in passing that the dose response curves for the daylight bleached quartz show a different relationship between luminescence and dose from those for the 500°C heated quartz. Initially the response of the former is approximately linear, up to about 25 Gy say, whereas the latter is clearly non-linear in this region.

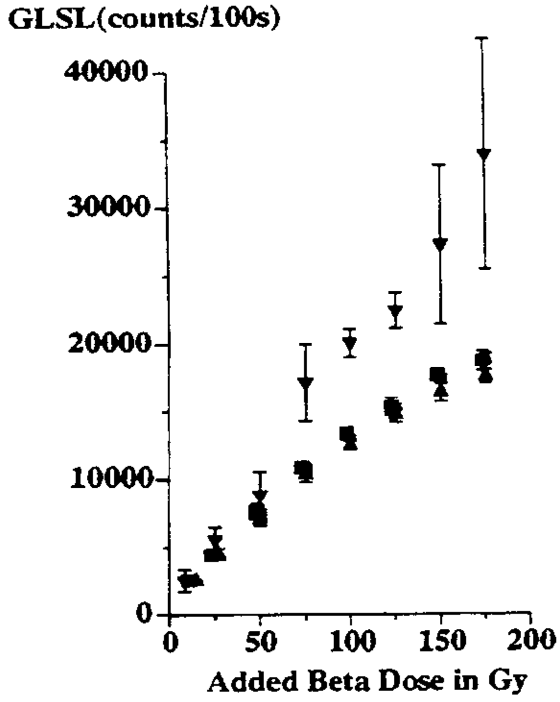

Figure 1
The dependence of the green light stimulated luminescence (GLSL) on beta dose for quartz previously bleached by daylight. The luminescence was measured for 100 s. Each point represents the mean of three measurements while the error bars indicate the spread in the three measurements. Four different normalization procedures are compared.

(1) samples were brought to the same total beta dose (175 Gy) before bleaching in the SOL-2 and application of the normalizing dose, indicated by squares.

(2) samples were brought to the same total beta dose (175 Gy), preheated and read for normalization with correction in the single aliquot manner, indicated by circles (which are indistinguishable from the squares on which they are superimposed).

(3) samples were bleached in the SOL-2 without bringing to the same total dose and the normalizing dose applied, indicated by upward pointing triangles.

(4) samples were brought to the same total dose (175 Gy) then bleached by heating to 450°C before application of the normalizing dose, indicated by downward pointing triangles and large error bars.

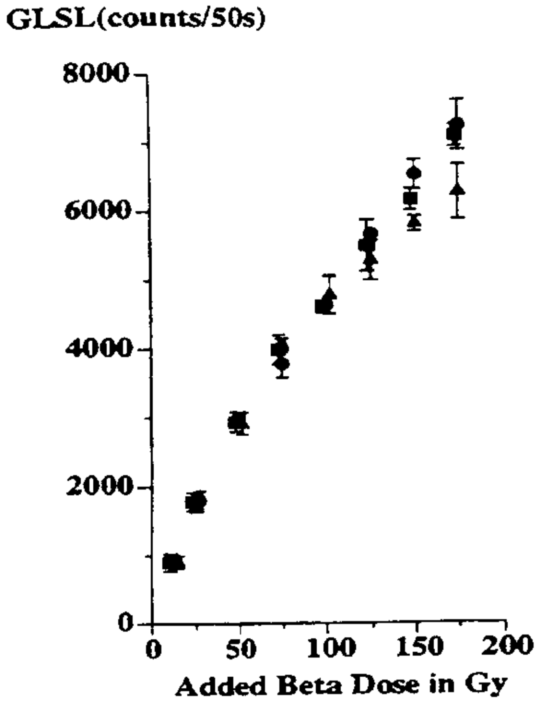

Figure 2
As fig. 1 but for 50 s green light stimulation, omitting the least successful normalization procedure involving heating to 450°C.

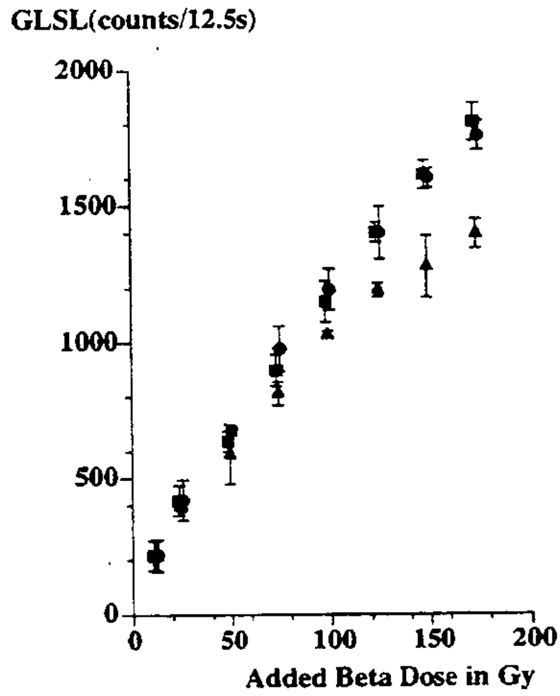

Figure 3
As fig. 2 but for 12.5 s green light stimulation.

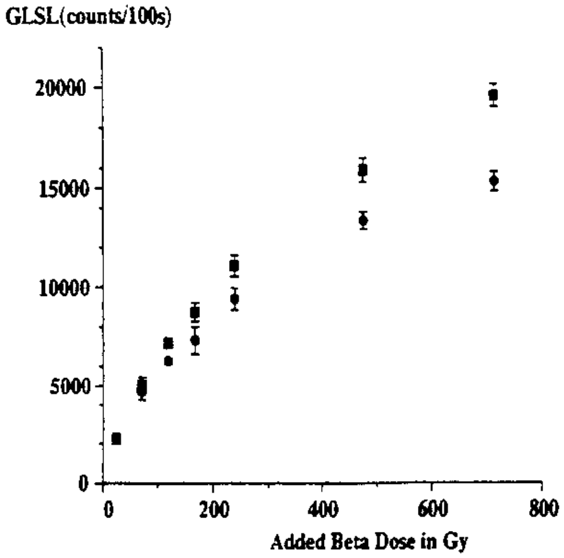

Figure 4
The dependence of the green light stimulated luminescence (GLSL) on beta dose for quartz previously bleached by daylight, as in fig. 1 but extending to higher doses at which saturation becomes more significant. Each point represents the mean of three measurements while the error bars indicate the spread in the three measurements. Two different normalization procedures are compared.

(1) samples were brought to the same total beta dose (700 Gy) before bleaching in the SOL-2 and application of the normalizing dose, indicated by squares.

(2) samples were brought to the same total beta dose (700 Gy), preheated and read for normalization with correction in the single aliquot manner, indicated by circles.

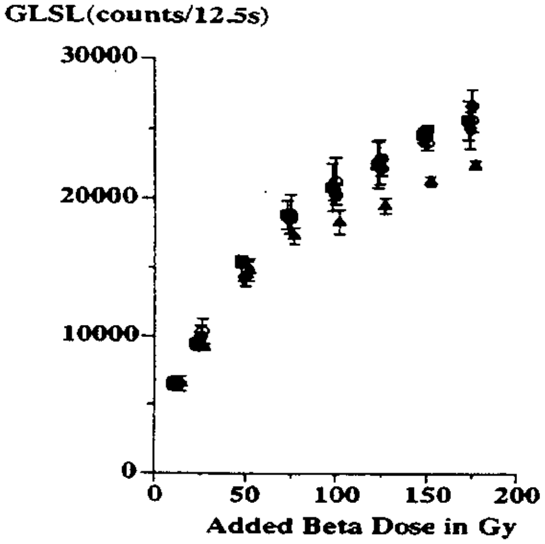

Figure 5
The dependence of the green light stimulated luminescence (GLSL) on beta dose for quartz previously bleached by heating to 500°C. The luminescence was measured for 12.5 s. Each point represents the mean of three measurements while the error bars indicate the spread in the three measurements. Five different normalization procedures are compared.

(1) samples were brought to the same total beta dose before bleaching in the SOL-2 and application of the normalizing dose, indicated by solid squares.

(2) samples were brought to the same total beta dose, preheated and read for normalization with correction in the single aliquot manner, indicated by solid circles.

(3) samples were bleached in the SOL-2 without bringing to the same total dose and the normalizing dose applied, indicated by upward pointing triangles.

(4) samples were brought to the same total dose then bleached by heating to 450°C before application of the normalizing dose, indicated by open circles.

(5) samples were bleached by heating to 450°C without being brought to the same total dose before normalization, indicated by downward pointing triangles.

Due to overlap not all symbols are inividually distinguishable.

Conclusions

Normalization involving sample bleaching by SOL-2 prior to application of the normalizing dose was successful provided all samples had been given the same total dose before bleaching.

Normalization involving bleaching the sample by heating prior to application of the normalizing dose was only successful for quartz which had been zeroed originally by heating.

A variant of the single aliquot method also provided a successful procedure for normalization within the dose range for which the luminescence response is approximately linearly related to dose.

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A substantially improved green-light-emitting diode system for luminescence stimulation

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Abstract. A compact and economical arrangement for the stimulation of luminescence by green light from light-emitting diodes is described and is shown to be of comparable sensitivity to the traditionally used argon ion laser system. The equipment is of particular relevance to the optically stimulated luminescence dating technique applied to quartz. Compared with a previously described system using light-emitting diodes, the new assembly provides a light intensity at the sample increased by a factor of 70 with the overall sensitivity of the system increased by a factor of 1000.

1. Introduction

Optically stimulated luminescence dating was introduced by Huntley *et al* (1985), who used light of 514.5 nm wavelength from an argon ion laser to stimulate luminescence at about 400 nm wavelength from quartz grains. It was shown that, for quartz grains extracted from sediments, this luminescence could be the basis for dating the time of deposition of the sediment in a manner analogous to the established thermoluminescence dating of sediments (as reviewed by Wintle and Huntley (1982)) and of pottery (as summarized for example by Fleming (1979), Aitken (1985), McKeever (1985) and Mahesh *et al* (1989)). In brief, luminescence would be bleached out of the crystals by exposure to sunlight at the time of deposition. Subsequent sedimentary deposits would exclude light and the latent luminescence would accumulate as the crystals absorbed energy from radiations from natural radioactivity in the surrounding soil. The optically stimulated luminescence intensity would depend on the time since deposition, on the sensitivity of the crystals to radiation and on the natural radioactivity of the surrounding soil. All three parameters can be measured in the laboratory and so the time since deposition can be deduced. Work on optically stimulated luminescence dating has recently been reviewed by Wintle (1993a, b). It is with the equipment for measuring the optically stimulated luminescence that this report is concerned.

In the process of detecting optically stimulated luminescence it is necessary to exclude scattered stimulating light from the photomultiplier detecting the luminescence, by use of suitable filters in front of the photomultiplier. Quartz and feldspars are the most commonly used minerals for optically stimulated luminescence dating. The quartz luminescence is peaked at about 365 nm wavelength with a full width at half height of about 60 nm (Huntley *et al* 1991). Insofar as the dependence of the sensitivity on the stimulating wavelength is concerned, the stimulated luminescence intensity from quartz falls exponentially as the wavelength increases, at least from 400 nm (Botter-Jensen *et al* 1994, Spooner 1994). Thus for the efficient detection of optically stimulated luminescence from quartz, the stimulating wavelength should be as close as optical filter properties permit to the luminescence wavelength. Hence the use of green light for stimulation which can be blocked from the luminescence-detecting photomultiplier by blue filters which can pass the luminescence. For feldspars the emission spectra depend on the type of feldspar, the commonly used Na and K feldspars showing a peak at about 400 nm (Huntley *et al* 1991, Botter-Jensen *et al* 1994). However, feldspars behave very differently from quartz regarding stimulation there being a marked peak in stimulation sensitivity in the infrared (Hutt *et al* 1988, Botter-Jensen *et al* 1994) even though they can also be stimulated by green light. The high yield and ease of separating luminescence from stimulating light has led to most dating using feldspars employing infrared stimulation which can be provided conveniently by GaAs light-emitting diodes, for example as described by Poolton and Bailiff (1989), Spooner *et al* (1990), Galloway (1991) and Botter-Jensen *et al* (1991).

Following from the original work of Huntley *et al* (1985), much work using green stimulation has employed an argon ion laser as light source (for example, Stokes (1992) and Berger and Huntley (1994)). Alternative, more economical and convenient sources of green light for

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stimulation have been investigated. One approach has been to use powerful white light from which, by use of filters, the green part of the spectrum has been selected for stimulation. A xenon arc lamp was used by Spooner and Questiaux (1989) and a halogen lamp by Botter-Jensen and Duller (1992); the latter system is being used increasingly (for example, Perkins and Rhodes (1994) and Wood (1994)). Galloway (1992) introduced a compact arrangement of 16 green light-emitting diodes for luminescence stimulation which has been in routine use ever since (for example, Galloway (1994a) and Liritzis *et al* (1994)).

Each stimulation system has advantages and disadvantages. The argon ion laser has the advantages of providing an appropriate intensity of monochromatic light at the sample with the disadvantages of technical complexity and consequent expense. The filtered light from the halogen lamp is also of appropriate intensity and the system can readily be altered by a change of filters to measure luminescence stimulated by colours of light other than green. The green-light-emitting diode (LED) system is the most compact and simplest of the three, but has hitherto provided a much lower intensity of stimulating light (by almost two orders of magnitude). This was compensated by longer measuring times, but inevitably resulted in a poorer ratio of luminescence signal to background with a consequent limitation on the lowest absorbed radiation dose that could be detected from quartz or feldspar crystals (Galloway 1994b). Newly available LEDs have allowed this limitation to be overcome.

2. The new green-light-emitting diode system

The original system (Galloway 1992) comprised 16 LEDs of type TLMP7513 (manufactured by III-V), each of which has a 25° emission angle and provides a luminous intensity of 300 mcd at 20 mA current with a peak in the emission spectrum at 565 nm (full width at half maximum 18 nm). Various other LEDs have been tried over the years, some of which have produced a modest improvement in system sensitivity, by a factor of about two or three. However, a dramatic improvement has now been obtained by use of the Nichia Chemical Industries Ltd of Japan type 110104 LED (supplied by MI Cables Ltd, 53 Carsegate Road, Inverness IV3 6EX, UK) which, according to the manufacturer's specification, has an emission angle of 15° and provides 3–6 cd at 20 mA current (30 mA absolute maximum) with a peak in the emission spectrum at 525 nm (full width at half maximum 40 nm). Initial tests with one LED showed that the spread in the emission spectrum into the blue region (< 400 nm) is sufficient to penetrate the filter stack, comprising Chance HA3, Corning 7-60, 7-59, Schott UG11 (each 4 mm thick) and BG-39 (0.5 mm thick) filters, which preceded the photomultiplier (EMI type 9635QA) used to count luminescence photons and, indeed, to swamp the counting system! Placing a green long-pass filter (Schott GG475) of 3 mm thickness in front of the LED removed the troublesome 'tail' of blue light with no significant influence on the green emission of interest for stimulation of luminescence. (The transmission properties of the filters used and the emission spectrum of the LEDs are illustrated in figure 3 later). The LED arrangement for luminescence stimulation, figure 1, is based on that used previously with the addition of a 5 mm diameter, 3 mm thick GG475 filter in front of each LED. An accurately machined Dural holder can accomodate 16 LEDs, each with a filter. The LEDs are connected in parallel and operated from a constant current source, which is switched on and off as required by the computer which also records the luminescence photon-counting rate.

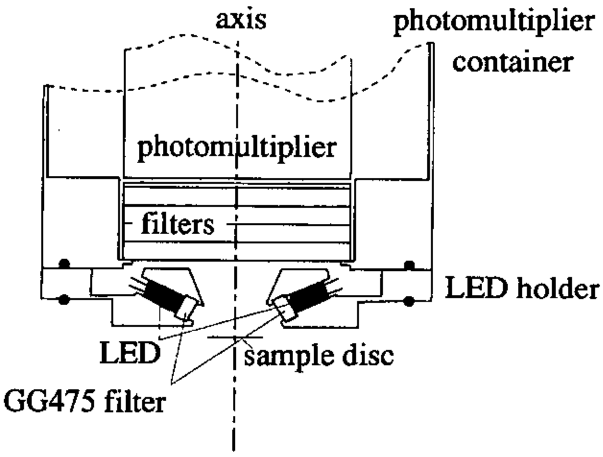

Figure 1. The mounting assembly for the Nichia type 110104 light-emitting diodes and associated GG475 filters, shown in relation to the sample to be stimulated by the green light, the filters used to separate the luminescence from scattered green light and the photomultiplier used to detect the luminescence. The assembly is cylindrically symmetrical about the axis and is machined from Dural.

3. The tests

Quartz, which had been bleached by daylight and given a known dose in the laboratory, was used for the tests. The quartz samples were prepared from 'acid-washed sand' (BDH Ltd) further treated with HF and HCl, and sieved to about 125 μm before deposition of about 15–25 mg per sample onto 12 mm diameter stainless steel discs. A random selection of samples was tested to confirm negligible feldspar contamination by looking for infrared stimulated luminescence (Spooner and Questiaux 1989, Galloway 1993). Quartz bleached by daylight was used because it provides a more critical test of the system than would quartz which has had luminescence removed by heating. The latter has a luminescence sensitivity (luminescence intensity per unit radiation dose) 30 or more times that of bleached quartz, whereas feldspar also has a higher sensitivity than does bleached quartz (relative sensitivities are quoted for example by Botter-Jensen and Duller (1992) and Galloway (1994b)).

The time dependence of the luminescence stimulated from quartz by the new system is shown in figure 2. The time taken to reduce the luminescence signal to half of its initial value provides a basic comparison of the effectiveness of the new system with any other, table 1. In

Table 1. The time taken by different green stimulation sources to reduce the luminescence from quartz to half of its initial value.

Stimulation source	Power at sample (mW cm^{-2})	Wavelength (nm)	Time (s)	Reference
16 LEDs (TLMP7513)		565 (18 FWHM)	1200	Galloway (1992)
16 LEDs (Nichia 110104)		525 (40 FWHM)	18	Present work
Argon ion laser	≃ 50	514.5	≃ 2	Huntley *et al* (1985)
	10	514.5	25	Godfrey-Smith *et al* (1988)
	45 max	514.5	≃ 4	Smith *et al* (1990)
	5–10 usual	514.5	40–20	Smith *et al* (1990)
Filtered halogen lamp	16	420–550	2.5	Botter-Jensen and Duller (1992)

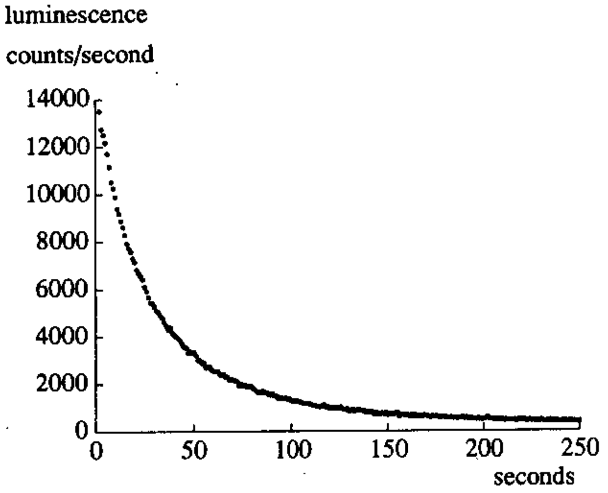

Figure 2. The decay in luminescence with time of exposure to the stimulating light, for quartz dosed to 75 Gy stimulated by the 16 Nichia 110104 LEDs each with a GG475 filter as in figure 1. The quartz sample was pre-heated for 1 min at 220 °C to remove unstable signal prior to measurement. The luminescence counting rate fell to half of the initial value in 18 s.

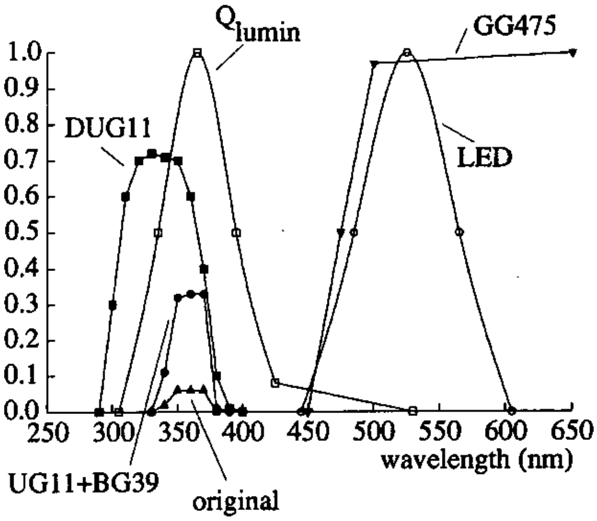

Figure 3. The transmission characteristics of filter combinations discussed in the text, based on the manufacturers' data (Schott and Corning). The combination labelled 'original' comprised 7-60, 7-59, UG11, BG39 and HA3 filters. Superimposed is the quartz luminescence emission spectrum (Q_{lumin}) from Huntley *et al* (1991) and the Nichia type 110104 LED emission spectrum (from the manufacturer's data). The vertical axis indicates the filter transmission or the relative emission intensity as appropriate.

this regard the new LED system is a factor of 70 better than its predecessor and comparable in performance to an argon ion laser. The energy per unit area required from an argon ion laser to reduce the green stimulated luminescence to half intensity is between about 150 mJ cm^{-2} (Smith *et al* 1990) and 250 mJ cm^{-2} (Godfrey-Smith *et al* 1988). It may be that this range of values results from a dependence on the mineralogy of the quartz or on the duration of any heating prior to green stimulation. However, from these values, the present LED system must be producing about 10 mW cm^{-2}, which is within the power range commonly used for dating with sedimentary quartz. Stokes (1992), for example, refers to the use of an argon ion laser system which provided a power density at the sample in the range 5–50 mW cm^{-2}, in the context of dating the deposition of young sediments using quartz. Smith *et al* (1990) referred to the power at the sample being usually in the range 5–10 mW cm^{-2}. The filtered halogen lamp system of Botter-Jensen and Duller (1992) has a short time to half intensity in relation to the power density at the sample due to the stimulating light extending to shorter wavelengths than it does in the other systems.

The stability of the stimulating light intensity with time was investigated by scattering the light from stainless steel in the sample position and replacing the colour filters in front of the photomultiplier by sufficient neutral density filters to reduce the intensity of scattered light entering the photomultiplier to a level at which photon counting of the scattered light was possible. Measurements of the variation of light intensity with time were performed over periods of 250 consecutive measurement intervals of 0.1, 1 and 10 s, so that the stability over durations of 25, 250 and 2500 s was investigated. A small overshoot of intensity at switching on was observed, of about 2%, which fell to half this value after 2 s and was imperceptible after 6 s. Apart from this reproducible small 'spike', the light intensity was constant within 2% for continuous operation (tested up to 42 min operation). Constancy within 2% from run to run throughout the day was also noted, with no particular control of room temperature.

Table 2. A comparison of performances with different filter combinations in front of the photomultiplier.

	Filter combination				
	7-60 (4 mm) 7-59 (4 mm) UG11 (4 mm) BG39 (0.5 mm) HA3 (4 mm)		UG11 (4 mm) BG39 (2 mm) HA3 (4 mm)	DUG11 (2 mm) HA3 (4 mm)	
	16 (TLMP7513) (Galloway, 1992)	4 (Nichia 110104)	4 (Nichia 110104)	4 (Nichia 110104)	16 (Nichia 110104)
Photomultiplier noise (cs^{-1})	9	9	9	9	9
+ filter phosphorescence (cs^{-1})	11	11	11	10	10
+ scattered light (cs^{-1})	16	16	15	30	100
Measured relative luminescence signal[a]	1	20	80	320	$\simeq$ 1000
Relative filter transmission		1	4	16	
Signal-to-noise ratio improvement	1	20	80	160	160

[a] Averaged from measurements on quartz samples given a range of β doses, with a measurement time of 100 s for the (Galloway 1992) system and 1 s for the new systems.

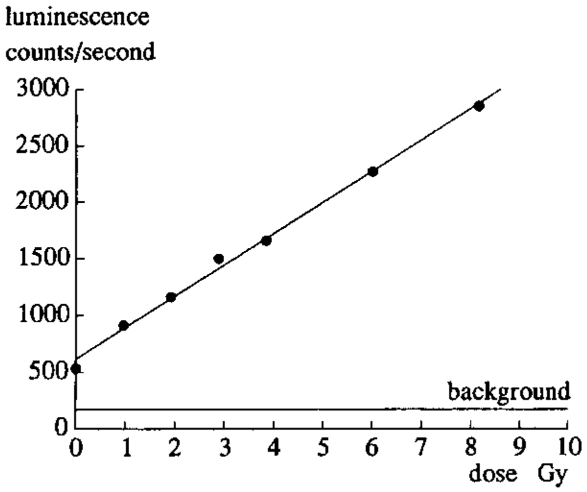

Figure 4. An example for quartz bleached by daylight, of the dependence of the luminescence on dose as measured by the new LED system of figure 1. The dose range covered here was too low to be measured with the original (Galloway 1992) system. Luminescence was counted for 1 s, with pre-heating of the samples for 1 min at 220 °C to remove unstable signal after exposure to a calibrated ^{90}Sr β-source. The finite counting rate at zero dose illustrates the phenomenon of recuperation (Aitken and Smith 1988).

4. The choice of filters

First tests of the new LED sytem were performed with the same combination of filters in front of the photomultiplier as had been used with the original LED arrangement of Galloway (1992). It is, however, appropriate to consider whether any advantage can be gained by use of a different filter combination, since the new system has a GG475 filter in front of each LED to cut off any light near the luminescence wavelength, figure 3. Basically it seemed that a UG11 filter should be suitable for passing the quartz luminescence more efficiently than did the original combination while still retaining discrimination against scattered green light. However, the UG11 filter, in common with most colour filters which transmit in the violet or ultra-violet region of the spectrum, also transmits in the red region. To suppress this red transmission, the UG11 filter was used in combination with a BG39 filter and the transmission of the combination is also shown in figure 3. A possibly more efficient alternative investigated was the Schott DUG11 filter, figure 3, which comprises a 2 mm thickness of UG11 filter glass with red absorbing metal oxide layers deposited on both sides of the filter. Comparison of the effectiveness of these possible filter choices was made using a preliminary test system which contained only four Nichia 110104 LEDs (each with an associated GG475 filter), identical to the final system of figure 2 except for the number of LEDs. The choice of filters in front of the photomultiplier depends only on the emission spectrum of the LEDs (after passing the light through the GG475 filter) and not on the number of LEDs. The comparative measurements are given in table 2. A heat-absorbing HA3 filter was always included since, in eventual routine use for dating work, it may be convenient to be able to heat the sample in the measuring position without concern for the possibility of damage to the filters. The UG11 and BG39 combination improved the photon-counting rate from the photomultiplier by a factor of four compared with the original filters, without worsening the background counting rate in which photomultiplier noise predominates. The DUG11 filter provides a factor of 16 improvement in signal compared with the original filters, with a doubling of the background rate in which scattered light now contributes more than the photomultiplier noise. Accordingly the DUG11 filter was adopted for use with the 16 Nichia 110104 system.

5. The overall system performance

Also included in table 2 are data on the original system and the complete new 16 LED system. The overall improvement in sensitivity to quartz luminescence stimulated by green light is about three orders of magnitude, a factor of 70 resulting from the change in LEDs used and a further factor of 16 resulting from the change in luminescence-selecting filters.

An indication of the performance of the new system in determining the dependence of luminescence on dose, up to 10 Gy, is given in figure 4. The dose range covered here was too low to be measured with the original (Galloway 1992) system. Each point was provided by a measurement of the luminescence for only 1 s, whereas 100 s measurement times had been used with the previous system. The small finite counting rate at zero dose illustrates the phenomenon of recuperation (Aitken and Smith, 1988).

6. Conclusion

The system described for the stimulation of luminescence from quartz by green light from 16 Nichia type 110104 LEDs each with its own small GG475 filter provides sensitivity comparable to that of the traditionally used argon ion laser systems, being 70 times as effective as the previous LED system. When used with a DUG11 filter to select the stimulated luminescence, the overall performance is about 1000 times as sensitive as the previous LED system. It is the most compact and economical system for green light simulation of luminescence and so should provide a most convenient tool for luminescence dating with quartz.

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Single aliquot dating of ceramics by green light stimulation of luminescence from quartz

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of the material proceeds independently for each component of added dose. An alternative method of data analysis permits all the necessary measurements to be made on only one aliquot [15]. Appropriate correction procedures for feldspars showing a significantly non-linear response are presented by Duller [16]. Duller [14] found that, in contrast to the success of the additive dose procedure, the regeneration process failed because of sensitivity change in the feldspar. While work has been done towards overcoming this problem with regeneration [17,18], the additive dose method is the subject of the present report.

Concerning application of the single aliquot additive dose method to the stimulation of quartz by green light, Galloway [19] showed an example of consistent functional forms resulting for the dependence of luminescence on dose when determined by single aliquot and multiple aliquot methods. Liritzis et al. [20] reported on a ceramic for which consistent ages were determined by single aliquot measurement on quartz and by thermoluminescence. That single aliquot and multiple aliquot methods give the same dependence of luminescence on dose has been demonstrated in detail by Hong and Galloway [21], both for quartz which was bleached by daylight and so relevant to sediment dating, and for quartz previously heated and so relevant to pottery dating. Further, significant differences were found between the appropriate single aliquot correction applicable to the stimulation of quartz by green light and to the stimulation of feldspar by infrared.

Naturally, most dating by optical stimulation has been applied to sediments, the field which inspired the development of the technique. Closer to the dating of a ceramic, Botter-Jensen and Duller [22] determined the age of a burnt stone by multiple aliquot additive dose measurements on extracted quartz stimulated by green light and obtained an age very close to the age determined by thermoluminescence. Two successful laboratory simulations of pottery equivalent dose determination by multiple aliquot additive dose green stimulation of quartz were reported by Galloway [19]. Consistent ages were determined by thermoluminescence and by single aliquot additive dose green light stimulation of quartz from a 3000 BC Greek ceramic [20]. The dating of ceramics by the single aliquot additive dose green light stimulation of quartz is discussed further here in relation to sherds from boreholes sunk in the north-western Peloponnese, Greece.

2. The samples

The samples came from bore holes sunk in a search for the lost city of Helike. Helike was the most important city of ancient Achaia, in north-western Peloponnese. It was founded in Mycenean times, and Homer refers both to the city and the area. It was destroyed by a catastrophic earthquake on a winter night in 373 BC. The land on which the city was built sank into the Corinthian Gulf and its inhabitants were completely annihilated by the disaster. Literary sources suggest that remains of the submerged city were visible under sea water at least until the Byzantine period [24]. They were subsequently buried under river-borne sediments. The approximate location of Helike has long been known but its exact site has yet to be found. Most previous efforts to locate Helike (1950–1974) concentrated on the sea bed [25,26]. The results of subsequent sonar research in the area lead to the return of the research on to the land [27,28]. Since 1991 several bore holes (up to 45 m depth) were drilled at selected sites in the plain between the deltas of the rivers Selinous and Kerynites. This was the area where Pausanias, in the second century AD, placed a village called Helike, at a distance of 40 stadia from Aegion, and described it as the site of the famous lost classical city. Most of the pieces of ceramic from the bore holes were so small (~1–2 cm) that the quantity of extracted quartz was insufficient for traditional multiple aliquot luminescence dating measurements. Consequently only a single aliquot approach was possible and so single aliquot additive dose measurements and related tests with green light stimulation were undertaken. Nine pieces of pottery were dated in this way. The resulting relationship between age and depth at which the piece of ceramic was found is compared with the age–depth relationship for seven other samples dated in other ways.

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Single aliquot dating of ceramics by green light stimulation of luminescence from quartz

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Abstract

The single aliquot additive dose method of equivalent dose determination, and hence of dating, as applied to the stimulation of luminescence from quartz by green light has been investigated. The quartz was removed from pieces of ceramic, extracted from bore holes in an area of archaeological interest in the Aegialia region, Northern Peloponesse, Greece. Various tests and an appropriate single aliquot correction procedure are discussed. It is concluded that the additive dose single aliquot method of determining equivalent dose, with correction for re-use of the aliquot, can be successfully applied to the green light stimulation of quartz for the purpose of dating. © 1997 Elsevier Science B.V.

1. Introduction

The thermoluminescence dating of ceramics is well established and described in several texts [1–4]. Thermoluminescence is bleachable by exposure to light which led to the development of methods for dating the deposition of sediments (for example, [5]). Interest in sediment dating produced the optically stimulated luminescence technique in which green light from an argon ion laser stimulated blue luminescence [6]. Soon afterwards, infrared was shown to be an appropriate stimulant of luminescence from feldspar [7]. Much work followed on sediment dating, conveniently summarised by Wintle [8,9], mostly based either on the stimulation of quartz by green light or on the stimulation of feldspar by infrared. In either case the additive dose procedure was usually followed, requiring many 'aliquots' of each sample (Refs. [10–13] serve as examples).

Concerning the infrared stimulation of feldspar, Duller [14] showed the feasibility of carrying out the additive dose procedure using a single aliquot of sample material with a correction for the loss of signal due to repeated preheating and reading of the same aliquot. Each reading of luminescence involved a brief stimulation which removed only a small fraction of the total luminescence available. Most of the latent luminescence remained unstimulated and was added to by the next added dose. The data for the correction for re-use of the material were measured using another aliquot of the sample. An essential aspect of this correction process is that the decay of luminescence due to re-use

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Sample preparation followed standard procedures: gentle grinding, initial selection of grain size, 10–15 min Calgon wash, 10–50 min of 40% HF acid etch, ~60 min HCl acid etch, wash, and final sieving to reject any fine grains which passed the initial selection by being clumped together. In this way quartz grains were extracted and feldspars removed. That feldspars were successfully removed was checked by the absence of infrared stimulated luminescence.

3. The experimental equipment

The system for measuring green stimulated luminescence has been described by Galloway [19,29,30]. It comprises 16 green light emitting diodes (type TLMP7513) passing a current of 22 mA per diode and providing approximately 0.2 mW cm^{-2} at the sample, with a peak emission at 565 nm (18 nm full width at half maximum). Luminescence was measured by a photomultiplier (EMI type 9635QA) preceded by a combination of filters, comprising Chance HA3 (4 mm thick), Corning 7-59 (4 mm) and 7-60 (4 mm), Schott UG11 (4 mm) and BG39 (0.5 mm), which give a transmittance peak at 360 nm with transmission exceeding 1% from 330 to 390 nm. The photomultiplier noise was about 11 counts s^{-1} and the total background rate about 16 counts s^{-1}, including scattered light. The background rate was measured frequently during the sequence of luminescence measurements and subtracted from them. The light emitting diode and photomultiplier combination was mounted on an automatic system which provided for exposure of the sample to a calibrated beta source, sample heating, and green stimulated luminescence measurement under computer control [31].

Tests for feldspar contamination were made using an infrared stimulation system comprising 16 type TSUS5402 (Telefunken) diodes with a peak emission at 950 nm and providing approximately 50 mW cm^{-2} at the sample [23,31]. The filter combination for luminescence detection comprised Corning 7-59 (4 mm thick) and Schott BG39 (2 mm thick), which gave a maximum transmittance at 370 nm with transmission exceeding 1% from 290 to 490 nm.

4. Single aliquot measurement and correction procedure

The single aliquot additive dose measurement procedure on quartz grains with stimulation of luminescence by green light consisted of a simple sequence, in which each stimulation of luminescence removed only a small part of the available luminescence. The sequence was: preheat and read natural signal; add beta dose, preheat and read; add further beta dose, preheat and read; continue in this way, adding dose, preheating and reading until the desired number of additive dose measurements have been made; preheat and read again several times without adding further beta dose. The additive dose measurements have to be corrected for loss of luminescence signal due to repeated re-use of the same aliquot, since each preheating not only removes unstable signal but reduces the surviving stable signal and each reading of luminescence by exposure to green light reduces (by a small amount) the signal surviving to the next added dose measurement. The correction procedures used have been described by Hong and Galloway [21] and followed from those developed for the infrared stimulation of feldspars by Duller [14] and by Galloway [15], in which the repeated measurements without further added dose serve either as a test of the success of the correction [14] or provide the information necessary for correction [15]. However, significant simplification emerged for the case of quartz stimulated by green light.

The essential information for the correction of single aliquot additive dose measurements is provided by the decay curve giving the factors, $f(n)$, by which the stable luminescence signal is reduced at the nth preheating and reading of the aliquot and that the $f(n)$ values are essentially dose independent. For the stimulation of quartz by green light, the factors $f(n)$ show an exponential dependence, $f(n) = e^{-b(n-1)} = r^{(n-1)}$, where $r = e^{-b} = f(n)/f(n-1)$, that is r is the ratio of any factor to the immediately preceding factor (see Fig. 1, and also [21]). One consequence of the exponential decay, for the correction of single aliquot additive dose measurements, is that the correction equations become the same regardless of whether or not the decay of each added component of

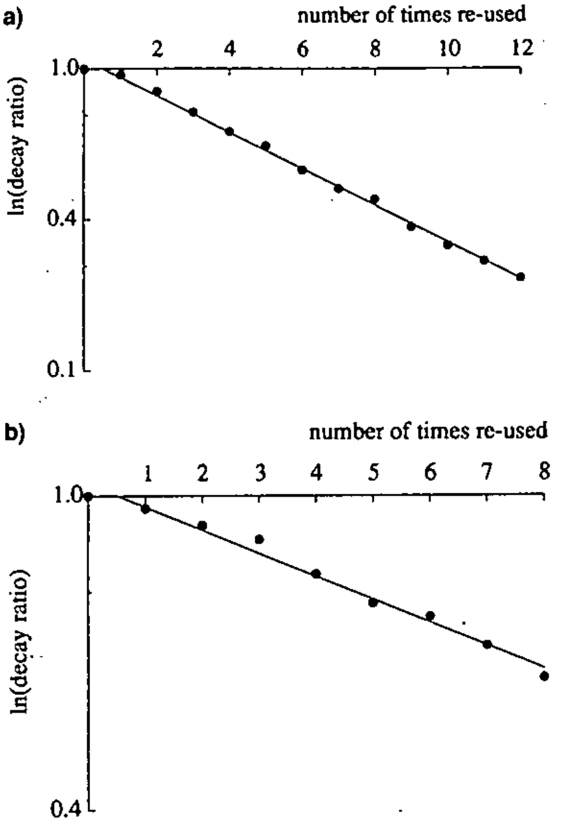

Fig. 1. Two decay curves for quartz showing exponential decay: (a) for sample B42 : 1 with preheating at 220°C for 1 min and 12.5 s measuring time; (b) for sample B24 : 1 with preheating at 200°C for 1 min and 100 s measuring time.

luminescence is regarded as being independent of the others. The correction required is simply,

$$_{\mathrm{corr}}L(D_n) = {}_{\mathrm{meas}}L(D_n) - r\,{}_{\mathrm{meas}}L(D_{n-1}) + {}_{\mathrm{corr}}\,L(D_{n-1}),$$

where $_{\mathrm{corr}}L(D_n)$ is the corrected value of luminescence resulting from the nth dose D_n and $_{\mathrm{meas}}L(D_n)$ is the measured value of luminescence. The distinction between the first and second correction methods of Duller [14], which was all important for the stimulation of feldspar by infrared, disappears for the stimulation of quartz by green light. Further, the decay factors $f(n)$ required to correct single aliquot measurements are replaced by r, which can be determined directly from the ratio of any sequential pair of preheating and luminescence readings with no added dose between (although of course better accuracy may come from averaging a sequence of measurements). Thus, unlike the situation with the infrared stimulation of feldspar, the decay factors can be determined directly (without the iterative process described by Galloway [15] from decay measurements made on the same aliquot after the additive dose measurements (Fig. 2). It may be noted, at least for the samples subject to the present study, that the decay in luminescence due to successive preheating and reading is much smaller for the stimulation of quartz by green light than for the stimulation of feldspar by infrared; compare for example $f(2) \sim 0.96$ in Fig. 1 or Fig. 2 with $f(2) \sim 0.86$ for the infrared stimulation of feldspar (from [14] or [15]). Consequently the magnitude of correction to the measured single aliquot additive dose measurements should be smaller with quartz than with feldspar and so in turn, the equivalent dose determined from corrected measurements should be less influenced by any uncertainties in the correction process.

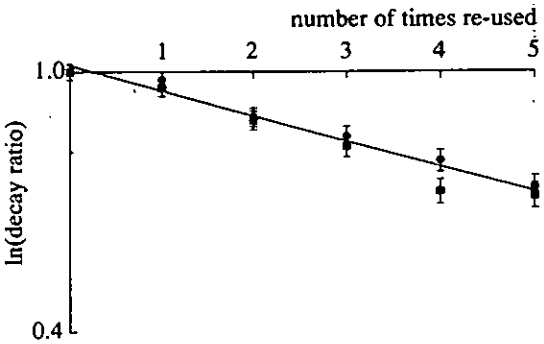

Fig. 2. Decay data for two aliquots of the same quartz (B18 : 1). One aliquot was dosed and the decay ratios measured (circles). The decay ratios for the other aliquot were measured after making an additive dose set of measurements (squares).

5. "Infrared cleaning" of quartz

Traces of feldspar can be present for two reasons in samples that are supposed to be purely quartz. Firstly, the chemical processing with HF acid to dissolve away the feldspar may have been insufficient. Secondly, the feldspar may be present as inclusions within the quartz grains and so be protected from HF treatment by the surrounding quartz. A sample of the processed material from the sherd can be tested for the presence of feldspar by infrared stimulation, which should produce luminescence from feldspar but not from quartz [32,33]. The green stimulated luminescence from feldspar is also bleached out by exposure of the feldspar to infrared [23], even though the reduction of the two signals is not at the same rate. Thus it should be possible to reduce to a negligible level the influence of any feldspar contamination on the green stimulated luminescence by exposure to infrared without affecting the green stimulated luminescence from quartz. To confirm that prolonged exposure to infrared had no adverse influence on quartz additive dose measurements, tests were carried out on material that was free from feldspar (as confirmed by infrared stimulated luminescence testing of another aliquot of the same material). The tests consisted of measuring several points of an additive dose curve, then exposing the quartz sample to the infrared emitting diode system for 3000 s and then continuing the additive dose measurements. The additive dose curve continued smoothly, unperturbed by the exposure to infrared (Fig. 3). It is concluded that prolonged exposure to infrared could be used to effectively "clean" a quartz sample slightly contaminated with feldspar prior to stimulation by green light without undesirable influence on the additive dose curve.

It was only necessary to apply infrared cleaning to three samples, K1, B25 : 3 and B24 : 1. For these samples 3000 s of infrared exposure preceded each reading of luminescence stimulated by green light.

6. Quartz response after bleaching

Sensitivity change in quartz follows bleaching [34]. It could however be of interest to see whether, sensitivity apart, the additive dose response curve after bleaching could indicate the shape of curve appropriate to the determination of the equivalent dose, that is, to confirm linearity, or to help determine the appropriate parameters to describe supra-linear or saturating response. The responses of three aliquots of the same material are compared in Fig. 4; one aliquot was bleached by Edinburgh daylight for 6 h and shows a supra-linear response; another aliquot was bleached for 1 h in a Hönle SOL-2 "solar simulator" and shows a saturating response with increased sensitivity compared to the daylight bleached material; the third was bleached by heating at 500°C for 1 min and also shows a saturating response with even higher sensitivity. This does not encourage the use of a simple laboratory bleaching method to determine the dose response!

7. Single aliquot additive dose measurements with green light stimulation on the Helike samples

Quartz samples from nine ceramics extracted from six of the Helike bore holes were subjected to single aliquot additive dose measurements with stimulation of luminescence by green light, as detailed in Table 1. Two of the ceramics, B25 : 1 and K1, gave quartz with low luminosity and so gave equivalent dose values from green light stimulation of low accuracy. The duration of exposure to green light for luminescence stimulation was 10 s for these samples. For better statistical accuracy in the measurements, a green light exposure time of 100 s was used for some of the other samples. (An exposure of 100 s to the green LEDs gives a similar yield of luminescence to a 1 s exposure to a typical argon ion laser system [29].) However the limited amount of sample material available made possible only one or two determinations of equivalent dose for each sherd, so that there was little opportunity to try to improve on the first attempts on each sherd. Four sherds, not listed in the table, provided sample material which proved not to respond to optical or thermal stimulation, even though the dose rates to which they had been exposed were comparable to those associated with measurable sherds. One, B36 : 1, gave little green stimulated luminescence but was datable by thermoluminescence. Another, K1, provided a little feldspar to which the single aliquot additive dose technique with infrared stimulation was applied in the manner of [15]. Other material from K1 was dated by thermoluminescence (Michael, personal communication). In all cases the samples were tested for absence of feldspar contamination

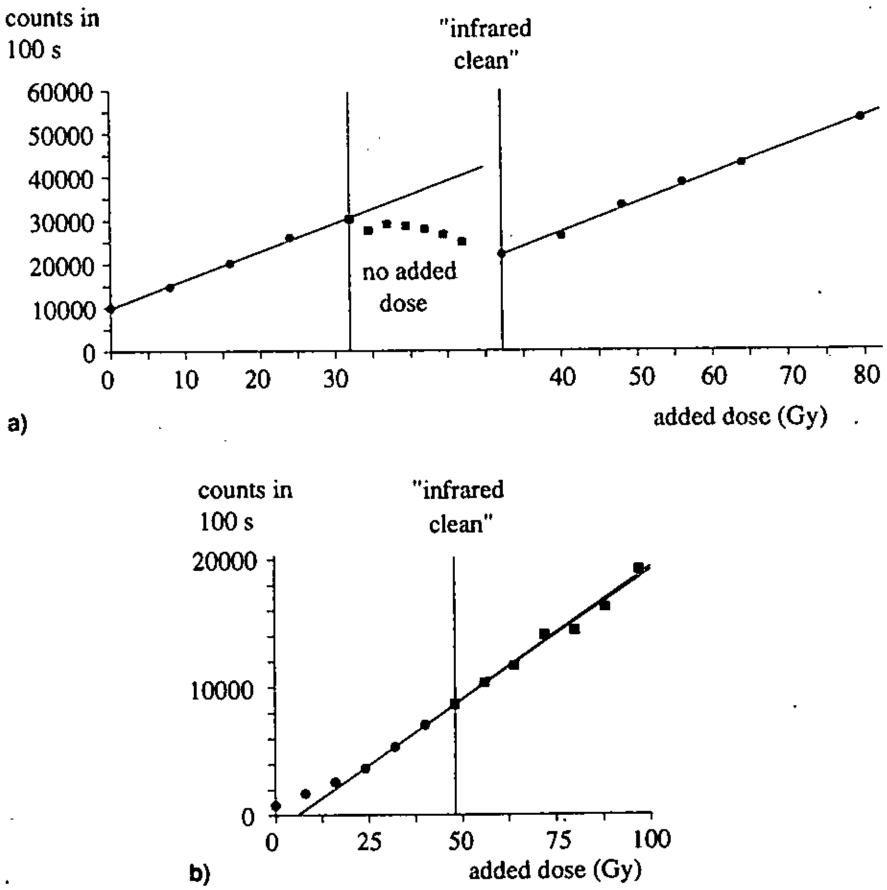

Fig. 3. Two additive dose growth curve measurements on quartz, interrupted but unperturbed by 3000 s exposure to infrared. In (a), uncorrected single aliquot additive dose data are presented from a sample of B25 : 3. The initial additive dose measurements up to 33 Gy are followed by seven repeated preheating and reading cycles without added dose, typical of the single aliquot procedure. The sample was then exposed to infrared for 3000 s and the green stimulated additive dose procedure continued. The two additive dose sections show the same sensitivity, 650 ± 20 counts per 100 s per Gy and 660 ± 20 counts per 100 s per Gy, respectively, unaltered by the infrared exposure. Corrected data for K2 (which is supralinear below 25 Gy added dose) is shown in (b), with the infrared exposure at 48 Gy having no detectable influence on the quartz sensitivity (207 ± 3 counts per 100 s per Gy before, and 203 ± 12 counts per 100 s per Gy after, infrared exposure).

by infrared stimulation. In four cases there was sufficient material to make a second determination of equivalent dose by green light stimulation, and infrared cleaning was applied prior to the second set of measurements. In none of these four cases was there a statistically significant difference between the two equivalent dose determinations and so the weighted mean is quoted in the table. Decay ratios due to repeated preheating and reading required for correction of the single aliquot additive dose data, such as illustrated in Figs. 1 and 2, were measured on the same aliquot after collection of the additive dose data. In addition, for samples K2, B42 : 1, B18 : 1 and B18 : 2, decay ratios were measured using a separate aliquot, with no significant difference being observed from the other set of decay ratios for the same samples. Examples of additive dose growth curves are shown in Figs. 5–8. Fig. 5 refers to sample B42 : 1 which, like samples B18 : 1 and B18 : 2, shows a saturating dose response. Fig. 6 shows the data for sample B25 : 3, which like the data

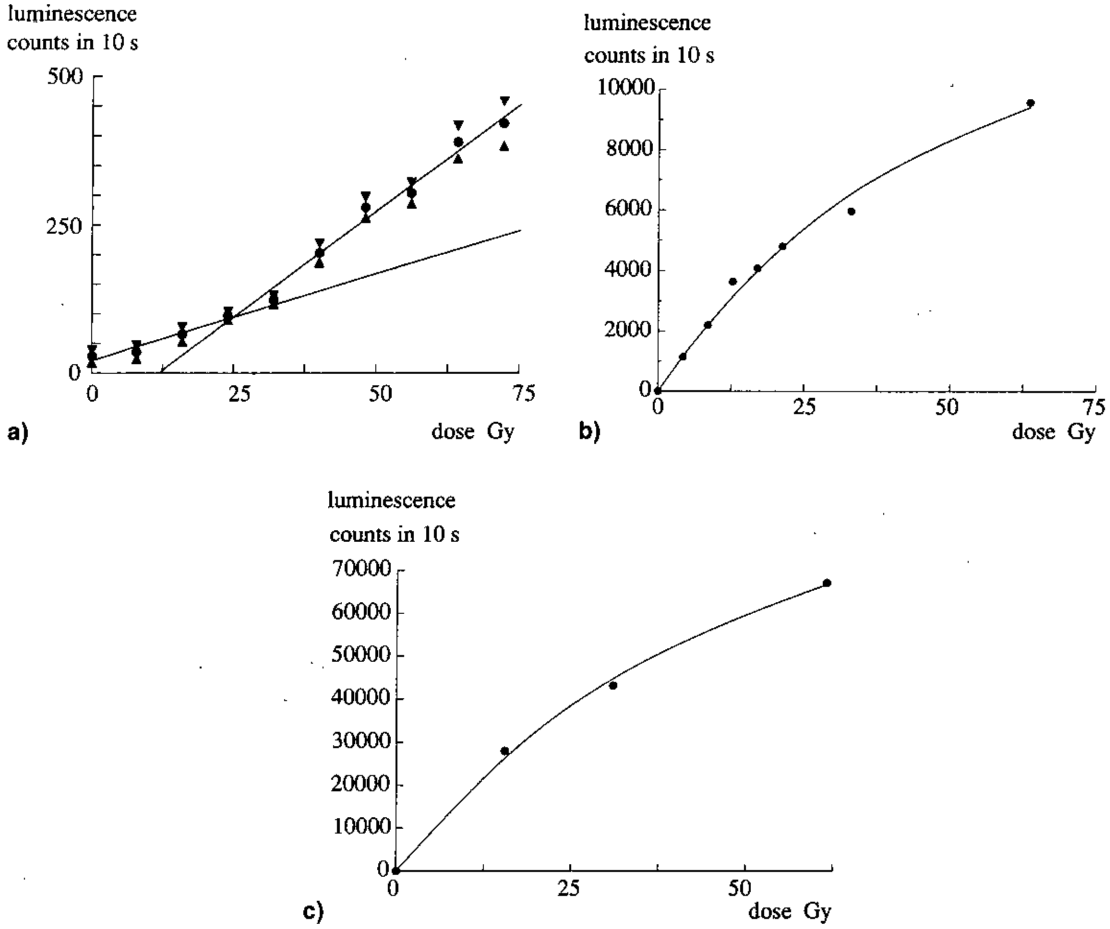

Fig. 4. The response of sample K2 after different bleaches: (a) by daylight for 6 h, showing a supralinear response at low dose and with an approximation to the response by two straight lines. The small non-zero intercept, if statistically significant, may be due to the recuperation phenomenon associated with bleaching and preheating ([35]). The result following bleaching for 1 h in a Hönle SOL-2 solar simulator is shown in (b) along with a saturating exponential fit to the measurements, luminescence = 12 120 (1 − exp(−0.024 dose)). The response following bleaching by heating at 500°C for 1 min is shown in (c) along with a saturating exponential fit to the data, luminescence = 88 800 (1 − exp(−0.023 dose)). The fit has essentially the same shape (exponent) in both (b) and (c), with (c) showing a higher luminescence sensitivity to dose.

for samples B25 : 1, K1, and B25 : 2, are well fitted by a straight line. Fig. 7 shows the corrected additive dose data for K2, which like the dose response of daylight bleached K2 material in Fig. 4(a), shows a supra-linear response and is extrapolated to give the equivalent dose by linear fitting to the data points up to 25 Gy added dose. Fig. 8 shows the corrected measurements on sample B24 : 1, which like K2, show a supralinear response and seem in this case to be appropriately extrapolated by a linear fit to the points up to 15 Gy added dose.

8. Age determination

Determination of the sample age from the dose extrapolated as equivalent to the natural luminescence from the sample requires knowledge of the dose rate to which the quartz crystals in the sample

Table 1
Details of the single aliquot additive dose green light stimulated luminescence measurements on samples from the Helike boreholes

Sample number	Grain size (μm)	Preheat [a] temp. (°C)	Read time (s)	Response function	Equivalent dose (Gy)	Dose rate (mGy yr^{-1})	Age (years)	Sample depth (m)
B25 : 1	106–212	200	10	Linear	6.3 ± 4.5	3.2 ± 0.1	2000 ± 1500	0.2
B36 : 1	60–150				3.5 ± 0.7 [b]	3.2 ± 0.2 [b]	1100 ± 230 [b]	0.75
K1	60–106	200	10	Linear	6.0 ± 3.0 4.0 ± 1.0 [d]	2.9 ± 0.1	2000 ± 1000 1380 ± 350 [d] 1800 ± 320 [e]	1.40 [c]
K2	106–250	200	100	Supralinear	5.4 ± 0.7 [f]	3.0 ± 0.1	1800 ± 250	1.45
B25 : 2	90–120	200	10	Linear	4.5 ± 1.5 [g]	2.2 ± 0.1	2050 ± 700	4.35
B42 : 1	70–150	220	12.5	Saturating	7.9 ± 0.3	2.7 ± 0.1	2930 ± 180	5.70
B18 : 1	70–150	220	12.5	Saturating	8.2 ± 0.3	2.5 ± 0.1	3290 ± 160	6.58
B18 : 2	70–150	220	12.5	Saturating	11.0 ± 0.4	2.8 ± 0.1	3930 ± 230	6.58
B25 : 3	70–106	200	100	Linear	10.3 ± 0.7 [f]	2.4 ± 0.1	4300 ± 350	7.54
B24 : 1	70–150	200	100	Supralinear	10.5 ± 1.5	2.3 ± 0.1	4570 ± 730	12.18

[a] Preheating was for 1 min.

[b] By thermoluminescence – no measurable green or infrared stimulated luminescence.

[c] 1st – 4th century Roman remains found at this level.

[d] By infrared stimulation of feldspar from K1.

[e] Thermoluminescence determination by Michael, personal communication, 1995.

[f] Weighted mean of two runs.

[g] Weighted mean of two runs; a thermoluminescence regeneration measurement indicated an equivalent dose ~4 Gy.

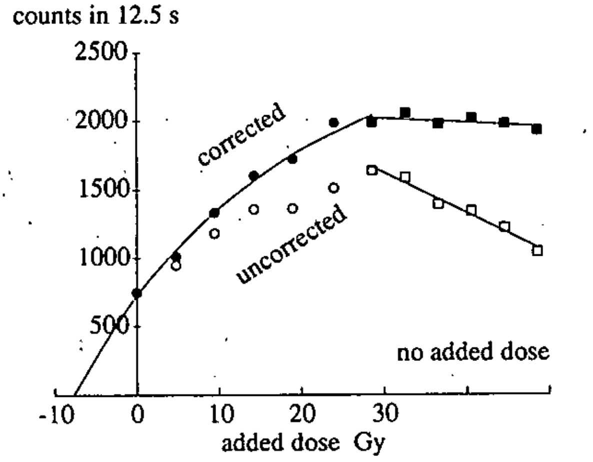

Fig. 5. Single aliquot additive dose data (uncorrected and corrected) for B42 : 1, with saturating exponential fit to the corrected points. Also shown, to the right of the figure, are the repeated preheat and read cycles which give the mean correction ratio r and the result of correcting these points by the mean ratio, which should ideally give a horizontal line.

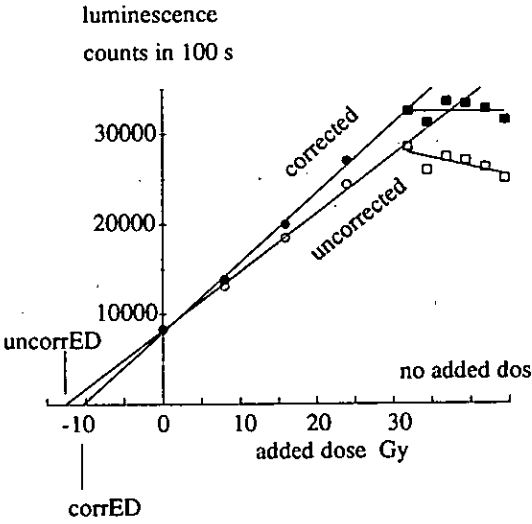

Fig. 6. Single aliquot additive dose data (uncorrected and corrected) for B25 : 3, with linear fit to the corrected points and to the uncorrected points for comparison. Also shown, to the right of the figure, are the repeated preheat and read cycles which give the mean correction ratio r and the result of correcting these points by the mean ratio, which should ideally give a horizontal line.

have been exposed. The dose rates quoted in the table comprise the beta dose rate from the material of the sherd, the gamma dose rate from the surrounding soil, and a cosmic ray component. The beta dose rate was measured using the calibrated plastic scintillation counter described by Galloway [36] and as discussed by Galloway and Liritzis [37]. A factor of 0.97 was assumed to allow for beta dose attenuation within the grains of quartz. (For most of the samples, the quartz grains were predominantly towards the smaller end of the initial size range in Table 1, making it appropriate to use a factor larger than the value of 0.9 suggested by Aitken [2] for 100 μm grains. However, even using a factor of 0.9 the ages in Table 1 are changed only by about 5%, substantially less than the quoted uncertainties.) Gamma dosimetry was made by spectrometry using a high resolution hyper-pure Ge detector following Galloway [38]. A small correction for probable water content, appropriate to the site and depth in the bore hole, was applied to both the beta and the gamma measured dose rates and is discussed in the archaeological interpretation of the results [39]. The essential distinction was between the samples found above the present water table and those found below it. The cosmic ray contribution was taken as 0.20 mGy yr^{-1} within the top metre, 0.15 mGy yr^{-1}

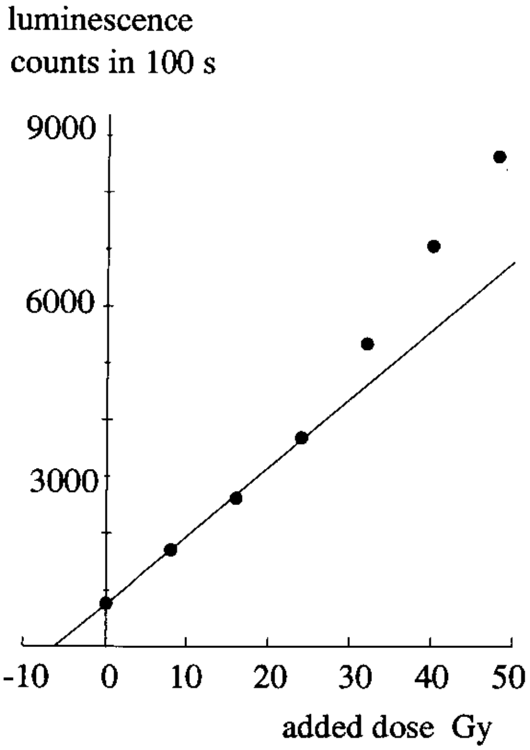

Fig. 7. Single aliquot additive dose data (corrected) for K2, showing supralinear response, with extrapolation by linear fit to points for added dose less than 25 Gy.

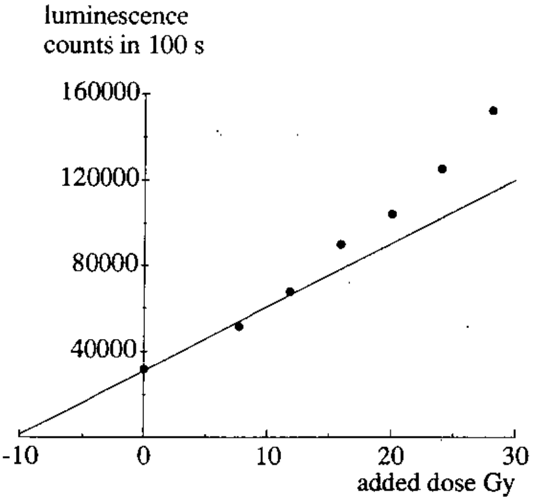

Fig. 8. Single aliquot additive dose data (corrected) for B24 : 1, showing supralinear response, with extrapolation by linear fit to points for added dose less than 15 Gy.

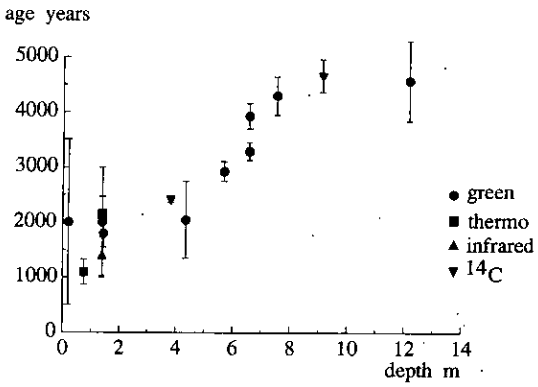

Fig. 9. The relationship between age and depth over the area in which bore holes were sunk. Circles refer to ages deduced from single aliquot green light stimulation of luminescence of quartz from pieces of ceramic; squares to thermoluminescence ages; the upward pointing triangle to single aliquot infrared stimulated luminescence; the two downward pointing triangles to ^{14}C dating.

for 1–8 m depth and 0.10 mGy yr^{-1} for the sample from about 12 m.

The ages determined for the sherds are plotted against depth in Fig. 9 and show a plausible roughly linear increase in age with depth. Also plotted are two radiocarbon ages [40] which are entirely consistent with the ages from the green light stimulation of the quartz single aliquots. Two ages determined by thermoluminescence and one determined by infrared stimulated luminescence are also plotted in Fig. 9. Overall, Fig. 9 shows that the additive dose method used for dating with green light stimulation of single aliquots of quartz provides ages which add significantly and consistently to the other age information on the site.

9. Conclusions

The additive dose single aliquot method of determining equivalent dose, with correction for re-use of the aliquot, can be successfully applied to the luminescence stimulated from quartz by green light for the purpose of dating. The single aliquot method can enable ages to be found when insufficient sample material is available for multiple aliquot optical or thermoluminescence dating. The decay factors, required for correction purposes, show an exponential dependence on the number of times of re-use of the aliquot. This makes unnecessary the assumption required in the case of infrared stimulation of feldspar, that each component of added dose decays independently of the other components. The decay factors required for correction can be measured on the same aliquot after the additive dose measurements have been completed. If necessary, the additional luminescence from feldspar inclusions in the quartz grains during the green light stimulation of the quartz can be avoided by exposing the sample to infrared to bleach all luminescence from the feldspar prior to green light stimulation of the sample.

The additive dose method with green light stimulation of a single aliquot of quartz should contribute significantly to future dating work.

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