Spatial Distribution of Environmental Dose for Luminescence Dosimetry: Theoretical Estimation and Applications

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By

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Year of submission: 2011

Certificate

I certify that the thesis entitled "Spatial Distribution of Environmental Dose for Luminescence Dosimetry: Theoretical Estimation and Applications" contains the results of original investigations carried out by **Mr. Naveen Chauhan** under my supervision. I am satisfied with the analysis of data and the outcome of the thesis and recommend the submission of thesis.

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Declaration

I hereby declare that contents of present thesis entitled "Spatial Distribution of Environmental Dose for Luminescence Dosimetry: Theoretical Estimation and Applications" comprises my own work and is original. The work has not been submitted to any University for award of a degree or diploma.

Signature of Candidate

Naveen Chauhan SRF, PRL Dedicated to My (Late) Mother and Father

Abstract

The present thesis focused on the estimation and quantification of spatial distribution of dose in natural sediments to explain the variation in natural doses and to explore the new avenues for luminescence dating. The work involved extensive use of mathematical, analytical, numerical, experimental and instrumental knowledge. In this work, several causes of distribution were investigated and possible reasons were explored for different grain sizes.

More specifically this thesis explores the causes of distribution of doses for the micron sizes single grains of quartz and it was found that the spatial fluctuations of inter grain distance of K-Feldspar beta sources at microscopic level can give a distribution in dose on account of statistical nature of dose deposition. In order to quantify this distribution, Monte Carlo based simulation codes were used to simulate the transport of beta particle through matter and compute the dose-depth profile for ⁴⁰K beta source. Using this positively skewed dose distribution was obtained. Further to this, the dose distributions were computed for more realistic, natural conditions by including the effect of porosity of soil and water content in the simulations. The results enabled estimation of age for different natural environmental conditions. This distribution in the single grain doses was then extended to estimate the distribution in the doses expected from single aliquots of quartz. In this study several important parameters like number of aliquots required for reliable dose estimation at different accuracy limit, maximum possible error and the spread expected in doses on account of β heterogeneity, the ratio of maximum and minimum doses etc. were estimated. The study suggested that there is significant scatter in the dose values obtained from single aliquots of quartz. In case the beta heterogeneity is the sole cause of distribution, the average value of the dose distribution for suggested number of aliquots will provide the correct age. The ratio of maximum and minimum doses can be used to distinguish the causes of distribution other than the beta heterogeneity. This work also suggested that beta dose distribution puts definite limit to resolution of luminescence dating.

In yet another work, we worked on extending the dating limits of guartz by dating interior of sub-cm size quartz grain. The work concentrates on the fact that the luminescence signal of quartz saturates at ~250Gy, however the older sample can be dated provided the natural dose rate is low. In sub-cm size, quartz grains the contribution of α and β is zeroed in outerfew mm thickness. The interior receive dose only because of gamma sources of surrounding environment resulting in the dose rate, which is 1/3 of the surrounding sediment dose rate. This lead to slower growth of luminescence signal in the interior region and the interior saturates later in time. Therefore, by dating interior the older sediments can be dated. In this work the beta dose-depth profile for subcm size grains was estimated for sources of ⁴⁰K, ²¹²Bi, ^{230m}Pa and ²¹⁴Bi and it was suggested that the grains having size greater than 4mm has an inner core which has contribution only because of the gamma dose and by analyzing this inner core dating of older samples is possible. In order to ensure the bleaching of the grains, transparency and laboratory bleaching experiments were performed which suggested grains having diameter of ~14mm are bleachable in natural environment provided they are exposed to light for sufficient time. The methodology was tested with a natural gravel sample and the results obtained confirmed the theory.

In another part of thesis, work related to spatially resolved luminescence technique was done in order to develop surface dating technique. The development of the technique-required resolution of issues related to transparency of material, estimation of natural and laboratory dose rates and measurement of the spatially resolved luminescence signal. The detailed work suggests that transparency issues can be resolved by careful selection of the sample and using appropriate measurement protocol. The dose rates to the surface sample were quantified and a program is written to compute the average natural and laboratory dose rate to the sample. In order to measure spatially resolved luminescence signal, an imaging system using Electron multiplying CCD (EMCCD) was developed. All the units of the system comprising, stimulation unit (heating and light stimulation), optical imaging unit, acquisition and data processing unit are built in-house. The system is capable of detecting

spatially resolved luminescence. The system was tested using dose recovery and for the known age sample.

In addition to these works, the commonly used SAR protocol was tested for sensitivity changes during measurement and it was found that there are significant changes, which occur during measurement of natural signal. These sensitivity changes are not corrected by the standard SAR protocol and lead to significant scatter in the estimated dose value. In order to correct for these sensitivity changes an improved NSC-SAR (Natural Sensitivity Corrected SAR) protocol is suggested. This protocol corrects for the sensitivity changes occurring during the natural measurement by means of NCF factor, which is ratio of the intensity of 110°C TL peak just before and after natural measurements. The use of this protocol significantly improves the dose distribution and each time the distribution become compact.

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Chapter-1

Introduction

1.1 Motivation and Background

Recent advances in radiation physics have enabled the effective use of radioactive sources for the benefit of humanity. Today nuclear radiation is being widely used in diverse areas ranging from a source of energy to radiation therapy, tracing of biochemical processes using radioactive tracer and for disinfecting the food grains by giving gamma dose (dose=energy/mass) etc. All the things, living or non-living, are continuously exposed to the radiation emitted by the natural radioactive sources like Uranium (U), Thorium (Th) and potassium

(K) present in the earth. Measurement of this radiation dose is an integral part of any use of nuclear radioactivity, both natural and manmade. An important application of radiation dosimetry is in geochronologyusing natural ubiquitous minerals viz. quartz, feldspars, carbonates and sulfates. It involves radiation dosimetry of radiation field arising from the decay of naturally occurring radioactivity viz., U, Th, K, Rb and cosmic rays. Exposure of natural minerals to ionizing nuclear radiation results in storing energy with time, which can be released on appropriate stimulation as luminescence. The total luminescence (or sum of light)is proportional to energy absorbed from the radiation field and hence is proportional to the radiation dose. If the radiation exposure is constant through time then the total radiation dose can be related to time duration of radiation exposure and hence age of sample.

1.2 Luminescence

Luminescence is the phenomenon of emission of light from an insulator followed by prior absorption of energy from ionizing radiations when stimulated either by heat or by light.

It differs from incandescence in sense that in incandescence, the light is emitted as long as the stimulating source exists. However, in case of luminescence the emitted light persists only for a finite time and stops thereafter, irrespective of the presence or absence of the stimulation source. Further, the emission of luminescence is contingent to sample being exposed to ionizing radiation for each stimulation cycle. Depending upon the time between the excitation and light emission, luminescence is termed as fluorescence and phosphorescence. In fluorescence this time difference is <10⁻⁸ s (McKeever, 1985) while in phosphorescence it is more. Both phenomenon have their own importance and are used widely in a variety of applications. Further, based on the nature of stimulation, luminescence is termed as radio-luminescence (due to exposure to ionizing radiations), photoluminescence (stimulation by light), bioluminescence (biochemical reactions in some insects or fishes like glow worm,fire flies etc.), triboluminescence (due to mechanical treatment of sample),

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chemiluminescence (chemical reactions, whereby excess energy is released in form of light), thermoluminescence (TL, (stimulation by heat after irradiation)) and optically stimulated luminescence (OSL, (stimulation with light after irradiation)).

In the present thesis, we shall concentrate on TL and OSL and will deal with radiation dosimetry using natural materials.

1.3 Defects in Crystals

Defects are the non uniformities/irregularities present in the crystal lattice, which result in the breakdown of the periodicity in its lattice.



Figure 1.1:i) Arrangement of atoms in ionic crystal. ii) Different types of defect produced in the crystal. a) Schottky defect b) Frankel defect c) Substitution defects d) F-centre e) R-centre

Fig. 1.1(i) shows a regular ionic crystal lattice made up of singly charged cations and anions that occupy alternate sites. Each cation is surrounded by 4 anions and vice versa. However, in general, no crystal is perfect and defects occur in the crystals. These can be,

1. *Planar Defects:* The defects occurring due to inter-faces present in regular lattice like grain boundaries, stacking faultsor external surfaces.

- 2. Linear Defects: Thesehave group of atomsdislocated in irregular positions like in screw or edge dislocation.
- 3. Point Defects: These are defects arising due to imperfections at atomic level and are present even at thermal equilibrium. The most common are the chemical impurities present in the crystal at atomic level. Point defects result in some interesting and useful properties like thermal and electrical conductivity, color of crystal, variation in mechanical strengths and plasticity. In addition, defects are also responsible for the luminescence properties. Some of the common defects are schottky defect (Fig. 1.1(ii)a), frankel defect (Fig. 1.1(ii)b), substitutional defects (Fig. 1.1(ii)c) etc.

In crystals thecharged ions or charges trapped at the ion deficient sites forms color centers. These color centers possess interesting property of giving color to crystals. The most common of the charge centers is F-centre, which is formed when an e^- is trapped in the negative ion vacancy (Fig. 1.1(ii)d). Sometimes two or more F centers form clusters to give R (Fig. 1.1(ii)e), M (cluster of 3) and N(cluster of 4) centers.

The presence of these defects allows the trapping of electrons and holes, resulting in storage of luminescence. Following section, describe the luminescence mechanism in more detail.

1.4 Luminescence Mechanism

1.4.1 Basic Principle

The luminescence phenomena in mineral can be understood with the band theory of solids, having Valence and Conduction band, and a Forbidden band of up to 10 eV for insulators (Fig. 1.2a).

Valence band is completely filled at absolute zero and in conduction band; the energy states provide free motion of the electrons in the crystal lattice under crystal field. In pure crystals forbidden band do not have any allowed energy states. However, in nature no crystal is pure and contains defects some of which provide localized metastable energy states within the forbidden band (Fig. 1.2b, c). These metastable states act as a trap centers for the electrons or holes created due to ionization of the crystal atoms. The sites where electrons are trapped are called electron-trapping center and likewise hole-trapping centre also exist. When the crystal is exposed to the ionizing radiations, then free electron and holes are created such that the electron goes to the conduction band while hole moves in the valence band. A few of these get trapped in the respective trap centers. The residence times of trapped charges in these traps depends on the nature of the traps and charge environment (Garlick and Gibson, 1948; Randall and Wilkins, 1945a; Randall and Wilkins, 1945b). The lifetime of the electron in a trap is given by

$$\tau = s^{-1} \exp\left(E_g / kT\right) \tag{1.1}$$

where *t* is the lifetime, *s* is the frequency factor (and is generally of the order of ~10¹²sec⁻¹, Aitken, 1985c), E_g is the energy trap depth (Fig. 1.2b), *k* is the Boltzmann constant and *T* is the absolute temperature. The lifetime of charges in traps can vary from sub-seconds to 10⁸ years and is strongly temperature dependent. On stimulation by heat or by light, the charges trapped in metastable states are evicted and some of these radiatively recombine with holes to emit light. The recombination site could be either of the traps or of new traps and are termed as recombination centre. The recombination occurs in the excited state of the atom, from where a de-excitation provides light and thus, spectral features are specific to recombination site. The intensity of luminescence is directly proportional to rate at which electrons are detrapped on stimulation (McKeever, 1985; Nambi, 1977)and is given by

$$I = C \frac{dn}{dt} \tag{1.2}$$

In this *I* is the intensity, *C* is the proportionality constant, n is number of electron present at an instant *t*. Two variant of stimulation are thermal giving rise to thermally stimulated luminescence and optical, giving rise to optically



stimulated luminescence. When a crystal is heated with a constant heating rate, we get a TL glow curve (Fig. 1.3a) and when stimulated with light we get OSL decay curve (Fig. 1.3b). Due to experimental abilities of pulsing the light sources, three variants of OSL exists which are CWOSL, POSL and LMOSL.

In **thermoluminescence** glow curve, we obtain peak at different temperatures. The peak temperature is related to the energy trap depth of metastable state and thepeak position on the temperature axis, informs on thetrap depth distribution in the crystal (Urbach, 1930). Garlick and Gibson, (1948); Randall and Wilkins, (1945a); Randall and Wilkins, (1945b) calculated the relationship between trap depth and the TL peak. Randall and Wilkins, (1945a); Randall and Wilkins, (1945b) calculated it based on first order theory considering that once electron is detrapped its recombination provides luminescence.Garlick and Gibson, (1948) introduced the theory for second order kinetics by including retrapping of detrapped charges.

The equation for the first order kinetics is

$$I = n_0 s \exp\left(-\frac{E_g}{kT}\right) \exp\left[-\left(s/\beta\right) \int_{T_0}^T \exp\left(\frac{E_g}{KT}\right) dT\right]$$
(1.3)

and that for the second order kinetics is

$$I = n_0^2 s \exp\left(-\frac{E_g}{kT}\right) / N \left[1 + \left(n_0 s / N\beta \int_{T_0}^T \exp\left(-\frac{E_g}{kT}\right) dT\right)\right]^2$$
(1.4)

In this, *l* is the intensity, n_0 is the initial concentration E_g is trap depth, *k* is Boltzmann constant, *T* is absolute temperature and *N* is concentration of available traps β is the heating rate. In a two level system of a single trap and single recombination centre, several transitions occur. There are three types of transitions i.e. band-to-band, band to centre and centre-to-centre transition.



Figure 1.3:a) TL glow curve (heating rate: 2°C/s) and b) OSL decay curve of quartz.

Fig. 1.4 gives the possibletransitions(McKeever, 1985), which occur during complete cycle of irradiation, storage and recombination. In this (a) gives excitation of electron from valence band to conduction band, (b) and (e) gives the trapping of electron and hole and (c) and (f) shows their eviction respectively. Transitions (d) and (g) are the transitions of hole or electron with recombination center respectively to give luminescence. In addition to this Nambi, (1977) also suggest that if electron and hole is evicted simultaneously

then they can recombine at some intermediate centre, which is then referred as the recombination center.



Figure 1.4:Different types of possible transitions (Mckeever, 1985)

Further, there are direct transitions like (i), which do not involve delocalized bands and electron in trap recombine with hole in recombination centre directly without involving CB or VB. In some of the phosphors, if electron and hole centers are near to each other such that their wavefunctions overlap, then there is a definite probability of tunneling with time resulting in fading of signal. This phenomenon is called anomalous fading.



Figure 1.5:Configuration coordinate diagram based on Mott and Seitz theory

Infew cases, it was found that non-radiative processes, in which the recombination centre loses its energy via phonon vibrations, are also possible. Generally, at higher temperature non-radiative transitions are favored. This can be explained on the basis of configuration coordinate diagram (Fig. 1.5) using Mott Seitz mechanism (McKeever, 1985). Configuration coordinate represents the displacement of atom from defect position and in its equilibrium position it occupies the minimum energy position (a). Normally, It goes to excited state at position (b) after absorbing energy without any adjustments as stated by frank Condon principle, loses energy E1 as a phonon vibration and occupies the minimum of excited level i.e. position (c). From there the electron again deexcites, come to (d) and finally regains its equilibrium position (a) after losing energy E2 as phonon vibrations. Now at elevated temperature there is finite probability that electron in excited state instead of coming to position (d) goes to position (e) and then tunnel to the ground state without emitting the light photon. From there it comes to equilibrium level after phonon vibrations resulting in non-radiative transition. This is called thermal guenching and can considerably affect the luminescence efficiency at higher temperature.

In the case of **Optically Stimulated Luminescence**, the energy to the trapped electrons is provided by the light photons. Unlike TL, it is a one shot process. If the energy of photon is less than the trap depth, the electrons will not be evicted and any photon having energy greater than trap depth can result in detrapping the electrons to conduction band. These detrapped electrons then recombine with holes and result in luminescence process. As soon as the phosphor is stimulated with light the concentration of the trapped charges decreases exponentially, hence the luminescence signal also decreases with time resulting in OSL decay curve (Fig. 1.3b). The rate of eviction depends upon the intensity of the light, and the photoionization crossection of the trap involved, which further depends on wavelength of light. Thus the intensity of luminescence

$$I = \frac{dn}{dt} \propto \phi \sigma(\lambda) \tag{1.5}$$

Where, *I* is the intensity, *n* is number of trapped charges, ϕ is stimulation light flux, σ is photo ionization crossections and λ is wavelength. In case there is only one photosensitive trap, then the light sum obtained using TL and OSL for prolonged duration should be similar. However in reality, situation is complicated by fact that, not all the TL traps may be OSL traps. In addition to this, there are other factors involved like thermal quenching, which change the light sum. The advent of OSL provides several advantages over long used TL. It helps in probing the trap centers which are light sensitive, hence useful for dating aeolian samples where resetting is mainly by the light not by heat. There are different modes of stimulation (like, CWOSL, LMOSL, POSL etc) which can be used for several kinds of measurements for understanding the physics of the process and the dating part. The OSL technique enabled dating of single grains of the sand. The short shine measurements, which are used for normalization in several situations, can be done only in OSL. Besides this, there are several others where OSL has an upper hand over the TL.

1.4.2 Generalized Trap Model

The simple model having one trap and one recombination centre explains luminescence, however many important properties cannot be explained by this simple model. Bailey, (2001) discusses a general kinetic model for explanation of TL and OSL. This model discusses the luminescence in quartz and takes into account several types of centers to explain the luminescent properties of quartz. These centre include low temperature peak centers (Level 1: 110°C peak, Level 2: 230°C peak), Fast (OSL_F) and medium OSL (OSL_M) component levels (Level 3 and 4), Deep level participating in thermal and photo transfer and are thermally disconnected (Level 5), unstable non radiative levels called reservoir levels participating in thermal quenching and thermal activation (level 6: R₁-centre and level 7: R₂-centre), thermally stable radiative recombination centers which is basically a luminescent centre and responsible for all the luminescence (level 8: L-centre) and one thermally stable non radiative recombination centre called killer centre (level 9). Fig. 1.6 gives the different types of the centers and the possible transition from each centre used by Bailey, (2001).

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Figure 1.6:Different types of centers and transitions proposed by Bailey, (2001)

1.5 Luminescence in Natural Minerals

In nature, Quartz and Feldspar are the two ubiquitous minerals, which are widely distributed, and this is because of their resistance to weathering. These two minerals have useful luminescent properties such as high luminescence sensitivity (luminescence per unit dose per mg); trap lifters of the $\sim 10^8$ years. A brief discussion on their luminescence behavior is given below.

1.5.1 Quartz

Silica forms ~13% of the weight (Krbetschek et al., 1997) of the Earth and hence is omnipresent in variety of location ranging fromgranites to hydrothermal veins and from volcanic rocks to sedimentary deposits. Depending upon the temperature and pressure conditions during formation and burial it can be of 14 structural types. A typical TL glow curve of quartz comprises glow peaks (at heating rate of 2-3°C) at 85, 110, 190, 230, 240, 310, 325,and 375°C (Aitken, 1985c; Fig. 1.3a). A typical Blue Green light stimulated OSL decay curve (Fig. 1.3b) comprises 3 or more components (Ankjærgaard et al., 2010a; Murari, 2008). It is suggested that OSL signal corresponds to 325°C glow peak and are correlated with 110°C glow peak (Murray and Roberts, 1998), however exact process involved is still unknown. The most common form of quartz is $[SiO_4]^{4-}$ with tetrahedral geometry. Impurities such as AI, Ga, Fe etc.act as trapping or

recombination centers. In addition, structural defects also participate in luminescence process. The Si⁴⁺ has ionic radii of 0.42 Å and is rarely substituted because of small size and high ionic charge; however, there are several ions like AI^{3+} , Ga^{3+} , Fe^{3+} , Ge^{4+} , Ti^{4+} and P^{5+} , which can substitute Si^{4+} . Out of these, AI is most common impurity, in order to compensate the charge monovalent impurities like H^+ , or alkali metal (M^+) like Li^+ , Na^+ etc are also present(Krbetschek et al., 1997). Charge compensation by H⁺ forms OH bond, which captures a hole to form complex at low temperature and reduces $[AIO_4]^0$ on irradiation at room temperature (Bøtter-Jensen, 2003). This [AIO₄]⁰ gives asmoky color to guartz(McKeever, 1984; Nassau and Prescott, 1975).Similarly, $[FeO_4]^0$ imparts purple to pale color. Impurities like Ge^{4+} and Ti^{3+} form (Ge^{4+}/M^+) and (Ti^{4+}/H^{+}) electron trapping centers. In addition to this there are E' centers (E₁', E₂', E₄') identified by Isoya et al., (1981). E₁' centre consist of an electron trapped at Si site next to oxygen vacancy, E₂' centre consist of trapped proton associated with oxygen vacancy and electron at Si site. E₄' is an oxygen vacancy in which hydride ion is bonded to Si atom and an electron is present at non-equivalent Si site. Several studies were done to associate different impurity centers with luminescence emissions, however, only a gualitative association is available so far. This is due to the overlapping of emissions from different centers. Thethree main emissionbandsare 360-420nm (near UV-violet), 460-480nm (blue) and 610-630nm (orange) (Krbetschek et al., 1997).

- 360-420nmband corresponds to 110°C TL peak and is associated with (H₃O₄)⁰ hole center. Besides this, there are peaks at 150-180°C, 200-220°C and 305-325°C that emit in this band. These peaks emit in other wavelength regions as well.
- 2. 460-480nm wavelength band is linked with $(ALO_4)^0$ hole center. It is associated with 375°C and also with 260-280°C and >450°C glow peaks.
- 610-630nm emission band is generally observed in the quartz samples from volcanic origin and no link has been established with any defect centre so far. Generally, glow peaks at 130, 240, 280 and 360°C temperature emit this wavelength band.

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Often in TL dating of heated quartz, the glow peak region of 300-400°C is used for dating, the preferred emission is 460-480 nm and occasionally 610-630 nm is used. For BGSL the preferred emission is 360-420 nm due to ease in its optical bleaching and the same is used for TL dating of optically bleached sample due to ease of bleaching of this emission.

1.5.2 Feldspar

Feldspars are aluminosilicates formed of AlO₄ and SiO₄ and are ubiquitous as well. These generally occur in a field with three end members, viz., Orthoclase (KAISi₃O₈), Albite (NaAISi₃O₈) and Anorthite (CaAl₂Si₂O₈). Out of these, Orthoclase (K-feldspars) have been used for dating. TL glow curve (Fig. 1.7a)of K-feldspar has glow peaks at 90, 110, 210, 280, 320 and 380°C.The emission ranges over entire UV-visible range with principle emission in UV, blue and red. Whenstimulated with Infra-red, luminescence can be excited from a deeper trap at 1.6-1.7 eV due to a resonance excitation to 280°C (1.4 eV), then thermal assistance further helps this charge to leak in to the conduction band for eventual recombination with emission of light (Fig. 1.7b). More recent studies have refined this explanation somewhat (Ankjærgaard et al., 2010b; Poolton et al., 2002; Thomsen et al., 2008). The structure of feldspar is complex and comprises number of substitutional impurities such as Ba, B, Cs, Ga, Fe, Li, Mg, Mn REE, Sn, Sr etc. thatsubstitute for K, Na, Ca, Al, Si, O (Heier, 1962; Krbetschek et al., 1997; Lyakhovich, 1972; Parsons, 1994; Rhodes, 1969). Thermally stable paramagnetic centers (Fe^{3+} and Mn^{2+}), and metastable states provided by impurities give its luminescence.

In dating, the blue emission window is used in both TL and IRSL, but there is a problem related athermal fading (anomalous fading) of luminescence signal with time. This fading is attributed to tunneling of e⁻ to the recombination centre resulting in lowering of luminescence signal in nature and hence underestimation of age. Several workers are contributing towards estimation for the fading (Huntley and Lamothe, 2001; Lamothe et al., 2003; Spooner, 1992; Thomsen et al., 2008; Visocekas and Guerin, 2006). In addition to this red emission of the

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feldspar is being probed (Fattahi and Stokes, 2003; Fattahi and Stokes, 2004; Krbetschek et al., 2002) and is found more stable.



Figure 1.7:a) TL glow curve (heating rate: 2°C/s) and b) OSL decay curve of feldspar

1.6 Dosimetric and Dating Aspects

As already discussed, the lifetime of some of the traps in quartz and feldspar is as long as 10⁸ years. These traps provide excellent opportunity to use them for natural dosimeter. The continuous irradiation allows luminescence signal to buildup in stable traps proportional to dose acquired. The acquired luminescence signal can be used to estimate the dose received by the dosimeter in natural environment. As the dose is deposited at a constant rate by natural radioactive nuclides, so the age can be estimated as

$$Age = \frac{Acquired \ Dose}{Dose \ rate} \tag{1.6}$$

The dose rate can be calculated by estimating the concentration U, Th, K and Cosmic rays considering ranges and stopping powers of ionizing radiations. The estimation of dose is complicated by the fact that different ionizing radiations have different ranges in sediment. These differences results in distribution in doses obtained from quartz and feldspar. This thesis work tries to estimate and quantify the distribution in the doses and hence develop new methodology for better understanding of the subject.

1.7 Scope of the Present Thesis

In the present thesis, dose distribution in natural radiation environment is studied by means of luminescence observed from the naturally occurring dosimeters, like quartz and feldspar. The study helped in

- understanding different kind of radiation environment for different sizes of quartz grains. The knowledge gained in this study is used to improve upon the existing protocols for making luminescence dating more reliable.
- quantifying the distribution in doses obtained from single grain and single aliquot analysis using Monte Carlo simulations.
- development of new methodology for dating the older sample using centimeter size quartz grains.
- development of an imaging system using Electron Multiplying Charge Coupled Device (EMCCD) for studying the distribution of doses spatially on surfaces. This development enabled studying spatial distribution of luminescence as a function of temperature/time.
- estimating and quantifying the changes in sensitivity during laboratory measurements. Experiments related to sensitivity changes showed systematic source of error in observing variability in doses.

The following chapters discuss the luminescence dating technique and relevant studies done for present thesis.

Chapter-2

Luminescence Dating: Experimental Protocols and Instrumentation

2.1 Introduction

Luminescence dating using the natural ubiquitous minerals like quartz and feldspar was introduced in 1960s for dating the heated archeological ceramic and bricks (Aitken et al., 1964; Aitken et al., 1968; Mazess and Zimmerman, 1966). This technique gained popularity for establishing the authenticity of antique archeological artifacts. Fleming, (1979) discussed the methods for identifying the genuine artifacts from the fakes. With time, the luminescence

technique found applications in quaternary sediments of climatic or tectonic origin. This was based on the fact that the TL signal from quartz and feldspar can be rapidly bleached by the sunlight and hence all sediments that are exposed to day light can be dated (Wintle and Huntley, 1979). This worked well but the difficulty was the presence of unbleachable residual signal. Singhvi and initial Wagner, (1986)discuss developments and applications of thermoluminescence in dating sediments. The possibility of observing optically stimulated luminescence was a game changer as it offered several additional possibilities over and above TL. The major advantage was the fact that only optically active traps were being probed, thereby obviating the need to subtract the residual luminescence. The second advantage was that an OSL signal can be pulsed, which enables multiple read out and the prospects of cumulative dosimetry(Ankjærgaard et al., 2010b).

Some of the experimental complexities related to overlapping of stimulation and detection windows were resolved by Huntley et al., (1985) and he succeeded in dating the quartz and feldspar samples using green argon laser light (emitting at ~514 nm)stimulation and violet detection at ~400 nm (Huntley et al., 1985). Further Hütt et al., (1988) showed that the feldspar samples can also be stimulated using infrared light (IRSL) at room temperature, this discovery helped in the rapid development of dating technique. After these important initial discoveries, several other possibilities and the protocols have been devised for development of dating technique to make it more widely applicable.

2.2 Luminescence Dating

Natural radioactive nuclides (like U, Th, and K) occur in trace amounts in all sediment and other geological materials. Their decay with time provides an omnipresent natural radiation field comprising ionizing radiations like α , β and γ rays. During their passage through the mineral lattice, these ionizing radiations ionize atoms in their path and create free electron and hole pairs. A small fraction of these free electrons during their free passage get trapped in electron deficient traps. Simultaneously holes present in valence band also get trapped at

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hole traps. As the mean lives of the radionuclides is ~ Ba and hence over a Ma year time their decay is negligible ensuring a constant radiation field. The traps having long lifetime (~ 10^8 yrs; Aitken, 1985c), keep on accumulating the charges unless they reach a saturation level (or equilibrium level). When provided sufficient energy either by heat or by light trapped charges are evicted from traps and some of them recombine with holes to give the light. The color of light as already discussed is characteristic to the nature of the centre where recombination takes place. The luminescence intensity (photons/sec) is proportional to the number of trapped electrons, which in turn is proportional to dose acquired by the crystal from ionizing radiations.Thus by measuring the natural luminescence signal and the luminescence sensitivity, the dose acquired by the crystal can be estimated.



Figure 2.1:Variation of luminescence signal of a crystal in natural environment

Fig. 2.1 shows the variation of luminescence signal in natural crystal during its antiquity in soil. In nature after a crystal crystallizes from the melt and get buried, it starts acquiring luminescence signal due to ambient radioactivity present in the soil. The luminescence signal increases with time, reaches an equilibrium level and remains there till it is reset to residual level either by heat or by light exposure event. Due to this resetting, the inherent clock reset to zero or a near zero value. When the sediment reburies in the soil and shielded from further light exposure, it again starts regaining luminescence signal due to irradiation by ionizing radiations. This continuesunabatedtill excavation. The natural luminescence and hence the corresponding radiation dose is estimated

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using appropriate methodology. The radiation dose acquired by the sample is deposited at a constant rate (i.e. dose rate) which is determined by estimating the concentration of radionuclides present in the sample, their decay products, energy of ionizing particles and stopping power of the samples. Estimation of both dose (D_e) and dose rate (\dot{D}) enables estimation of time (i.e. the age) of irradiation of sample i.e.,

$$Age = \frac{D_e}{\dot{D}}$$
(2.1)

This acquired natural dose (also called palaeodose) is estimated in terms of equivalent laboratory beta dose, which produces luminescence signal similar to natural luminescence level and hence is termed as equivalent dose (D_e) . The \dot{D} is estimated after measuring the elemental concentration U, Th, K (Adamiec and Aitken, 1998) and including the contribution of cosmic rays (Prescott and Hutton, 1994). While computing the \dot{D} several factors need to be folded in, to find a correct estimate of the age of the sample.

Now in order to find the age the most important thing is correct estimation of the D_e and \dot{D} which can be done as follows,

2.2.1 Estimation of D_e

Several protocols have been devised to make reasonable estimate of the D_e taking into account the possibility of changes in sensitivity (Luminescence per unit dose per unit mass). In initial stages additive dose method like Multiple Aliquot Additive Dose (MAAD, Aitken, 1985c; Singhvi and Wagner, 1986;Lepper et al., 2003; Vandenberghe et al., 2004; Ward et al., 2003) and multiple aliquot regeneration (MAR) methods were used. Later with the possibility of OSL and pulsed stimulation, single aliquot based additive (SAAD, Duller, 1991; Duller, 1994) and regeneration (SARA, Mejdahl and Bøtter-Jensen, 1997) were developed. Later on single grain regeneration methods were developed which

helped in finding D_e from single grain of few hundred microns. MAAD techniques had the advantage of an age based on a large number of grains (10⁵), whilst the single aliquot/single grain method helps elucidate the heterogeneity in dose and in luminescence properties.

In the MAAD protocol, incremental beta doses are given in addition to natural dose and a growth curve of luminescence intensity with dose is constructed. The D_e is estimated by extrapolating the growth curve on negative x axis. Fig. 2.2 shows the D_e estimation using MAAD protocol. This method



Multiple Aliquot Additive Dose (MAAD)

Figure 2.2:Determination of D_e using multiple aliquot additive dose method (MAAD)

ensures that all the samples are measured with the same sensitivity and that an apriori knowledge of the physics and mathematics of the luminescence vs. dose exists.

The MAR methods tend to replicate the nature. Here the natural signal is read out and then the signal is regenerated, and a regenerated growth curve is constructed. The natural intensity is then interpolated on this curve to obtain a palaeodose with the proviso that no sensitivity change occurs during the regeneration process. This is rare and often a correction is needed. Protocols like the Australian slide method (Prescott et al., 1993), seek to blend the advantages of both the additive dose and regeneration dose methods. An important aspect of these methods are that these rely on a large number of replicate samples and this calls for inter aliquot normalizations. These procedures have been reviewedby Jain et al., (2003).

Some of the other methods which are used for dose evaluation includesphoto transferred thermoluminescence (PTTL, Murray, 1996), thermally transferred OSL (TTOSL, Wang et al., 2007; Pagonis et al. 2011; Adamiec et al., 2010) dating protocol, Post IR IRSL protocol (Buylaert et al., 2009). In these entire measurements, different criterion are applied to make the luminescence signal sample and/or aliquot independent by means of weight normalization, zero glow normalization, second glow normalization and short shine normalization (Aitken, 1985c). All these protocols applied to samples provide a robust estimation of doses. However nowadays single aliquot protocol (Murray and Wintle, 2000) is the most widely and routinely used protocol. Single aliquot /single grain methods are the preferred methods as these provide a means to examine various heterogeneity in the samples and permit robust age estimation with improved precision.

2.2.1.1 Single Aliquot Regeneration (SAR) Protocol

Murray and Wintle, (2000) describes the basic SAR protocol (Fig. 2.3). This protocol enables the measurement of a dose using a single aliquot, on the premise that the luminescence behavior during laboratory irradiation and in nature is similar and hence OSL response during natural and laboratory measurements can be measured and corrected for sensitivity changes. The protocols involves measurement of the natural signal and then regeneration of the growth curve with due care for sensitivity change that accrue on due to preheating and optical stimulation for readouts. The sensitivity changes during the repeated measurement cycle of irradiation, heating and OSL recording can be monitored by means of small test dose administered after each regeneration dose. The signal corresponding to natural and regeneration doses (R_i; i=N, 1, 2, 3, 4, 5....), is normalized with respect to OSL signal corresponding to this test dose (TD). In the normalization it is assumed that any sensitivity change during the measurement cycle is reflected in the TD signal and administration of smalltest dose do not alter the sensitivity of the sample; hence, both the natural or regeneration signal and TD signal are recorded at same sensitivity. This assumption has been further tested in this thesis and based on this improved

protocol has been established. The sensitivity corrected natural luminescence signal (L_N/T_N) is interpolated on the laboratory generated and sensitivity corrected (L_i/T_i) vs. dose calibration curve to obtain the equivalent beta dose (D_e) (Fig. 2.4). In SAR protocol, preheat at temperature 'T' for a fixed time is used after a regeneration dose to remove the contribution of shallow traps, which



Figure 2.3:Single aliquot regeneration (SAR) protocol as suggested by Murray and Wintle (2000)

are unstable at geological time scale (Murray and Wintle, 1999; Roberts et al., 1994; Wintle and Murray, 1999). The temperature and duration of preheat is decided by means of preheat plateau test (Murray and Wintle, 2000). In the protocol, two additional tests are done to check the accuracy of the sensitivity correction and for the thermal transfer of the charges (i.e. recuperation). If the sensitivity correction using the test dose signal is working then the order of the

regeneration dose should not matter. Thus, one of the regeneration doses is repeated and the ratio of the L_i/T_i for the two signals is computed. If this ratio is within 10% of unity, the measurement is accepted or else is rejected. In second test, one of the regeneration dose is taken as zero (i.e. no dose is given) and corresponding OSL signal is measured. The signal corresponding to zero dose is generally a small fraction of the estimated D_e . However if its contribution is accountable then a correction in dose need to be applied. So finally using a dose sequence of N, R1, R2, R3....0, R1 we can get a growth curve and estimate of D_e value.



Figure 2.4:Determination of D_e using SAR

2.2.2 Estimation of *D* and critical factors

Estimation of dose rate (\dot{D}) is based on the measurement of elemental concentrations and computation of range energy relationship for a given grain size, and mineral type (due to difference in stopping power). Fig. 2.5 shows the decay scheme and decay series of natural radionuclides. Table 2.1 lists the number of particles emitted and the average energy per particle.

Radio nuclide	Decay particles	Average energy per decay (MeV)				Average dose per decay(Gy/ka)*			
		α	β	Y	total	α	β	Y	total
238	8α, 6β and	42.7	2.28	1 78	46.76	2.685	0.143	0.112	2.94
0	Ŷ	42.7	2.20 1.70	40.70	(1.146)	(0.057)	(0.0025)	(1.206)	
²³⁵ U	7α, 4β and γ	41.1	1.27	0.67	43.04	16.6	0.515	0.269	17.384
²³² Th	6α , 4β and	35.7	1 33	2 32	30 35	0.732	0.0273	0.0476	0.8069
	Y	00.7	1.00	2.02	00.00	(0.305)	(0.0091)	(0.0178)	(0.3319)
⁴⁰ K	89% β and 11% γ		0.501	0.156	0.606		0.782	0.243	1.025

Table 2.1:The number of particles emitted, the average energy per particle and dose rate contribution for 1% K, 1ppm ²³⁸U, and 1ppm ²³²Th

Alpha particles ($_4$ He²⁺) deposit most of their energy by ionization and excitation resulting in generation of e⁻, which further deposit their energy. Being heavier in mass, alpha particles move along a straight track without deviating much from it. These particles have +2 units charge so they have very high ionization cross-section and linear energy transfer (LET). Due to this, a large number of electrons are generated along α particle track resulting in saturation of all the available traps surrounding it. The excess charges are lost and only result in heating the crystal. The saturation implies that for the energy deposited the number of trapped charges are substantially lower and hence yield lower luminescence. Thus, the efficiency of luminescence generation in case of alpha particles is low and need to be considered while computing the dose rate.

Beta particles interact with matter by ionization andby interacting with orbital electrons through coulomb interaction. Being smaller in mass, they are scattered (elastically and in-elastically) randomly by the atoms present in crystal. Thus, these particles follow a random trajectory and deposit their energy throughout the crystal volume. These particles can induce bremsstrahlung radiations due to their acceleration towards nucleus and consequent emission of electromagnetic X-rays.

Gamma rays being neutral interact with matter generally by photoelectric effect, Compton scattering or by pair production. Similar to β particle it also deposits its energy throughout the crystal.

Thus total annual dose rate comprises all the components i.e.

$$\dot{D} = a\dot{D}_{\alpha} + \dot{D}_{\beta} + \dot{D}_{\gamma} + \dot{D}_{cr}$$
(2.2)

where 'a' is thealpha efficiency of luminescence production per unit Gy of alpha dose with respect to that for beta dose (Aitken, 1985c; Zimmerman, 1971) and can be estimated by formula suggested by Aitken and Bowman, (1975) as,

$$a = \frac{D_{\beta}}{13sT_{\alpha}} \tag{2.3}$$

Here D_{β} is the equivalent beta dose, which induces same amount of luminescence signal as T_{α} minutes of alpha dose. s is the source strength in μm^{-1} ²min⁻¹. This 'a' value is important for estimating the dose rate for samples having diameter of grains lower than the range of alpha particles. Conversion of elemental concentrations to radiation dose rate is done using infinite matrix assumption. Adamiec and Aitken, (1998); Aitken, (1985b); Aitken, (1985c); Aitken Bowman, (1975); Bell. (1976) and provide the conversion factors.Complexities that arise due to range energy relations and the surrounding matrix are discussed below.

Grain size: The fact that different ionizing radiations have different ranges implies that the dose delivered by them is spatially attenuated. The range of α ~20 µm, β ~2 mm, γ ~30 cm (Fig. 2.6); so the dose rate will depend on the grain size and physical location of grains from radioactivity.In µm size grains dose is deposited by all the three ionizing radiations and Cosmic rays (CR). While for ~100µm size grain, alpha dose is limited only to the outer skin and interior receives dose only from β , γ and cosmic rays.



Figure 2.5:a) 40 K Decay scheme b), c) and d) Natural decay series of 232 Th, 238 U and 235 U respectively



►Z

<u>9</u>2

¹⁹Rn

²¹⁵At

^{∎211}Po

²⁰⁷Pb



Figure 2.6:Ranges of different ionizing radiations

To remove the complexities, the outer 20 μ m alpha skin is generally removed by an HF etch and the residual fraction is used with the assumption that it received only the beta, gamma and cosmic ray dose rate. For ~cm size grain both α and β are limited to exterior skin of 2 mm and interior has dose only because of γ and



Figure 2.7:Variation of beta dose attenuation factor as function of grain diameter computed on the basis of Mejdhal, (1979)

CR. This dose is 1/3 of the total dose for sub mm size grains and hence has important implication of extending the datable range up to 3-4 times. This work was proposed and established in this thesis. During their passage through matter, the beta and gamma rays attenuate exponentially and hence delivered dose reduces with distance.Mejdahl, (1979)calculatedattenuation factor for

different grain sizes (Fig. 2.7) and estimated the factors by which dose rate is reduced when alpha skin is etched away. The attenuation of gamma dose is also observed (Aitken, 1985b), however comparing the range of gamma and grain size, it is generally considered to be constant within a grain.

Effect of moisture: The presence of water in the void spaces affects the dose rate significantly. The water in voids does not carry any radioactivity but attenuates the radiation dose from the radioactivity in the sediment. Therefore, a correction to the dose rate estimation is made to estimate the dose rate correctly. This is calculated considering saturation water content (W) measured in laboratory and expressed as

$$W = \frac{Weight of water}{Dry weight}$$
(2.4)

W along with a factor *F* (Aitken, 1985c), which is the average soil water content as a fraction of this saturation water content (*W*) are used to calculate the correction factors. Using these two factors and the nuclear tables, the α , β and γ dose rates (Zimmerman, 1971) are corrected as

$$\dot{D}_{\alpha} = \frac{\dot{D}_{\alpha dry}}{1 + 1.5WF}$$
(2.5)

$$\dot{D}_{\beta} = \frac{D_{\beta dry}}{1 + 1.25WF} \tag{2.6}$$

$$\dot{D}_{\gamma} = \frac{D_{\gamma \, dry}}{1 + 1.14W_1 F} \tag{2.7}$$

Here W refers to sample and W_1 to soil.

Disequilibrium in the radioactive decay series:While estimating the dose rate, it is generally considered that the radioactive series are in secular equilibrium throughout the burial, which means that all the members of the series have same

activity. However, a series can be in disequilibrium if any of the members of radioactive series is lost or added. One such possibility is the escape of radioactive isotopes of Radon (Rn), resulting in absence of members following the Rn in the series. As Rn is gaseous, it can escape out of the system. In addition, there could be disequilibrium due to the leaching of members by moving water etc. In order to estimate the dose rate correctly quantification of the disequilibrium is necessary (Adamiec and Aitken, 1998; Olley et al., 1996).

Aforementioned discussion enables a reasonably robust estimation of dose rate and this coupled to the palaeodose D_e provides the age.

2.3 Sample Preparation

Sediment sample collected and stored in dark light tight metal pipes (Chandel et al., 2006) are opened under subdued red light conditions. The top and bottom ~3 cm layer of the pipe, which may be accidently exposed to light during sample collection, is used for radioactivity analysis and the interior is used for luminescence measurements.

Soon after the collection, the water content of sample as received and the saturation water content is measured. The dried samples are weighed and used for radioactivity measurements using thick source alpha counting, γ ray spectrometry or high resolution γ ray spectrometry (to assess the activity of individual members of the decay chain). For the estimation of disequilibrium condition of series the samples are sealed in airtight sample holders for 2 weeks and then long chain gamma counting using HPGe counting is done for decay series.

The second part of sample is treated with 1N HCl followed by $30\% H_2O_2$ to remove the carbonates and organic material respectively. The sediment is then sieved in different grain fractions. Moreover, as far as possible the medium grain size is used for the estimation of the palaeodose.Considering dosimetric aspects, the preferred methods are thin 4-11 µm grains for fine silt sediments and the 90-150 or 180-210 µm grain size for coarser sandy sediments.

Coarse grain technique:This technique was first given by Ichikawa, (1965), but later developed by Fleming, (1979). In this the course grain fraction of sediment obtained after HCI and H_2O_2 is sieved in range 90-150µm and then quartz and feldspar fractions are separated by using Sodium polytungstate (Na₆O₃₉W₁₂.H₂O) solution of density 2.58 g/cc. The method exploits the density difference between quartz (2.65 g/cc) and feldspar (2.54 g/cc). The densityseparated fractions are etched with 40% HF for 80 min followed by reaction with 12N HCl (to remove fluorides) for 30 min to remove the outer α -dosed skin of 20 µm and dissolve feldspars. The purity of quartz is checked by IR stimulation. The samples are mounted on stainless steel discs with the help of non-luminescent silicon oil and analyzed to find out D_e.

In case of feldspar, fraction separated using sodium polytungstate is either etched with 10% HF for 40 min to remove α skin or used as such and a correction for α skin is applied.D_e estimation is made using the standard protocols either using TL or IRSL. During analysis the dose value from feldspar are corrected for anomalous fading using formalism given by Huntley and Lamothe, (2001); Kars et al., (2008).

Fine grain technique:In this grains of size 4-11 μ m are used for analysis (Zimmerman, 1971). The fine grain sample (basically polymineral grains) extracted after HCl and H₂O₂ treatment is de-flocculated in 0.01N sodium oxalate with multiple use of ultrasonic bath for desegregation. Then stokes column settling method is adopted for the separation of 4-11 μ m fraction with stokes settling times of 2 and 15 min. Finally, this 4-11 μ m grains are mounted on the Aluminium disc by re-suspending the grains in alcohol and putting ~1 ml of this volume with equal volume of alcohol in 1 mm glass vial having Aluminium disc at the bottom. Finally, the sample is dried at 45°C in the oven. After drying, discs are used for the analysis. In this technique as the grain sizes are smaller than α range, so alpha contribution in Eq.2.2 is taken in to account by measuring the alpha efficiency using the vacuum alpha irradiator.

2.4 Luminescence Dating:Instrumentation

The main elements involved in luminescence dating instrumentation are,

- 1. Stimulation system
- 2. Light detection system
- 3. Irradiation source
- 4. Particle detection and counting system

Following section details these elements.

2.4.1 Stimulation System

Sample stimulation is done either by heat or by light, or both. In both the cases feedback control electronics is used.

2.4.1.1 Heating System

Heating system consists of a heating plate made up of Kanthal (an alloy of iron chromium and aluminium) or of Nichrome (alloy of chromium and nickel) which is used for resistive heating. Heating system is generally capable to heating the sample up to 700°C at heating rates ranging from 0.2-10°C. The variable heating rates provides flexibility in controlling the luminescence output and optimizes retrieval of desired information. The temperature of heating system is monitored by using a thermocouple made up of Chromel-Alumel. For a good heating system the temperature profile should be reproducible to better than1%. This is achieved by feeding the output of thermocouple to an error amplifier that provides an output proportional to the difference and this drives the power transistors to compensate the current to the heating element. In general heating is done at linear heating rate. The other preferred option is holding the sample for a preset time at a given temperature. Temperature accuracies of $\pm 1^{\circ}$ C is generally desirable for measurements.

2.4.1.2 Light Stimulation System

In general, it is found that shorter the wavelength of light more is its photoionization cross-section. Hence, shorter wavelengths are efficient in stimulating the sample and are generally used for stimulation. The choice of stimulation light is governed by the emission of the sample. In general high intensity blue LEDs (~470 nm) and Nd:YAG (532 nm) green laser light are used for stimulation of Quartz and IR LEDs emitting at either of 880 nm or 930 nm are used for feldspars. There can be several stimulation modes like,

- i) Continuous wave stimulation where the light intensity is constant during measurement (CWOSL, Fig. 2.8a),
- Linear modulation in which stimulation intensity increases linearly with time (LMOSL, Fig. 2.8b) helps visual identification of different components of OSL having different photo ionization crossections.
- iii) Pulsed stimulation where the stimulation is pulsed and offers possibilities of measuring during the off time thereby increasing the spectral window (POSL, Fig 2.8c).

2.4.2 Light Detection System

Light detection system in general consists of a photo multiplier tube (PMT) along with a suitable combination of detection filters. In luminescence dating a bialkali PMT (EMI 9235QB) that has a spectral response in the near visible UV to red is used. Fig. 2.9 shows the quantum efficiency curve of the PMT. The PMT is generally used in photon-counting mode to provide improved signal to noise ratio and additional improvement is achieved by cooling the PMT if needed. Typical S/N ratios are 10 or more for quartz and 100 or more for feldspars.Discrimination against stimulation light entering the PMT is achieved by means of optical filters, which are mostly color glass, and occasionally interference filters. Following are the combination of the filters used for the luminescence measurements from quartz and feldspar,

1. Combination of Schott BG-39 and Hoya U-340 is used to detect the UV emission from quartz when stimulated with blue light



Figure 2.8:a) Continuous wave stimulation and corresponding CWOSL signal, b) Linearly modulated stimulation and corresponding LMOSL signal, c) Pulsed stimulation and its corresponding POSL signal. In this pulsed stimulation is applied for 1s, and pulse width (generally of ~ms to ~ns) is shown exaggerated.

- Combination of Schott BG-39 and Corning CS 7-59 is used to detect the blue emission from feldspar when stimulated with IR light
- 3. If the Intensity of luminescence light isvery high then some times, quartz neutral density filters (ND filters) are used to reduce the light level

Fig. 2.10 shows the transmission of filters along with the stimulation light range and emitted wavelength range for quartz and feldspar.



Figure 2.9:Response of Bialkali type EMI 9235QB photo multiplier tube.

2.4.3 Irradiation Source

The two commonly used source used for luminescence dating are radioactive isotopes ⁹⁰Sr for β irradiation and ²⁴¹Am for α irradiation. Fig. 2.11 shows the decay scheme of both these isotopes.

⁹⁰Sr decays to ⁹⁰Y by emitting a β particle with maximum energy of 0.546 MeV with an half life of 28.8 yr, which further decays to ⁹⁰Zr by emitting a β with maximum energy 2.27 MeV and a half life of 64 hrs (Fig. 2.11). The long life ofthis source enables it to be used for longer time and useful for laboratory purpose. In commercially available sources, either a thick layer of ⁹⁰Sr is deposited on 1 mm thick silver plate and from front is covered with a protective covering of 0.1 mm silver or alternatively, the activity is embedded in a glass matrix to ensure safety in long-term usage.

 241 Am alpha source emits 5.48 MeV alpha particles with a half-life of 432.6 years (Fig. 2.11). This isotope is commercially available in form of 1 µm thick layer backed with 200 µm silver foil and front face protected by 2 µm thick gold-palladium alloy protective covering.



Figure 2.10:Stimulation lights and Transmission curve of different types of filters used for a) Quartz and b) Feldspar

2.4.4 Particle Detection and Counting System

Particle counting systems are used to find the concentration of radioactive nuclides by computing the counting rate and thus the decay rate of different radionuclides. These are basically scintillation counters in which ionizing radiations are detected and then counted using counting unit. Generally thick



Figure 2.11:Decay scheme of ⁹⁰Sr and ²⁴¹Am Source

source α pair counting technique (appendix J, Aitken, 1985c) is used to estimate the concentration of natural ²³⁸U and ²³²Th. Inthis aZnS(Ag) screen, having thin coating of ZnS(Ag) deposited on top of transparent tape is used as a scintillator. This is placed on top of PMT, which is followed by counting system. The counting system has additional units to count and estimate the concentration of ²³⁸U and ²³²Th activity by using fast and slow pair counting units respectively. Similar to α counting, γ counting is used to find out the concentration of K in sediments using NaI(TI) as scintillator. In this the gamma ray photons emitted by sediment is compared with a known standard and concentration is found by comparing the count rate of two.

In addition to this, several other instruments can be used to find the concentration of radionuclides like, High purity Germanium detector (HPGe), Silicon Surface Barrier (SSB) detector, ICPMS etc.

2.5 Luminescence Dating: Instruments

2.5.1 Risø TL/OSL Reader (Model DA-20)

Risø TL/OSL reader is an automated commercial system used for TL/OSL measurements and designed mainly for dating geological sample (Bøtter-Jensen

et al., 2003). It consists of a basic hardware unit and a controller unit designed to control the action of system. In this system, there is provision of using 48 single aliquot or single grain discs. Heating system comprises a heating strip made up of low mass Kanthal, specifically machined with a slot to hold a sample disc of 9.65 mm diameter. It can heat the sample up to 700°C at a heating rate varying from 0.1 to 10°C/s. The continuous flow of nitrogen helps in maintaining the nonoxidizing environment and cooling the heating plate. It consist of a optical stimulation unit consisting of 28 blue LEDs (in a cluster of 4) emitting at 470±20 nm and delivering a power of 50 mW/cm²at sample position. It also has 21 IR LEDs (in cluster of 3) emitting at 870±40 nm delivering a power of 145 mW/cm²(Bøtter-Jensen et al., 2003). Fig. 2.12 shows the basic stimulation unit and block diagram of acquisition unit of the TL/OSL reader. Bray et al., (2002) and Bøtter-Jensen, (2000) have estimated the optical crosstalk to be about 0.014% and 0.006% respectively. The detection assembly consists of EMI 9235QB PMT having sample to PMT distance of about 55 mm and making a solid angle of about 0.4 steradians and a filter mounting assembly, which can hold different combination of filters. In this arrangements filter can be easily replaced to observe luminescence in different detection wavelength ranges. TL/OSL reader is also equipped with 90 Sr β source (Fig. 2.13). Irradiation source is placed in rotating stainless steel wheel, which is pneumatically controlled. The entire arrangement is enclosed in a lead shield. A thin beryllium window (0.125 µm) separates source from the measurement chamber. The instrument is provided with a graphical user interface (GUI) to set the protocols to be followed and providing the instruction to controller unit to carry out measurements. Another analysis GUI software is used to analyze the data acquired during the measurements.

2.5.2 Daybreak TL/OSL Reader

This is also automated commercially available system used to do TL/OSL measurement and specifically designed for dating the natural samples (Bortolot, 2000). It can hold and sequentially measure 60 single aliquot discs, one at a time. Its stimulation unit consists of a heating assembly and optical stimulation

unit. Heating element is made up of Nichrome plate and can heat up to 500°C at variable heating rates. Heating is generally controlled by two temperaturevery controlled stages enabling precise temperature control using thermoelectrically (TEM) stages. A Chromel-Alumel thermocouple welded beneath the heater plate is used to monitor the temperature. Optical system consists of 20 high intensity green LEDs emitting at 515±40 nm and delivering a power of about 30 mW/cm² at sample position.IR stimulating system consist of 10 diodes emitting at 880 nm fitted with RG830 glass filters to suppress the high wavelength light detectable by the PMT. It delivers a power of 50mW/cm² at sample position. Detection unit contains a bialkali PMT along with a filter assembly. Filters can be readily changed to make measurement in different detection windows. It has a very compact ⁹⁰Sr based beta irradiator with provision to irradiate at elevated temperature. A GUI based software is used to control the tasks performed by the system and a FORTRAN based program is written to give a set of instruction and make measurements in the system. An analysis software is used to analyze the data acquired.

2.5.3 Alpha Counters

These are basically scintillation counters used to estimate the concentration of U and Th, by means of thick source alpha pair counting technique (Appendix J, Aitken, 1985c). In this technique, alpha particles emitted by U and Th series are counted to find the counting rate. The distinction between the two is generally made based on the pairs of ²²⁰Ra and ²¹⁶Po, which are members of Th decay chain and emit alphas subsequently within a time interval of 0.21s. This pair is thus used to determine the activity of the Th series, which can thus be used to find the activity and hence the concentration of U series from the total count rate. In this counter 42 mm diameter ZnS(Ag) screen is used as a scintillator, which is in direct contact with finely powdered sediment. The scintillations produced are detected by a PMT, signal is amplified and counted. In these counters, a threshold discriminator setting is applied such that at threshold position, the count rate is 0.82 times the count rate for U series at 0 V threshold. Similar value corresponding to Th should be 0.85.



Figure 2.12:Stimulation and acquisition unit of Basic TL/OSL reader



Figure 2.13:⁹⁰Sr β source arrangement used in Risoe TL/OSL reader

2.5.4 Gamma Counters

These are generally used to estimate the concentration of K (%), by comparing the sediment sample against a known concentration standard. The counter used could be scintillation counter (Like Nal (TI) based scintillation counter) or High Purity Germanium (HPGe) detector. In this HPGe counter can also be used to estimate the concentration of U and Th along with the K. These are also used to find out the series equilibrium condition by measuring the activity of several isotopes of decay series



Risoe TL/OSL Reader







Daybreak Alpha counter

Chapter-3: Dose Distribution in Sediments

Chapter-3

Dose Distribution in Sediments

3.1 Introduction

Sediments are a mixture of different types of minerals produced from rocks by different processes depending upon environmental conditions. Rocks exposed on the surface of earth are subjected to mechanical disintegration and chemical weathering. Agents of wind and water (like rivers, ocean current, glaciers, landslides etc.) continuously erode, transport and deposit the eroded material at different locations. Even the hard minerals are weathered by continuous action of air and water. The minerals like quartz and orthoclase feldspar break into smaller sizes during the process of mechanical weathering and transportation. The resultant mechanically broken or chemically weathered collective material is termed as sediments. Sediments are transported by wind and water and get deposited at different places. As harder minerals are more resistant to breaking during transportation, they form the majority of the constituents of the sediments. During transportation, broken fragments undergo several changes like size reduction, rounding and sorting. In addition, they are exposed to light and occasionally even new mineral formation takes occurs. Either of these events leads to resetting of the luminescence signal. After the burial of the sample under the sediment load, it is shielded from the light exposure leading to a subsequent buildup of luminescence signal due to continued irradiation from the ambient radioactivity present in surroundings and the cosmic rays. As shown by equation, (2.2), chapter 2, most of the dose is deposited by ionizing radiations namely, α , β and γ radiations. The ranges of ionizing radiations in the sediment matrix vary over several orders of magnitude. Alpha particles have a range of about 20 µm, while beta rayshave a range of about 2-3 mm andy rays have a range of about 30 cm in the sediment matrix (Aitken, 1985c, Fig 2.6). In sediments, the grains sizes are variable and can range from < 1µm to several centimeters. Owing to their different ranges, different ionizing radiations deposit different doses in grains of different sizes. Fig. 3.1 shows the doses deposited in different size grains considering a 1 ppm U, 1 ppm Th and 1% K and cosmic rays (CR)(Adamiec and Aitken, 1998; Prescott and Hutton, 1994). It can be seen that the dose in the interior of fine grains (4-11 μ m) is deposited by all the radiation while for a 100 μ m size grain contribution in the interior mainly comes from β , γ and CR, and α is limited to outer skin. For still larger size ~1 cm dose in the interior is because of y and CR, while other two are limited by their range. Thus the variation of ranges coupled with the distribution in grain sizes results in distribution in doses at single grain level. The quantification of this dose distribution is important in order to make reliable age estimates and is the subject matter of investigation in the present thesis. More specifically the following aspects were examined in detail,



Figure 3.1:Doses deposited in different size grains considering a 1 ppm U, 1 ppm Th and 1% K and cosmic rays (CR)

- dose distribution for sub-millimeter (~200 μm) size single grains and single aliquots formed by ~100 such single grains, and
- 2) dose distribution inside cm size grains

This analysis, suggested improvement in the existing methodologies for the dating of sediments and proposes a new methodology to date the cm size quartz grains that would lead to extension of the dating range for coarser grained sediments.

3.2 Dose Distribution: Sub-Millimeter Size Grains

Ideally, the grains from same sediment stratum in a similar radioactive environment should give identical D_e values and the dose distribution should be a delta ($\delta(\overline{D})$) function peaked at D_e . However, considerable scatter was observed in doses obtained from single grains of natural quartz or feldspar (Fig. 3.2).Several different possible pre-depositional and post-depositional scenarios have been considered to explainthese variations (Arnold and Roberts, 2009; Bateman et al., 2003; Bateman et al., 2010; Duller et al., 2000; Duller and Bøtter-Jensen, 1997; Murray and Roberts, 1997; Nathan et al., 2003; Olley et al., 1998; Olley et al., 1999; Roberts et al., 2000; Thomas et al., 2005; Vandenberghe et al., 2003). These include, heterogeneous bleaching of the grains before burial, sensitivity changes during measurement protocols, uncertainties in instrumental measurements, mixing of the grains from different provenances or bio-turbation. But the observation that even carefully selected samples from desert region where total predepositional bleaching is expected, the D_e depicts scatter in the dose values, indicating the presence of other sources of variability besides the aforementioned factors.



Figure 3.2:Dose distribution observed in natural well bleached sample (Desert sample)

One possible cause that was identified by Mayya et al., (2006) and Morthekai, (2007) was the spatial fluctuation of β emitters in the sediment matrix (Fig. 3.3).



Figure 3.3:Random distribution of quartz (white circles) and feldspar (black circles) grains in the sediment matrix resulting in heterogeneous dose deposition (Mayya et al., 2006).

Most of the β dose is contributed by a few K-feldspar grains with up to 14% stochiometric K, distributed randomly in the sediments matrix. As the range of

βparticle is comparable to inter grain distance, so a feldspar grain near to quartz (or feldspar) grain will deposit more dose as compared to the feldspar grain situated at a larger distance.Different quartz grains have different configuration of the feldspar grains around them suggesting different dose deposition. Thus, these fluctuations in inter-grain distances can result in distribution in the doses estimated from single grains of quartz and analogously for feldspar.



Figure 3.4:Dose distribution function obtained by Mayya et al. (2006)

Nathan et al., (2003) used MCNP-4C Monte Carlo electron/photon transport models to estimate the dose distribution in single grains measurements. His results though deviated from the experimental data showed that such fluctuations can result in significant distribution in dose values and can lead to erroneous estimation of palaeodoses.Mayya et al., (2006)presented a mathematical model that considered the dose deposited by beta and gamma radiations from U, Th and secondary particles of cosmic rays as being spatially uniform, and the beta dose from randomly distributed ⁴⁰K carrying feldspar mineral grains (hotspots) being non-uniform. The heterogeneity in beta dose deposition was computed by examining the dose distribution in quartz originating due to fluctuations in the K-feldspar (hotspots) position. In this work a positively skewed dose distribution (Fig. 3.4) was obtained and based on this, a modified age equation was proposed. However, in the development of theory, several simplifying assumptions were made which were not valid sensu-stricto and could imply second order correction in the real world. These are:

- Approximations of specific energy loss (dE/dr) of beta particles by its mean value (E/R) where R is the range of beta particle in quartz and E is it's kinetic energy, and
- Neglecting the dependence of dose distribution on the packing density (porosity) of sediment matrix.

Improvement based on relaxing these assumptions are attempted to realize the full potential of the suggestions by Mayya et al., (2006). This will render the theory more rigorous and more widely applicable. Also, a small computational error in the work of Mayya et al., (2006) in the numerical evaluation of the integrals involving range distribution function needs to be rectified. Thus, in the present thesis improvement over aforementioned assumptions wasattempted using both the Monte Carlo based particle transport code and an analytical approach.

3.2.1 Monte Carlo Simulations

As mentioned before, Mayya et al., (2006) assumed dE/dr ~ E/R to estimate the dose deposited by a beta source averaged over the entire β energy spectrum. However, this assumption is an approximation as, during the slowdown of β particle, the mass-collision-stopping power (MeV-cm²/gm) increases, resulting in more energy deposition and the E/R assumption gets modified. To quantify the energy deposition by the β particle as a function of distance, Monte Carlo techniques were used. Monte Carlo methods are considered to be accurate as they mimic the transport of the radiation in matter using random sampling techniques. In this, the sampling of the initial parameters and the processes involved is done on the basis of statistical approaches, thus providing a closer approximation to nature. In our present work Monte-Carlo based EDKnrc user-code (Rogers et al., 2005) of EGSnrc code system (Kawrakow and Rogers, 2000) was used for calculating the beta dose distributions. This code utilizes Class-II condensed history Monte-Carlo techniques. The cross section dataset needed for the Monte-Carlo simulations was generated using PEGS4 program. The simulations were carried out to calculate the dose absorbed by a quartz grain at different radial distances for a

point source of ⁴⁰K. The Monte-Carlo simulations utilized the PRESTA-II electron-step-length algorithm and EXACT boundary-crossing algorithm (Kawrakow and Rogers, 2000). ESTEP, the parameter which defines maximum fractional continuous energy loss per step, was set to a default value of 0.25. In the simulations; the low energy threshold for electron transport was set to ECUT=521 keV (i.e. 10 keV kinetic energy) and the photon transport cut-off parameter set to PCUT=1 keV. For the present work a geometry having, point ⁴⁰K source (Fig. 3.5) at origin surrounded by concentric spherical shells of thickness 10 μ m was used. The spherical shells were made up of Quartz (SiO₂) of density 2.65 gm/cm³The beta energy spectrum of ⁴⁰K was taken from Kelly et al., (1959). The modules for estimating the energy deposited in different regions were used. $\left\langle \frac{dE}{dr} \right\rangle$ (*r*) was calculated for different energies of electron viz., 1.35, 1.25, 1.15, 1.05, 0.95, 0.85, 0.75, 0.65 MeV and was compared with the assumption $\left(\frac{dE}{dr} \sim \frac{E}{R}\right)$. Fig. 3.6 shows one such comparison for 1.35 MeV and it is clear that it has a shape different from a step function. Similar trends were observed for lower energies.



Figure 3.5:The geometry used for the simulations. In this ⁴⁰K source at the center is surrounded by concentric spherical shells of quartz.

For sediment samples, simulations were carried out for the complete energy spectrum of 40 K.The Energy spectrum for 40 K was considered as a histogram

with ~ 66 KeV energy resolution. The probability distribution curve was generated by digitizing the data of 40 K spectrum from the Kelly et al., (1959).



Figure 3.6: The energy deposition function dE/dr as estimated by the Monte Carlo simulations compared with the function used by Mayya et. al. (2006)

Using this, averaged specific energy loss, viz., $\left\langle \frac{dE}{dr} \right\rangle(\xi)$ was computed as a function of normalized distance. The normalization was w.r.t. the maximum range of ⁴⁰K beta particles. The variations for $R_m \times dE/dr(MeV)$ obtained by the simulations and the earlier method (Mayya et al., 2006) was compared (Fig. 3.7). This unit is used in order to compare the similar terms on y axis. It shows that, at greater distances, the dose contribution by the K⁴⁰ hotspots is larger than that estimated by Mayya et al., (2006) i.e. quartz grains at larger distances receive somewhat higher doses. Fig. 3.8 shows the variation of energy deposited per unit volume ($EPV = dose \times density$) as a function of scaled distance on a logarithmic scale. In logarithmic scale, both functions have almost similar shape, however, there is a significant disagreement when scaled distance (ξ) ~0.3 which reduces near ξ ~1. In our calculations, the $\left\langle \frac{dE}{dr} \right\rangle(\xi)$ calculated using Monte Carlo simulation is used to find the dose distribution function, as discussed below.



Figure 3.7: The comparison of energy deposition function for the ⁴⁰K source obtained by Monte Carlo simulations with the Mayya et al. (2006). In this y axis is normalized in order to compare similar quantities on both sides



Figure 3.8:Variation of Energy deposited per unit volume (EPV) in different concentric shells of quartz by point source of ⁴⁰K. The comparison with earlier work shows significant difference when scaled distance is ~0.3.

3.2.2 Dose Distribution in Single Grains: Improvement in $\frac{dE}{dr}$

Fig. 3.3 shows a typical of arrangement in the sediment matrix. Here r_i is the distance of a quartz grain from ith feldspar grain. ρ_s is the density of the

sediment matrix. Now,the energy deposited by a β particle at a radial distance r_i from ⁴⁰K point source having range between *R* and *R* + *dR* is given by:

$$dE_i = P(R)dR \times \left(\frac{dE}{dr}\right)_{r=r_i} dr \times \frac{dA}{4\pi r_i^2}$$
(3.1)

Here p(R)dR is the range spectrum of ⁴⁰K β particles, dr is thickness of grain at r and dA is the cross-sectional area of the grain. Energy deposited by the complete ⁴⁰K spectrum having continuous energy, varying from 0 to 1.35 MeV is

$$E_{i} = \int dE_{i} = \int_{r_{i}}^{R_{m}} P(R) dR \times \left(\frac{dE}{dr}\right)_{r=r_{i}} dr \times \frac{dA}{4\pi r_{i}^{2}}$$
(3.2)

So the dose deposited in the grain is given by dividing the above equation by $\frac{1}{\rho_s dAdr}$ which is the mass of the volume element dAdr. So the equation modifies to

$$D_i = \frac{1}{4\pi\rho_s r_i^2} \int_{r_i}^{R_m} P(R) dR \times \left(\frac{dE}{dr}\right)_{r=r_i}$$
(3.3)

The term inside the integral represent $\frac{dE}{dr}$ averaged over complete β range spectrum at a distance $r = r_i$

$$D_i = \frac{1}{4\pi\rho_s r_i^2} \left\langle \frac{dE}{dr} \right\rangle_{r=r_i} \qquad (r_i < r < R_m) \tag{3.4}$$

It is more convenient to express the above equation in terms of the following dimensionless variables,

$$x = \frac{R}{R_m}, \quad y(x) = \frac{E}{E_m}, \quad \xi_i = \frac{r_i}{R_m}$$
 (3.5)

Eq.(3.4) can now be re-expressed as

$$D_{i} = \frac{1}{4\pi\rho_{s}} \frac{1}{R_{m}^{2}} \left[\frac{1}{\xi_{i}^{2}} \left\langle \frac{dE}{dr} \right\rangle_{\xi = \xi_{i}} \right] \qquad (\xi_{i} < \xi < 1)$$
(3.6)

where $\left\langle \frac{dE}{dr} \right\rangle_{\xi=\xi_i}$ denotes the energy deposition by a ⁴⁰K-feldspar hotspot, at a

distance ξ_i hence it can be written as a function of $\xi_i \left(i.e. \left\langle \frac{dE}{dr} \right\rangle (\xi_i) \right)$. This is the quantity which is calculated using Monte Carlo simulation based particle transport codes. In the work by Mayya et al., (2006), $\frac{dE}{dr}$ for a mono-energetic beta particles was approximated by $\frac{E}{R}$, and as already seen in Fig. 3.7, this approximation can affect the results significantly. Eq. (3.6) can be further written as

$$D_i = D_c g\left(\xi_i\right) \qquad \left(\xi_i < \xi < 1\right) \tag{3.7}$$

Where, D_c is the characteristic dose defined as

$$D_c = \frac{E_m}{4\pi R_m^3 \rho_s} \tag{3.8}$$

and $g(\xi)$ is the dose-distance relationship function

$$g\left(\xi_{i}\right) = \frac{1}{\xi_{i}^{2}} \left[\frac{R_{m}}{E_{m}} \left\langle \frac{dE}{dr} \right\rangle \left(\xi_{i}\right)\right] \qquad \left(\xi_{i} < \xi < 1\right)$$
(3.9)

Where, $\left\langle \frac{dE}{dr} \right\rangle (\xi_i)$ is the energy deposition obtained by Monte Carlo simulation based particle transport codes.Finally, dose to a given grain due to all the hotspot can be obtained by summing over all the K-feldspar sources as,

$$D = D_c \sum_{i=1}^{N} g\left(\xi_i\right) \tag{3.10}$$

All the grains having the same configuration of feldspar grains around it will receive the same dose, or alternatively the dose distribution function $\phi(D)$ will be δ function as presented below:

$$\phi(D) = \delta\left(D - D_c \sum_{i=1}^{N} g(\xi_i)\right)$$
(3.11)

In following, we followed the procedure outlined by Mayya et al. (2006) for obtaining the dose distribution function for different possible feldspar configurations: by using Monte-Carlo generated function for $g(\xi_i)$. As mentioned, Eq. 3.10 and 3.11 give the dose deposited and the corresponding distribution in a single grain from a fixed and randomly distributed feldspar grains.

However as infinite number of such possible configurations exist; the actual distribution is weighted to sum over all these configurations taking into account their probability of occurrence. Thus the above equation modifies to

$$\phi(D) = \int_{0}^{\xi_{\infty}} \dots \int_{0}^{\xi_{\infty}} P(\xi_{1}, \xi_{2}, \dots, \xi_{N}) d\xi_{1} d\xi_{2} \dots d\xi_{N} \times \delta\left(D - D_{c} \sum_{i=1}^{N} g(\xi_{i})\right)$$
(3.12)

Where $P(\xi_1, \xi_2, ..., \xi_N)$ is joint probability of occurrence of configuration in which K-feldspar hotspots are at distances $\xi_1, \xi_2, ..., \xi_N$ from a given grain. Considering the concentration of the K to be low, the probability of occurrence of individual feldspar grains will be independent of each other and hence the corresponding joint probability density decomposes into a product of individual probability densities. We further assume that the individual probability of occurrence is uniformly distributed in space; i.e. their probability of occurrence in a small volume element in space is proportional to the ratio of the volume of the element
and the accessible volume covered by the maximum beta particle range. In a dimensionless notation, it is

$$P(\xi_i)d\xi_i = \frac{4\pi\xi_i^2 d\xi_i}{4\pi\xi_{\infty}^3/3} = \frac{3\xi_i^2}{\xi_{\infty}^3}d\xi_i$$
(3.13)

With these, Eq. 3.12 is modified to

$$\phi(D) = \int_{0}^{\xi_{\infty}} \frac{3\xi_{1}^{2}}{\xi_{\infty}^{3}} d\xi_{1} \dots \int_{0}^{\xi_{\infty}} \frac{3\xi_{N}^{2}}{\xi_{\infty}^{3}} d\xi_{N} \times \delta\left(D - D_{c} \sum_{i=1}^{N} g(\xi_{i})\right)$$
(3.14)

In order to reduce the above N-fold integral further, Mayya et al., (2006) proposed the use of Laplace transformation technique based on the premise that dose being a positive quantity its distribution should be zero for negative D. This is a principal requirement for the applicability of Laplace transformation. The Laplace transformation from $D \rightarrow s$ decomposes the N-fold integral to the Nth power of a single integral. Finally, it follows that if we express the dose distribution function in terms of the scaled dose units as $\phi(D/\overline{D})$ its Laplace transform $\phi^*(s)$ satisfies the following equation:

$$\phi^{*}(s) = e^{\mu [f(s)-1]}$$
(3.15)

where, μ is the mean number of hotspots ($\mu = 892 \times k$, where *k* is K %) within the maximum range, R_m and the function f(s) is related to the dose-distance function $g(\xi)$ through the relationship

$$f(s) = 3\int_{0}^{1} \xi^{2} e^{-sg(\xi)} d\xi$$
 (3.16)

In order to find out the final dose distribution, the Laplace inversion $(s \rightarrow D)$ of the function on the RHS of equation, (3.15) is carried out. In present study numerical inversion programme developed by Mayya et al., (2006) was used.

The crucial function f(s) defined in equation, (3.16) is evaluated using function $g(\xi)$ (equation, 3.9) which is computed using the values of $\left\langle \frac{dE}{dr} \right\rangle(\xi_i)$ obtained from Monte Carlo simulation of electron/photon transport. For evaluating the integral, the $\left\langle \frac{dE}{dr} \right\rangle(\xi_i)$ values were fitted to a polynomial function given below.

$$p(r) = 5.21765 + 7.34693r - 28.05728r^2 - 76.6174r^3 + 244.60605r^4 - 214.6201r^5 + 62.10964r^6$$
(3.17)



Figure 3.9:The dose distribution function $\phi \left(\frac{D}{D} \right)$ obtained using Monte Carlo simulations for different concentrations of the K. There is systematic shift of the distribution function towards higher dose side as compared to Mayya et al. 2006

The Laplace inversion of $\phi^*(s)$ yields the required dose distribution $\phi(D/\overline{D})$ for different concentrations of K (Fig. 3.9). Fig 3.9 also shows comparison of the obtained dose distribution function with that from Mayya et al., (2006). The present results show a shift in peak towards higher doses by about 25%, 18%

and 13% for K concentration of 0.3%, 1% and 3% respectively, when compared to the Mayya et al., (2006)results. This is due to greater energy deposition at larger distances (Fig. 3.7) as compared to the estimates based on mean energy approach (Fig. 3.9). As the number of feldspar grains at larger distances is comparatively larger (due to larger volume) than the proximal ones (whose contribution is estimated to be smaller than mean energy approach), so on the whole, a higher dose is deposited in the quartz grains. The shift in dose distribution function towards higher dose increases the minimum dose rate and hence, decreases the age.

3.2.3 Effect of the Porosity and Water Content

The dose distribution so far was calculated by assuming a homogeneous, quartz equivalent medium in which the hotspots are distributed randomly. However, in reality, porosity and moisture content also affect the dose deposition. In order to realize the natural conditions, the effect of porosity and water content in soil was investigated. A porosity of 15% and 30% was incorporated in the Monte Carlo simulations by using a geometry having alternate spherical shell of quartz and air (Fig. 3.10). The thickness of air shell is considered such that the volume of porous shell is porosity times the volume of inner quartz shell. Simulations were also carried out to find the dose distribution while all the voids are filled with



Figure 3.10: The geometry used in simulation to incorporate the effect porosity and study the effect of water content on dose distribution function.

water. The dosedeposition functions for these calculations are shown in Fig 3.11a,b,c.The effective range of the β particle is higher for higher porosity and lower for higher moisture content for a given porosity.



Figure 3.11:Dose distribution function $\phi\left(\frac{D}{\overline{D}}\right)$ computed for sediment matrix having 30% porosity for different concentrations of K.

The dose distribution function for porous sediment matrix (as indicated by *'Porous (air in pores)'*)graph, (ϕ (*Scaled dose*) vs *Scaled dose* plot; Fig. 3.11a,b,c) shifts towards higher dose as compared to solid quartz. Dose distribution function when the pore spaces are filled with water *'Porous (water in pores)'*(

 ϕ (*Scaled dose*) vs *Scaled dose* plot; Fig. 3.11a,b,c); lies in between these two extremes, but is almost overlapping with the solid quartz distribution graph. Further, the relative shift decreases as concentration of potassium increases. The shift in the dose distribution function is due to the increase in the range of β particles in porous and moist sediments relative to solid quartz. As the effective volume (within the R_{max}) contributing to beta dose increases the average dose deposited in a particular grain increases. The increase in the deposited dose shifts the dose distribution function to higher side. As the potassium content increases, the relative shift decreases due to decrease in inhomogeneity with increase in concentration.

3.2.4 Implications: Single Grain Dose Distribution

Fig. 3.9 shows a shift in the dose distribution function towards higher dose side with the use of the more realistic function for dE/dr obtained using Monte Carlo simulations. This improvement suggests an increase in the minimum-scaled dose (δ). The ages thus calculated by the relation proposed by Mayya et al., (2006)

$$T = \frac{D_{\min}}{\left[f + \delta(1 - f)\right]\overline{\dot{D}}}$$
(3.18)

is lower as compared to the results suggested earlier. In this expression D_{\min} is the minimum D_e of experimentally observed values, f is the fraction of uniform dose, δ is the value of the minimum-scaled dose extracted from the dose distribution functions (Fig.3.9) and $\overline{\dot{D}}$ is the average dose rate to the soil. The change in δ values arising from the modification of energy deposition function is shown in Fig. 3.9d for different K concentrations. Thus, the shift in distribution function can be attributed to increase in contribution from the sources at higher distances.With an increase in concentration of potassium, δ values increases. The value of δ at a particular concentration can be calculated using the following empirical relation obtained by fitting the asymptotic curve to δ values estimated for different concentrations,

$$\delta = 0.66 - 0.53 (0.11)^x \tag{3.19}$$

where *x* is the K(%)

It may be noted that the δ increases from a value of 0.22 (for x=0.1) to a maximum value of 0.66 (for large x). Thereafter any further increase in concentration of the K leads to increase in peak height and decrease in Full Width Half Maximum (FWHM). This as expected, the effect of spatial fluctuations weakens with increase in K concentration and distribution approaches to δ distribution about an average dose (\overline{D}).

Porosity plays an important role in the deciding the δ value. Fig. 3.9d provides the variation of doses with the porosity of the sediment matrix for different concentrations. It can be seen that for a given concentration, the δ value increases with decrease in density of the soil. The δ value is higher for a porous soil and while for the moist soil, it lies in between the two extreme cases. As suggested by the equation, (3.18) the age will have to be computed according the natural conditions. For moist conditions graph for '*Porous (water in pores)*' (Fig. 3.9d) will give the reliable results, while for dry samples '*Porous (air in pores)*' (Fig. 3.9d) graph will be appropriate. The values of δ for different concentration can be obtained from following empirical relations. For dry soil, '*Porous (air in pores)*'

$$\delta = 0.68 - 0.46 (0.06)^x \tag{3.20}$$

for Moist soil, 'Porous (water in pores)'

$$\delta = 0.68 - 0.51(0.11)^x \tag{3.21}$$

herex is the K (%)

As the concentration increases, the relative shift in the distribution functions for different densities decreases. This is because with increase in the concentration, the inhomogeneities arising from the differences in beta range in different medium becomes unimportant.

In order to see the variations in the age due to present analysis we tried to apply the method to results of Murray and Roberts, (1997). The age calculated on the basis of minimum dose value (D_{min} =14.7 ± 2.2 Gy) and corresponding dose rate is 2.32 Gy/ka for K = 1.3%, f=0.44 (Mayya et. al. 2006)and δ =0.63 (from Eq.3.17) is 8.0 ± 1.4ka. The age calculated by Mayya et al., (2006) for the same sample was 9.3 ± 1.4ka. However, the age obtained by Murray and Roberts, (1997) from average dose and dose rate 9.8 ± 0.5 ka. It is to be noted that age obtained from present study is a bit farther from the experimental results and different from the method by Mayya et al., (2006), but this age is theoretically more correct. However theory needs further refinements, and any further improvements, which are to be done, should be done using this new theory.

3.2.5 Implications: Distribution in Single Aliquots

The discussion above shows that spatial fluctuation of β sources around quartz grains lead to an inherent spread in palaeodosesobtained by individual quartz grains. In luminescence dating of sediments, SAR protocol, (Murray and Wintle, 2000; Singhvi et al., 2011) based on single aliquots (having several such heterogeneously irradiated single grains) are used for analysis. In order to obtain a statistically robust palaeodose, several aliquots/grains of a given sample are analyzed. However, because of inherent scatter at single grain level, it is expected that the D_e obtained from such single aliquots also have distribution in doses. The understanding and quantification of spread in the single aliquot doses helps improving the existing analysis techniques. Hence, in this work, we used Monte Carlo simulations to predict the extent of spread in palaeodoses arising due to heterogeneity of beta dose. Specifically, we computed,

1. the amount of spread in palaeodoses of single aliquots.

- 2. theminimum number of aliquots required for a robust estimation of palaeodose and estimate associated maximum possible expected error.
- 3. the maximum spread in mean of palaeodose distribution of aliquots due to fluctuation in the spatial distribution of beta emitters.
- 4. ratio of maximum to minimum palaeodoses that possibly can be used to distinguish between the spread in palaeodoses that arises exclusively due to spatial fluctuation of beta emitters, such that the spread beyond this could be attributed to other factors such as incomplete bleaching and sensitivity changes (Galbraith, 1990; Singhvi et al., 2011).

In order to quantify the spread a Monte Carlo based numerical model was developed which estimates the spread in palaeodoses using statistical parameters such as mean, standard deviation and the ratio of minimum to maximum value. The palaeodose estimates were made by randomly sampling the single grain doses from the dose distributions and averaged to give the final doses. The following sections discuss the procedures followed, the results obtained and their effects in dose estimation methodology.

3.2.5.1 Model to simulate single aliquot doses

Treating '*x*' (dose) as a random variable, single grain doses were randomly sampled from single grain distribution using inverse transformation method (Bevington and Robinson, 2003). In this method, the Cumulative Probability Distribution Function (CDF 'r = F(x)') for a random variable '*x*'can be obtained from the probability density function $\phi(x)$,

$$r = F(x) = \frac{\int_{-\infty}^{x} \phi(x) dx}{\int_{-\infty}^{\infty} \phi(x) dx}$$
(3.22)

F(x) was normalized with respect to the total area of density function (varying from $-\infty$ to $+\infty$), and thus *r* is a uniform random variable in the range between 0

and 1. In this formalism 'x' is an independent random variable and 'r' is dependent variable. Inverse transformation of Eq. 3.22 holds with 'r' as an independent random variable with values between 0 and 1 and 'x' as dependent variable, i.e.

$$x = F^{-1}(r)$$
 (3.23)

Fig. 3.12a shows the graph of 'x' vs. 'r'. Further, for a given random value 'r' the value of x was calculated using Eq. 3.23, where F^{-1} values were interpolated by a 3rd order polynomial. *Mathematica 5.1* was used for carrying out the computations and all Monte-Carlo simulations.



Figure 3.12:(a) Plot of scaled dose 'x' vs. 'r[= F(x)]'. (b) The histogram of randomly generated palaeodose distribution for 1000 single grains and the corresponding theoretical single grain palaeodose distribution function

The uniform random number 'r' was generated from 0 to 0.99999 using the inbuilt function '*Random*' available in the *Mathematica 5.1*. The 'Random' function uses Marsaglia|Zaman subtract-with-borrow generator for generation of random numbers. These random generators have period of 10^{200} to 10^{500} and are detailed in *http://www.mathcom.com/corpdir/techinfo.mdir/q210.html#q 210.6.2*. Each generated random dose corresponds to a probable single grain palaeodose. Fig. 3.12b shows the distribution of randomly generated palaeodoses for 1000 single grains, and compares these with the corresponding theoretical dose distribution function.

In generating palaeodose for a single aliquot with several grains, the case of an aliquot comprising 100 single grains was considered. Given that in nature, typically about 5-10% grains contribute to the total luminescence light sum (Duller et al., 2000), and that the distribution of the bright grains in the multigrain aliquots is random, the number of bright grains for each aliquot was generated randomly by considering their number to vary from 0 to 10% of total number of grains. The palaeodose values for the single aliquot were then computed as the average of the palaeodoses that were generated for each of the aliquot with variable number of bright, randomly irradiated grains. These results were analyzed for a variety of aspects as discussed below.



Figure 3.13:Flow diagram showing the procedure followed to find the single aliquot doses for N aliquots

3.2.5.2 Number of Aliquots Required for Palaeodose Estimation

In SAR protocol, it is often difficult to determine the number of aliquots that should be measured for a reasonable approximation to the palaeodose. Towards this, single aliquot palaeodoses were computed for a large number of aliquots using the above methodology (Fig. 3.13). To estimate the minimum number of aliquots whose average palaeodose closely approximates the mean value of single grain palaeodose distribution, average palaeodose for a predefined number of randomly generated single aliquots was computed and tabulated for different ranges around the mean of single grain dose distribution. Fig. 3.14 (branch-I) illustrates the procedure followed. About 1000 different sets of single



Figure 3.14:Branch-I: procedure to generate 1000 different palaeodose set for N aliquots and finding probability for having palaeodose values within a preset range of mean dose value. In this case, the ranges taken are ±1%, ± 5%, ±10%. Branch-II: It gives a method to find out the set maximum and minimum palaeodose values out of 1000 generated sets for a given number of aliquots.

aliquot palaeodoses were generated for a fixed number of aliquots and average palaeodose was computed. Of these, sets lying within a range of $\pm 10\%$, $\pm 5\%$ and $\pm 1\%$ of single grain mean palaeodoses were counted to obtain the



probability of finding the average palaeodose within defined range of mean of single grain distribution. Fig. 3.15a shows the results for a typical case of 1% K

Figure 3.15:(a) Variation of probability to obtain average dose within ±1%, ± 5%, ±10% range of mean of single grain palaeodoses for 1% K. In this 95% probability is taken as a cut off to consider the number of aliquots suitable for dose evaluation. (b) shows the comparison for different K concentration at aforementioned limits.

which suggest that, to obtain average palaeodose value within $\pm 10\%$ of the mean value of single grains average dose, ~9 aliquots will be sufficient and for a $\pm 5\%$ range about 35 aliquots are needed (here 95% probability is taken as the cutoff). For $\pm 1\%$ range, ~900 aliquots would be needed. Given that this is impractical, a limit on the practically achievable precision is to be anticipated. As a reasonable compromise between the measurement time and the accuracy, the use of $\pm 5\%$ range at 95% probability, 35 aliquots are needed for the case of 1% K. This number will increase to 63 for 0.3% K and decrease to 24 for 3% K (Table 3.1; Fig. 3.15b).

K (%) concentration	Number of Aliquots Required			
	±10% range	±5% range	±1% range	
0.3	16	63	>1000	
1	9	35	~900	
3	5	24	~500	

Table 3.1:Number of aliquots required to obtain an estimate of dose value at different range limits for different concentrations.

Mayya et al., 2006 suggested that as the potassium concentration increases, the scatter in single grain palaeodose distribution decreases because the dose from K-feldspar beta emitters becomes spatially homogeneous at single grain level and hence lesser number of aliquots are required. The data in Table 3.1 accords with this observation.



Figure 3.16:(a) Variation of minimum and maximum average dose values as a function of number of aliquots for 1% K. Shaded region gives the number of aliquots having >95% probability for dose values lying within ±5% of mean single grain palaeodose.
(b) and (c) shows the comparison of minimum and maximum average dose values as a function number of aliquots for different concentrations.

3.2.5.3 Variation in Average Palaeodose

Discussion above shows that even for 95% probability of obtaining average palaeodose value within a particular range for given number of aliquots, there is always a ~5% probability that palaeodose values would lie beyond the desired interval. We estimated the minimum and maximum average palaeodose values for given number of aliquots around the single grain mean palaeodose using the scheme given in Fig. 3.14 (branch-II).Typically, 1000 different sets of a pre-defined number of single aliquots were generated. Out of these, sets with maximum and minimum average palaeodose values were selected. Fig. 3.16a shows the variation of minimum and maximum average palaeodose values as a function of number of aliquots for 1% K. As expected, an increase in the number of aliquots leads to a decrease in the maximum average dose value and increase in minimum average value. Both converge to single grain mean dose.

K (%) concentration	Maximum possible error (%)			
	±10% range	±5% range	±1% range	
0.3	18.1	8.5	-	
1	19.2	9.2	1.7	
3	19.0	8.4	1.5	

Table 3.2:Maximum possible error expected on the basis of beta dose heterogeneity model for different concentrations and different range limits.

The shaded region in Fig. 3.16a gives numbers of aliquots that have palaeodose within ±5% range of the mean dose of single grains. Figs. 3.16b and 3.16c give the variation of maximum and minimum average dose values as a function of K concentration. As expected, the average value of the minimum and the maximum palaeodose for 3% K concentration is close to the single grain mean value of the palaeodose. Importantly all the curves approach mean single grain dose asymptotically, suggesting that there has to be a trade off in terms of measurement time and marginal improvement in the precision. The maximum and minimum average dose values define the limit for the experimental precision that can be expected. Table 3.2 provides associated maximum possible error (%) in estimating the palaeodose for different concentrations and at different

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range levels for suggested number of aliquots. This maximum possible error is calculated by following relation

$$Maximum \ possible \ error = \frac{Maximum \ average \ dose - Minimum \ average \ dose}{2(average \ dose)}$$
(3.24)

3.2.5.4 Spread in the Palaeodoses

To quantify the nature of palaeodose spread, so that spread beyond these theoretical limits could be justifiably ascribed toother causes like partial bleaching (e.g. Murray and Roberts, 1997), palaeodoses for 1000 different sets for a fixed number of single aliquots were simulated and standard deviations for each aliquot set was computed. Fig. 3.17 gives the flow diagram of the method.



Figure 3.17:Flow diagram showing the procedure to find the sets having maximum and minimum SD value out of 1000 generated sets

Fig. 3.18 shows typical histogram for the sets having maximum and minimum standard deviation (SD) for the case of a set comprising 35 aliquots. For uniformity, the scaled palaeodose values were divided into 10 bins from scaled dose of 0.5 to 2.2.



Figure 3.18:(a) Dose histogram for the set of aliquots having maximum SD value for different number of aliquots. (b)Dose histogram for sets having minimum SD values

Fig. 3.19a shows the variation of maximum and minimum standard deviation (SD) as a function of number of aliquots. The result suggests that maximum standard deviation decreases and the minimum standard deviation increases with increase in number of aliquots and both asymptotically converge towards a common SD value of ~0.15 (for 1000 aliquots). As expected, this value is lower in comparison to the SD value of single grain distribution, which is ~0.25. A finite SD for large number of aliquots indicates an inherent limit to the precision of single aliquot palaeodose. Other sources of scatter will add to this. Figs. 3.19b and 3.19c show the effect of the K concentration on the SD and as expected, SD is lower for higher concentration.

Generally, for heterogeneously bleached samples, the minimum valuerecorded from among a range of observed values is used to compute the age. However, it is equally likely that a well-bleached sample also mimics such a distribution due to beta dose heterogeneity. In such cases the use of minimum dose would lead to an underestimation, hence due care should be taken while analyzing such samples. The present practice to arrive at a decision on the bleaching status of a sample is based on the examination of the nature of the spread of palaeodoses on histogram or by the use of radial plot (Galbraith, 1988; Galbraith, 1990).

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Figure 3.19:(a) the variation of maximum and minimum standard deviation (SD) as a function of number of aliquots. (b) and (c) compares the same for different concentrations of K.

Though necessary, these may not be sufficient and a way out will be to use the additional proxies and information derived from the analysis of modern analog of the deposition process, that can help in distinguishing sources of the distribution. As an illustration, of the inferences above, the case of 35 aliquots (with 100 grains and \leq 10% of these contributing to the total light sum), from a sediment with 1% K content was considered and the palaeodoses were generated several times. Fig. 3.20 shows the nature of the spread for different sets. This suggests



Figure 3.20:The variation in shapes of dose histogram obtained for set of 35 aliquots for a concentration of 1% K.

that the shape of palaeodose histogram may not be sufficient to decide the model to be used for dose analysis.

For a sample with a palaeodose of 50 Gy, the model generated minimum palaeodose is ~17 Gy and the maximum value is ~152 Gy. Since the spread is large, the conventional wisdom would suggest that such a sample will normally be considered as heterogeneously bleached and hence the use of standard protocols may lead to erroneous ages. The use of the ratio (*R*) of the maximum and minimum palaeodose to account for the maximum possible variability due to beta dosimetry effects provide an additional check for cause of distribution. Based on a simulation of 10⁶ single aliquot palaeodose histories for 1% K, the minimum-scaled palaeodose obtained is 0.31 and maximum palaeodose is 3.2 (i.e. R~10). Thus, ratio R ≥10 suggests that sources other than 40 K are contributing to the spread in the palaeodoses. In natural samples, in addition to the heterogeneous beta dose contribution by 40 K, uniform dose by Uranium, Thorium and 40 K gamma are also deposited. So while evaluating the ratio contribution of this uniform dose need to be subtracted from the distribution.

3.2.5.5 Experimental Verification

To illustrate this further, we examine two samples; one from beach sand from E. Timor and the second was dune sand from the Niger in Sahara desert, Africa. Table 3.3 shows their U, Th and K concentrations. Fig. 3.21 shows the



Figure 3.21:Dose histograms obtained for the samples from two different natural conditions. (a) Dune sands from the Sahara desert (b) Beach sands from Australia

palaeodose histograms. To remove the contribution of the uniform dose, the minimum dose value of the distribution was considered to have contribution from heterogeneous beta dose and uniform dose. It was assumed that other sources leading to variable doses, did not contribute to the minimum dose. The fraction of uniform dose in the minimum dose value was evaluated using the respective dose rate fraction and was subtracted from all other dose values to get the palaeodoses distribution due to heterogeneous sources. The minimum dose value for the dune sand was 10.8 Gy while the maximum dose value was 12.4 Gy. After removing the contribution due to uniform component the value for heterogeneous components are 2.37Gy and 3.98Gy and hence the ratio is 1.7 suggesting that, the sample has the spread in palaeodoses only because of the beta heterogeneity and hence the average value of the doses should provide accurate results. Adopting similar approach for the beach sand, it is found that the maximum and minimum doses after removing uniform dose component are 1.38Gy and 21.2Gy and the ratio, is 19.8. This clearly indicates that the sample has other sources of distribution in addition to the beta heterogeneity and appropriate model need to be applied. Thus, we find that the spread in single aliquot palaeodoses can be predicted based on beta heterogeneity concept and proper analysis protocol can be then selected using ratio of maximum and minimum doses along with the dose histogram and radial plot.

Isotope	Beach Sand from E.Timor	Dune sands from Sahara	
Uranium (ppm)	0.68 ± 0.08	0.6± 0.2	
Thorium (ppm)	2.94± 0.23	0.4 ± 0.04	
Potassium (%)	0.71 ±0.05	0.14 ± 0.01	
Fraction of K beta dose	~40%	~22%	

Table 3.3:The concentration of radioactive elements for the two samples E. Timor beachsand and Sahara dune sand along with their respective K beta dose fraction

3.2.5.6 Discussion

Heterogeneity in the palaeodose due to spatial fluctuation of the beta sources around different quartz grains results in a distribution of the single aliquot palaeodoses. It is inferred that if beta heterogeneity is the sole cause of variation, the average of the distribution gives a realistic estimate of the palaeodose regardless of the nature of variability. Aspects like, minimum number of aliquots required for realistic palaeodose values, convergence of maximum and minimum average dose values and SD values, anomalously high palaeodose values etc., can be explained on the basis of fluctuations in dose in single grains.

However, this study presents the case when only K sources are heterogeneously distributed in the sediment matrix. As in nature, other radioactive sources, which are generally uniformly distributed, also contribute to the beta and gamma dose. For the case of simultaneous presence of both the components, the distribution in doses gets affected by the uniform component, which dilutes the scatter in the single aliquot dose distribution. This uniform component needs to be subtracted to infer the extent of spread due to heterogeneous K - beta dose.

Occasionally it is found that in palaeodose histogram or radial plot, some of the palaeodose values are anomalously higher than rest of the palaeodose values. These palaeodoses are attributed to the presence of some zircon or highly radioactivity grain (McFee and Tite, 1998) present in vicinity of quartz grains, as these grains receive a higher palaeodose values. This study suggests that anomalously high doses can also arise on account of heterogeneous beta dose deposition as shown in Figs. 3.18 and 3.20.

3.2.6 Conclusions: Distribution in Sub-Millimeter Size Grains

The present analysis affords following inferences:

- An important outcome of this study is the observation that beta dose heterogeneity perhaps can account for a large spread and hence bleaching heterogeneity need not always be implicated.
- 2. The dose deposition function calculated using Monte-Carlo simulations suggests a higher value of δ , which results in lower value of the ages calculated on the basis of simplified model proposed earlier.
- 3. The porosity has noticeable effect on the δ values when concentration is lower, but at higher concentration the δ values are almost same. So, at

lower concentrations the conditions of the sampling site (like dry, moist or dense) have to be considered while calculating the age.

- 4. The concept of beta heterogeneity presents a paradigm shift from the conventional considerations so far for dose determination using single aliquots. Also it implies that when other sources of variability are not present average value of the dose distribution provides more realistic estimate of the palaeodose irrespective of the shape of distribution.
- 5. The spread in palaeodose places a limit on the precision of single aliquot measurements and typically, about 35 aliquots are needed for a palaeodose value within ±5% of the mean of single grain value. It is suggested that number of aliquots at ±1% accuracy limit would need analysis of about ~900 aliquots.
- 6. The distribution of doses on histogram or radial plot may not be sufficient to predict the source of variability. However the use of ratio of maximum to minimum beta dose due to ⁴⁰K can be used as an additional proxy for identifying nature of variablity.
- If ratio of maximum to minimum beta dose of ⁴⁰K dose value is more than 10 then factors other than beta source fluctuations are responsible for variation in doses.
- 8. Heterogeneity of beta dose can also lead to anomalously high palaeodose. These are at times ascribed to the presence of zircon grains with high internal radioactivity and associated beta dose.

The work on single aliquot distribution is published as Chauhan and Singhvi (2011).

3.3 Dose Distribution: Sub- Centimeter Size Grains

As alluded to different ranges of ionizing radiation implies that grains of different sizes receive different doses. The attenuation of doses inside the grains makes dosimetric computations grain size dependent, but provides opportunity to make use of low dose rate region in larger size grains. The upper limit for the luminescence age is defined by a combination of the saturation dose (Chawla et

al., 1998) and the stability of the luminescence signal. Quartz has demonstrated a stable luminescence signal (~10⁸ka, Aitken, 1985c) but has a low saturation dose for OSL measurements, which implies an upper age limit of \leq 100 ka. This puts a limit on dating the older sediments. Though feldspar provides an opportunity to date older sediments because of higher saturation dose, but it suffers from athermal fading, which limits its applicability. The other possibility that enabled the dating of older events using guartz is in low annual dose environments (Huntley and Prescott, 2001) which are not routinely available. We explored a possibly simpler alternative of using large grains, where the interior receives only a fraction of the annual dose seen by a standard 100µm grain, (Fig. 3.22a; Aitken, 1985c; Mejdahl, 1979). This implies a slower progression to saturation, and consequently of dating over an extended time range. Typically, in a sediment matrix with ~1 ppm 232 Th, ~1 ppm U and ~1% K, the β dose contribution for a typical grain size of 100 μ m is ~70% and the remaining 30% is from gamma and cosmic rays. About ~85% of the beta dose is contributed by 40 K, ~13% by U-series and ~2% by 232 Th-series (Adamiec and Aitken, 1998).



Figure 3.22:(a) Contribution of doses in different regions for millimeter (mm) size quartz grain.(b) Simulation geometry for obtaining dose depth profile in variable size quartz grains embedded in radioactive sediment matrix. The quartz grains were subdivided in concentric spherical shells (broken lines) to compute the dose-depth profile.

In a typical sediment, dominant contributors to the beta dose are 40 K, 212 Bi (232 Th-series) and 234m Pa and 214 Bi (U-series). Table 3.4 lists their maximum beta energies (β_{max}), corresponding ranges under Continuously Slowing

DownApproximation (CSDA), and the net contribution to beta dose for unit concentrations. This section deals with the conceptual development with the above isotopes in view of the fact that the other isotopes make minor contributions to the absorbed dose. The depth dependence of beta dose rates from the above radioactive sources was computed using Monte Carlo simulations and analytical approach. We also identified possible limiting factors including the extent of photo-bleaching of geological luminescence, in view of possible attenuation of light penetration in large grains.

Radionuclide	Decay series	Max. beta energy, β _{max} (MeV)	CSDA range, R _m (mm)	Branching ratio	Net dose %
⁴⁰ K	K	1.35 ^a	2.9	0.893	85
²¹² Bi	Th	2.25 ^b	5.3	0.64	0.6
^{234m} Pa	U	2.28 ^b	5.3	1	4.7
²¹⁴ Bi	U	3.27 ^b	7.9	1	3.8

Table 3.4:List of different isotopes contributing beta dose in the interior of the quartz grain.Also given are their maximum beta energies (β_{max}), CSDA (Continuously Slowing Down Approximation) ranges in quartz of density 2.65 g/cm³ and percentage beta dose contribution for unit concentrations.^aAitken (1985), ^bEckerman et al., (1994) and^cESTAR computer program

3.3.1 Depth Dose Calculations

In order to estimate the minimum grain size, the ranges of beta particles emitted by different radioactive isotopes inside the quartz grains are to be estimated. The depth of the beta-irradiated portion, will further decide the minimum size of the quartz grain that should be used for the analysis. In order to find the dose depth profile, Monte Carlo simulations were used. These simulations were further verified by the analytical formulations, using the point source dose depth profile (estimated by Monte Carlo simulations) and hence computed dose depth profile due to sediment matrix inside the quartz grains of different sizes.

3.3.1.1 Monte Carlo Simulations

In this Monte-Carlo based EDKnrc user-code (Rogers et al., 2005) of EGSnrc code system (Kawrakow and Rogers, 2000) was used for calculating the beta dose distributions. The simulation parameters are similar to the work described in section 3.2.1. The simulations to calculate the dose absorbed by a quartz grain were carried out for each of ⁴⁰K, ²¹²Bi, ²³⁰Pa and ²¹⁴Bi.In the first set of simulations, a point radioactive source was considered in an infinite quartz medium. The absorbed dose arising from each source was computed for concentric spherical shells of 10 μ m thickness. This yielded dose as a function of radial distance ξ . Fig. 3.23 shows the MonteCarlo calculated point source based dose function g(ξ) (Gy/particle) for ⁴⁰K as a function of the distance ξ from the source. The influence of the inverse square dependence of g(ξ) on ξ was removed by multiplying g(ξ) by ξ^2 .



Figure 3.23:Monte Carlo-calculated dose values $g(\xi)$ shown as a function of radial distance ξ from a point ⁴⁰K beta source in an infinite quartz medium. The influence of inverse square of distance on the calculated $g(\xi)$ is removed by multiplying $g(\xi)$

by ξ^2 . $g(\xi) \times \xi^2$ is expressed in units of Gy-mm²/particle

In the second set of simulations, the absorbed dose in a quartz grain was calculated when the spherical quartz grains of different diameters (diameters between 0.1 mm and 10 mm) were irradiated by an infinite spherical radioactive

sediment matrix. Beta emitting sources were randomly sampled from this spherical radioactive shell. The geometry used in the simulations is depicted in Fig. 3.22b. The sediment matrix and quartz were assumed to comprise SiO₂ with density of 2.65 g cm⁻³. The beta energy spectrum of ⁴⁰K was taken from Kelly et al., 1959 and those of ²¹²Bi, ^{234m}Pa and ²¹⁴Bi were taken from Eckerman et al., 1994. Up to 10⁸ beta-particle histories were simulated.Statistical uncertainties (1 σ) on the dose estimates ranged between 0.02% and 6%.

3.3.1.2 Analytical Approach

Figs. 3.24(a-d) show the irradiation geometry for larger and smaller grains and explain the parameters used in analytical calculations. Here, *R* is the radius of quartz grain, *r* is the distance between the grain centre and a point inside the quartz grain where dose is to be evaluated, R_m is the maximum range, ξ is the distance between a point in the radioactive sediment matrix and a point *r* in quartz, θ is the angle between ξ and the dotted line (as shown in Fig. 3.24a and 3.24b) and θ_0 is the maximum angle that the dotted line can make with ξ . The expression for the dose rate (Gy.s⁻¹) at *r* due to a small volume element (dV) at a distance ξ for a unit radioactivity concentration of $Q_v = 1Bqcm^{-3}$ is given by

$$d\dot{D}(r) = Q_{\nu} \times \delta V \times g(\xi)$$
(3.25)

Where $g(\xi)$ (Gy/particle) is the Monte-Carlo derived point source beta dose deposition function (as explained in section 2.1). The total dose rate $\dot{D}(r)$ can be obtained by integrating equation, (3.25) over the volume of sediment matrix as given below,

$$\dot{D}(r) = \int d\dot{D} = 2\pi Q_{\nu} \times \int \xi^2 g(\xi) d\xi \times \int_{0}^{\theta_0} \sin\theta \, d\theta$$

= $2\pi Q_{\nu} \times \int \xi^2 g(\xi) d\xi \times (1 - \cos\theta_0)$ (3.26)



Figure 3.24:Schematic representations of different volumes contributing to quartz grain ofradius R. r is the distance from center where dose is to be evaluated; ξ is the distance of source from r. θ is angle which ξ makes with the dotted line passing through the centre of the spherical system and varies from 0 to $\theta_0 \cdot \theta_0$ is the maximum angle that the dotted line makes with the ξ vector. Rm is the maximum range of beta particle in quartz. (a) Geometrical picture of grains having R > Rm. (b) Geometry showing the relation between θ_0 , ξ , r and R.(c) Geometrical picture for grains such that R+r > R_m> R and (d) Geometrical picture for grains such that R+r < R_m

From Fig 3.24b

$$\cos\theta_{0} = \frac{R^{2} - (r^{2} + \xi^{2})}{2\xi r}$$
(3.27)

Two distinct cases can be considered as described below:

Case 1: For grains with radius $R > R_m$ (Fig. 3.24a), the dose contribution at any point in the quartz grain is due to the shaded region bounded by the quartz surface and the sphere of radius R_m centered at the point r. For this case, the dose rate was calculated as follows:

$$\dot{D}(r) = 2\pi Q_{\nu} \int_{R-r}^{R_{m}} \xi^{2} g(\xi) d\xi \left[\frac{(\xi+r)^{2} - R^{2}}{2\xi r} \right] \qquad (R > R_{m}) \qquad (3.28)$$

Case 2: For grains with radius $R < R_m$, two possibilities arise, namely, $R + r > R_m > R$ (Fig. 3.24c) and $R + r < R_m$ (Fig 3.24d). For the case $R + r > R_m > R$, the expression for dose rate is given by,

$$\dot{D}(r) = \dot{D}_{1}(r) = 2\pi Q_{v} \int_{R-r}^{R+r} \xi^{2} g(\xi) d\xi \left[\frac{(\xi+r)^{2} - R^{2}}{2\xi r} \right] \qquad (R+r > R_{m} > R)$$
(3.29)

For the case, $R+r < R_m$ the expression for dose rate is given by,

$$\dot{D}(r) = \dot{D}_1(r) + \dot{D}_2(r)$$
 $(R + r < R_m)$ (3.30)

where

$$\dot{D}_{2}(r) = 4\pi Q_{\nu} \int_{R+r}^{R_{m}} \xi^{2} g(\xi) d\xi$$
(3.31)

3.3.2 Beta Dose Rate Distribution

For a given thickness of the radioactive sediment matrix, the active volume varies with grain diameter. Thus, to exclude the influence of active volume on the dose rates while comparing dose-rate distributions in different size grains, the

dose rate presented in this section is based on $Q_v = 1 Bqcm^{-3}$. The dose rate at r = R can be interpreted as the surface dose rate.



Figure 3.25:Comparison of Monte Carlo and analytically calculated values of dose rate(Gy·s⁻¹) for an activity concentration of $Q_v = 1 Bq \cdot cm^{-3}$ for 0.1 mm and 4 mm diameter quartz grains shown as a function of distance from the surface of grain along radius. These grains are irradiated externally by ⁴⁰K beta particles distributed uniformly in an infinite spherical sediment matrix. Top X-axis is for 0.1 mm case and bottom is for 4 mm case. Y-axis shows the dose deposited in Gy.s⁻¹.

For all the beta sources, the surface dose rate for larger diameter grains constitutes about 60% of the corresponding value of 0.1 mm diameter grain. Fig. 3.25 compares the Monte-Carlo derived and analytically calculated dose rate values (Gy.s⁻¹) for 0.1 mm and 4 mm diameter grains for ⁴⁰K, as a function of the distance from grain surface towards the centre of the grain. In the case of 0.1 mm diameter grain, the dose deposition is constant along the radius and the differences between analytical and Monte-Carlo values can be attributed to statistical uncertainties. For a grain of diameter 4 mm the beta dose rate at depth of 2 mm reduces to ~0.2% of its value for 0.1 mm diameter grain. Hence for a 10 mm diameter quartz grain, the interior volume of the grain (~6 mm diameter) does not receive beta dose and such grains should provide sufficient sample amount for analysis. Fig.3.26 presents the normalized dose-rate values for ²¹²Bi,

^{234m}Pa and ²¹⁴Bi for 6 mm diameter grains as a function of radial distance from the surface of grain.For each of the radionuclides, the dose-rate values are



Figure 3.26:Monte Carlo-calculated values of dose rate (Gy.s⁻¹) for an activity concentration of $Q_v = 1 Bq \cdot cm^{-3}$ for ²¹²Bi, ^{234m}Paand ²¹⁴Bi sources that are uniformly distributed in infinite spherical sediment matrix. The dose-rate values are shown as a function of distance from the surface of 6 mm diameter grain. The dose-rate values of each source are normalized to dose rate of 0.1 mm diameter grain

normalized to the dose-rate value of 0.1 mm grain. At a depth of 2 mm, the normalized values are about 2%, 5% and 2.5 % for ²¹²Bi, ²¹⁴Bi and ^{234m}Pa, respectively. Using the beta dose fraction in Table 3.4, the dose-rate contribution at a depth of 2 mm is 0.01% for ²¹²Bi, 0.2% for ²¹⁴Bi and~0.1% for ^{234m}Pa. This suggests that at 2 mm depth, beta doses from ²³⁸U-series and ²³²Th-series are insignificant. Hence, typically, the grain size should exceed 6 mm diameter to obtain sufficient sample from the grain interior.

These mathematical and computational results suggested the minimum grain size to be used for the analysis. The maximum grain size, which is to be used, is decided by the bleachability of luminescence signal in large size quartz grain. The bleachability of luminescence signal of quartz grain in natural environment depends upon the transparency (thus attenuation of light inside the quartz grain) of grain and the time duration of the light exposure in the nature. In

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order to find the bleachability of luminescence signal transparency experiments were performed to predict depth of light penetration inside a quartz grain.

3.3.3 Bleaching Experiment

The optical transparency and hence the photo-bleachability was determined using ILX Light wave optical multimeter having a detection range of 350-1650 nm. For our purpose we used blue light having peak intensity of 447nm. Light from a LED source was collimated using a 1 mm pin–hole. Quartz slices of variable thicknesses were kept in front of the collimated light and transmitted light was detected using photometer with a silicon detector. Detector was placed at a distance of 1 cm from the sample.



Figure 3.27: The transmission of quartz studied by a collimated blue light beam. The intensity is normalized w.r.t. to the smallest thickness of slice of quartz

Light incident on the quartz slice gets isotropically scattered by internal surfaces and cracks. The isotropic distribution suggests that light scattering facilitates bleaching of the geological luminescence. Measurements on two different colored quartz grains viz., milky white (Fig. 3.27) and blackish grain, indicated light penetration of 7 mm and 2 mm (97% attenuation). Fig. 3.28 shows the bleaching of 90-150 μ m grains under a sun lamp. For this short shines (0.1s) were recorded and averaged for (0.02s) after exposing to sun lamp. The figure shows that under normal conditions luminescence signal is bleached in ~5 min.

As the transparency experiments shows a 97% reduction in the light, it implies a bleaching time of ~170 min (i.e. ~3 hours) for the interior of the grain. This implies that for a 4π optical bleaching geometry, depending on their transparency, grains having diameter less than 14 mm can be expected to be bleached over a period of several hours.

In order to further verify the bleachability of large size quartz grains, a laboratory-controlled experiment was performed. The quartz grains of size ranging from 1–1.4 cm were taken and annealed at 450°C for 4 hours. The sample wrapped in light tight aluminium foil is then given ~100 Gy gamma dose.



Figure 3.28:The short shine (0.1s) recorded after different bleaching time of quartz grains under solar simulator lamp.

The gamma-irradiated grains were bleached under the sunlamp for 3 hours. The exterior portion is etched away and interior portion is analyzed. Fig 3.29 shows the OSL signal for unbleached grain and the interior portion (initial size ~1.5 cm) of the same grain after bleaching for 2 hours under sunlamp. It is seen that within two hours the signal in the interior of the grain reduces to near zero value. This experiment suggests that large size grain can be bleached in nature provided it get sufficient light exposure.

3.3.4 Experimental Verification

In order to test the proposed theory, geological gravel samples from Portugal were analyzed. The gravel sample contained well rounded pebbles (variable sizes) of different minerals. There was significant portion of the quartz grains, which were utilized for the analysis. The sediments samples above the gravel sequence were initially dated with OSL dating technique and gravel



sample is expected to be greater than 200 ka. The older sediment sequence makes it viable to use the developed procedure.

Figure 3.29:Bleaching of the stone sample under solar simulator. The stone sample was given gamma dose ~120Gy and then bleached the sample under solar simulator for 2 hours. The graph shows the OSL decay curve of unbleached dosed quartz and the bleached sample. The stone was irregular in shape having minimum dimension of about 11.7 mm.

3.3.4.1 Sample Preparation

Sample collected under light tight conditions were processed and grains of size 1-1.4cm were sieved. Out of these quartz grains, which are milky white in color, translucent and well rounded, were selected. The different sides of the grain were measured with vernier caliper and recorded. the grains were then put in 30% Hydrofluoric acid (HF) and etched with constant stirring. Stirring is done so that quartz grains are etched uniformly. It took 40 hours to etch the outer 2 mm skin of the quartz grains. It is noteworthy that the quartz grains etch out non-uniformly and hence, careful measurement of different dimensions needs to be taken. The etched grainswere then gently crushed under water in agate mortar to minimize the loss of signal due to heat. The crushed sample was then treated with mild HF for 10 min to remove the surface defects created during crushing,

followed by an HCI treatment to remove the fluorides. The sample was again sieved to get 90-150 μ m grain size. Many a time the sample quantity was very small and in such cases only one large sieved was used.

3.3.4.2 Dose Measurements

Sieved quartz grains of size 90-150µm were then analyzed using the SAR protocol (section 2.3, Chapter, 1). A preheat of 220°C for 10s followed by stimulation by blue light at 125°C was used. The test dose TL signal was used



Sample: LAVAD 2.1 (stone-4)

Figure 3.30:a) OSL decay curve b) Glow Curve c) Recycling ratio of different discs d) Histogram of dose distribution for stone 4 of Sample LAVAD-2.1 from Portugal.

to correct for the sensitivity changes. Large size quartz grains have generally poor sensitivity (typically 80-100cts/s or less) and hence, S/N ratio was poor. However it is possible to obtain one out of 5-6 quartz grains with acceptable S/N

ratio. The selection of such a grain made the process time consuming. Fig. 3.30 shows the OSL Decay curve, Glow curve, recycling ratios and dose histogram for one of the stone sample (stone-4 LAVAD-2.1).

3.3.4.3 Dose Rate Computation

The dose rate of the sample was generally computed by using the concentration of U, Th, K and taking the contribution of cosmic rays into account and for computation of the gamma dose rate infinite matrix assumption is made considering the radioactivity sources are distributed homogeneously throughout the matrix. However, in nature for the large size quartz grain the radioactivity sources (sediments) are occupying only the void spaces in between the grains so in the computation of gamma dose rate the infinite matrix gamma dose rate is to be multiplied by the packing fraction. This packing fraction can be estimated by knowing the size of the void and the size fraction of the sediments comparable or lower than the size of the void, which can be done using grain size analysis. In present case the size of quartz grain was considered to be 10mm, which using the following formula gives the size of void as 2.25 mm.

$$Radius of \ void = 0.414R \tag{3.32}$$

Where R is radius of grain. Thus using this data the natural dose rate of the sample can be estimated.

For the present case for LAVAD-2.1 the U, Th, K concentrations were found to be 1ppm, 3 ppm and 4 % respectively. The grain size analysis shows the fraction of grains in size <3 mm is ~17%. Using this along with the cosmic rays contribution the dose rate is found to be ~ 0.17Gy/ka

3.3.4.4 Results and Discussions

The sensitivity corrected luminescence signal was used to obtain the growth curve (Fig. 3.30b). The Fig. 3.30d shows the histogram of the dose values obtained for stone. Using this grain an average dose value of about ~36Gy was obtained. Using the dose rate of 0.17Gy/ka as calculated in previous

section an age of 217 ka was obtained. This age is in accordance with stratigraphy sequence. In order to cross check this age value, 90-150 μ m grain size fraction was also used and using this obtained a dose value of 180 Gy and dose rate of 0.85Gy/ka. The age obtained is 230ka, which is within the experimental uncertainties. This proves the theory.



Figure 3.31:Dose distribution observed from different stones of LAVAD-2.1, having different sensitivities

However, it has been observed that there are very few stones, which have good response; others vary significantly in the sensitivity and the doses. Fig. 3.31shows the histogram obtained for different stones of similar sample i.e. LAVAD-2.1 and quite a different behavior was observed. The sensitivity of these stones was lower as compared to stone-4, and a lot of unexpected scatter in the doses was observed. To get good results, it is recommended to use a wellbehaved grain with respect to sensitivity. In addition to this, care while etching the sample is needed as the etching is generally non-uniform. Also for smaller grains having size less than 10mm, the non uniform etching can lead to breaking of grains and hence continuous monitoring of the grains size needed. While

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selecting the grains the care must be taken that grain should be well rounded, semitransparent (which can be identified by holding it against filtered subdued red light) and minimum thickness of grain along any axis should exceed twice the beta range (more appropriately it should be greater than 6 mm). Vandenberghe et al., (2008)suggested that some of the quartz grains can have internal radioactivity. For such cases appropriate correction will have to be incorporated in dose-rate estimation and these effects can also be computed.

3.3.5 Conclusions: Dose Distribution in Centimeter Size Grains

The present study demonstrates that the beta dose in a grain due to ⁴⁰K decreases with depth and is insignificant at a depth of 2 mm. The beta dose contribution of ²¹²Bi, ^{234m}Pa and ²¹⁴Bi of ²³⁸U series at this depth is also insignificant. For grains exceeding 4 mm diameter, the interior of the grains receive only the gamma dose and a small contribution for higher energy beta particle from the U and Th series members, and this fact can be exploited for extending the dating limit by three fold. The experimental results for optical transparency suggest that a grain size of 1.4 cm diameter can be bleached by light if it gets sufficient light. The feasibility of the technique was tested for natural sample and results were found in accordance with the proposed theory. This thus concludes that we can use ~cm size grains for extending the dating limits of quartz.The theoretical concept of the work has been published as Chauhan et al., (2009)

Chapter-4: Spatially Resolved Luminescence Dating

Chapter-4

Spatially Resolved Luminescence Dating

4.1 Introduction

Generally, for luminescence dating, we need to separate the grains of specific mineral and of specific grain sizes. This requirement limits the application of the luminescence dating to samples where grains can be separated in the first place. Initial efforts for the luminescence dating of surfaces were made a few years ago (Greilich et al., 2005) but a routinely applicable methodology and system has not yet been achieved. The potential application of this approach will be the dating of rock samples from a variety of geological situations like glaciated terrains, dating of the fusion crust of meteorites, dating of

complex carbonate with detritus in them, archeological stone tools and sculptures etc. If developed this would imply substantive improvements in areas important in climate change, geology and archeological studies, (Fig 4.1).



Figure 4.1:New possibilities using surface dating technique (Greilich et al., 2005)

In the surface dating technique, the luminescence signal is taken as a 2D image using a CCD camera and then a pixel specific analysis is done to obtain a mineral/phase specific age. Different pixel groups of surface are used to obtain multiple ages.

While notionally simple, in practice luminescence dating of surfaces require several critical inputs that include a proper computation of dose rate (including appropriate assessment of geometry effects, internal dose and the solid dose), depth of bleachability from surface and transparency aspects. As luminescence measurements do not change the chemical composition, it is possible to further analyze sample using other chemical techniques. For samples with complex mineralogy, the instrumentation would make it possible to analyze specific phases.

In addition, even different phases of growths such as complex calcretes could be studied. Thus, by dating the quartz inclusions in various layers in carbonate nodules, it will be possible to find the accretion rate of carbonate nodules. The key elements in the dating of surfaces using luminescence are,

1. Estimation of the transparency of the sample

- 2. Estimation of the Dose Rate
 - i. Estimation of Natural dose rate
 - ii. Estimation of net laboratory dose delivered as a function of depth and hence compute average dose for the sample
- 3. Development of 2DLuminescence Measurements at high resolution

This thesis work examined aforementioned issues and developed basic elements as discussed below.

4.2 Transparency of the Sample

Fig. 4.2 shows a schematic of the effect of transparency in luminescence dating studies. In this case two important parameters are depth of the sample from where the luminescence is emitted and the depth of beta ray penetration. Both of these depend on the nature of material.

The attenuation of the light inside a medium is governed by the Beer Lambert's law such that light attenuates exponentially as a function of depth i.e.

$$S = S_0 \exp(-\mu z) \tag{4.1}$$

Where *S* is the stimulation intensity of light at a depth *z* inside the medium and μ is the attenuation coefficient. For high transparency materials with low attenuation coefficient for light, the penetration depth is higher than the β range of the laboratory irradiation source (i.e. Optical depth > β range). When such a sample is measured in the laboratory, then while measuring natural signal, luminescence is contributed by the regions up to optical depth of stimulation light as shown in the Fig. 4.2, however the laboratory-regenerated signal using a β source, is limited only up to the maximum range of β particle and associated x rays. Thus, the regenerated growth curve will be valid for β -irradiated region not for the entire region and its use will provide erroneous estimations by overestimating the dose as the luminescence signal for natural measurement is contributed by a larger volume of the sample.

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Figure 4.2:The dating issues related to material having optical depth > the beta range. Here S_0 is initial intensity and S is the intensity at depth z for stimulating light and I(t) is luminescence intensity at time 't'.

An important quantity is the variation of luminescence intensity as a function of the transparency and sample thickness. This can be derived by estimating the luminescence intensity at a particular point for a given period of time (t). If I(t) gives the instantaneous luminescence intensity at time t that decays exponentially (Fig. 4.3) as,

$$I(t) = I_0 e^{-\lambda t} \tag{4.2}$$

Where I_0 is initial intensity and λ is the OSL decay constant. This can be expressed in terms of total light sum as integral over the measurement time from 0 to ∞ .



Figure 4.3:The OSL decay curve having initial intensity as I_0 and intensity at time t is I(t). λ is the decay parameter.

Thus

$$I_{sum} = \int_{0}^{\infty} I_0 e^{-\lambda t} = \frac{I_0}{\lambda}$$
(4.3)

This implies,

$$I(t) = \lambda I_{sum} e^{-\lambda t} \tag{4.4}$$

So, the OSL intensity for a given time period t_m is given by

$$I = \int_{0}^{t_{m}} \lambda I_{sum} e^{-\lambda t} dt$$

$$= I_{sum} \left[1 - e^{-\lambda t_{m}} \right]$$
(4.5)

In this, the decay constant λ depends on the power and the photoionization of the stimulation light. More is the stimulation power or higher the photoionization crossections, the faster will be the decay and hence higher will be the value of the decay constant i.e.

$$\lambda \propto S(\nu) \tag{4.6}$$

or

$$\lambda = \eta S(\nu) \tag{4.7}$$

Here S(v) is the power and η is the efficiency for a given frequency v of stimulating light. Therefore, the intensity at a given point due to S(v) is given by

$$I = I_{sum} \left[1 - e^{-\eta S t_m} \right]$$
(4.8)

This is the intensity due of OSL signal at a given point. Now for a thick slice, this intensity needs to be integrated over the entire thickness. Considering i(z) as the areal signal density having similar form as *I*, the intensity of the sample of thickness z_m is given by

$$I_{sample} = \int_{0}^{z_m} i(z) dz$$
(4.9)

In addition to this, the stimulating intensity $S(\nu)$ decreases as a function of the depth in accordance with the Beer–Lambert's law (equation, 4.10), hence the OSL decay constant changes with time.

$$S(\nu) = S_0 e^{-\mu z} \tag{4.10}$$

Where μ is attenuation constant and S_0 is the initial power of the stimulation signal. The intensity of emitted luminescence also gets attenuated as the light emitted from deeper regions travels to the surface. In order to compute the effect of transparency and the thickness of the sample on the net luminescence production, the areal luminescence signal density, and the attenuation coefficient are needed. Considering equation, (4.4), the luminescence signal intensity from a layer of thickness *dz* at a distance *z* at a given time *t* is given by

$$I' = i(t, z, \tau) dz = \lambda i_{sum} e^{-\lambda t} dz$$
(4.11)

Where i_{sum} is the total integrated intensity from 0 to t. Substituting the values of λ and *S* from equation, (4.10)

$$I' = i(t, z, \tau) dz = \eta S_0 e^{-\mu z} i_{sum} e^{-\eta S_0 e^{-\mu z} t} dz$$
(4.12)

Now this luminescence emitted by thickness dz at depth z is attenuated while reaching the surface according to Beer–Lamberts law. This implies that, the intensity of light coming out due to dz element after traversing z distance is,

$$I'' = i(t, z, \tau) dz \times e^{-\mu z} = \eta S_0 e^{-2\mu z} i_{sum} e^{-\eta S_0 e^{-\mu z} t} dz$$
(4.13)

Thus, the total intensity from the sample of thickness z_m in total time t_m duration is given by

$$I = \int_{0}^{z_{m}} \int_{0}^{t_{m}} i(t, z, \tau) e^{-\mu z} dz dt$$

$$= \int_{0}^{z_{m}} \int_{0}^{t_{m}} \eta S_{0} e^{-2\mu z} i_{sum} e^{-\eta S_{0} e^{-\mu z} t} dz dt$$
(4.14)

The solution of this equation provides the variation of luminescence with thickness and the transparency.

Defining,

$$C_1 = \eta S_0 i_{sum} e^{-2\mu z}$$
 and $C_2 = \eta S_0 e^{-\mu z}$

Then equation, (4.14) becomes,

$$I = \int_{0}^{z_{m}} dz \int_{0}^{t_{m}} C_{1} e^{-C_{2}t} dt$$
(4.15)

and its solution provides,

$$I = \int_{0}^{z_{m}} C_{1} dz \left| \frac{e^{-C_{2}t}}{-C_{2}} \right|_{0}^{t_{m}}$$

$$= \int_{0}^{z_{m}} \frac{C_{1}}{C_{2}} \left(1 - e^{-C_{2}t_{m}} \right) dz$$
(4.16)

Substituting for C_1 and C_2 , and solving

$$I = \int_{0}^{z_{m}} \frac{\eta S_{0} i_{sum} e^{-2\mu z}}{\eta S_{0} e^{-\mu z}} \left(1 - e^{-\eta S_{0} e^{-\mu z} t_{m}}\right) dz$$

$$= \int_{0}^{z_{m}} i_{sum} e^{-\mu z} \left(1 - e^{-\eta S_{0} e^{-\mu z} t_{m}}\right) dz$$

$$= i_{sum} \int_{0}^{z_{m}} e^{-\mu z} \left(1 - e^{-\eta S_{0} e^{-\mu z} t_{m}}\right) dz$$

$$= i_{sum} \left[\int_{0}^{z_{m}} e^{-\mu z} dz - \int_{0}^{z_{m}} e^{-\mu z} e^{-\eta S_{0} e^{-\mu z} t_{m}} dz\right]$$

$$= i_{sum} \left[I_{1} + I_{2}\right]$$

Where

$$I_{1} = \int_{0}^{z_{m}} e^{-\mu z} dz \quad and \quad I_{2} = -\int_{0}^{z_{m}} e^{-\mu z} e^{-\eta S_{0} e^{-\mu z} t_{m}} dz$$

Solving $I_{\rm 1}$ and $I_{\rm 2}$ separately,

$$I_{1} = \int_{0}^{z_{m}} e^{-\mu z} dz = \left| \frac{e^{-\mu z}}{-\mu} \right|_{0}^{z_{m}} = \frac{1}{\mu} \left(1 - e^{\mu z_{m}} \right)$$
(4.17)

In I_2 let $C_3 = \eta S_0 t_m$

So

$$I_2 = -\int_{0}^{z_m} e^{-C_3 e^{-\mu z}} e^{-\mu z} dz$$
 (4.18)

substituting

$$x = C_3 e^{-\mu z}$$

and
$$dx = C_3 e^{-\mu z} (-\mu) dz$$

or
$$\frac{dx}{(-\mu C_3)} = e^{-\mu z} dz$$

when $z = 0$ then $x = C_3$
 $z = z_m$ then $x = x_m = C_3 e^{-\mu z_m}$

we get

$$I_{2} = -\int_{C_{3}}^{x_{m}} e^{-C_{3}e^{-\mu z}} e^{-\mu z} dz$$

$$= -\int_{C_{3}}^{x_{m}} e^{-x} \frac{dx}{(-\mu C_{3})}$$

$$= \frac{1}{\mu C_{3}} \int_{C_{3}}^{x_{m}} e^{-x} dx$$

$$= \frac{1}{\mu C_{3}} \left| -e^{-x} \right|_{C_{3}}^{x_{m}}$$

$$= \frac{1}{\mu C_{3}} \left(-e^{-x_{m}} + e^{-C_{3}} \right)$$

$$= \frac{1}{\mu C_{3}} \left(e^{-C_{3}} - e^{-C_{3}e^{-\mu z_{m}}} \right)$$

$$= \frac{1}{\mu \eta S_{0}t_{m}} \left(e^{-\eta S_{0}t_{m}} - e^{-\eta S_{0}t_{m}e^{-\mu z_{m}}} \right)$$

(4.19)

Thus, the total intensity is given by

$$I = i_{sum} [I_1 + I_2]$$

= $i_{sum} \left[\frac{1}{\mu} (1 - e^{\mu z_m}) + \frac{1}{\mu \eta S_0 t_m} (e^{-\eta S_0 t_m} - e^{-\eta S_0 t_m} e^{-\mu z_m}) \right]$ (4.20)

 $I = \frac{i_{sum}}{\mu} \left[1 - e^{\mu z_m} + \frac{1}{\eta S_0 t_m} \left(e^{-\eta S_0 t_m} - e^{-\eta S_0 t_m e^{-\mu z_m}} \right) \right]$ (4.21)

Fig. 4.4 shows the variation of intensity computed in equation, (4.21) as a function of the attenuation coefficient and the thickness of the sample. It shows that for a given attenuation coefficient the signal contribution increases and finally saturate indicating the maximum depth of penetration of stimulating signal and hence contribution from an infinitely thick sample. However, for a given thickness the luminescence decreases exponentially with attenuation coefficient. It therefore implies that materials with higher attenuation coefficients (i.e. low transparency) are suitable for surface dating technique but in such samples, S/N ratio is expected to be lower as signal is contributed by a thin layer. On the other hand, materials having low attenuation coefficients can be used provided; the thickness of the sample is less than the range of β particles and remains constant during measurement. It is also implicit that the transparency of the material does not change during the measurement cycle as, a small change in the transparency effect the luminescence signal exponentially.

4.3 Dose Rate Estimation

4.3.1 Natural Dose Rate Estimation

For the luminescence dating of surfaces, dose rate estimation needs due care for several factors. A surface represents boundary between two different regions having different U, Th and K concentration (Fig. 4.5). Therefore, to determine dose rate to the surfacesample, the dose rate contribution from both of the regions need to be evaluated individually and then summed up to get the







final dose rate. Natural dose is contributed by α , β and γ radiations and as the samples/grains remain contiguous, irradiation across boundary needs assessment and ideally, the spatial distribution of the radioactivity is needed.

The alpha dose to the surface due to external region can be eliminated by removing the 20 μ m thick skin, either by etching or by polishing. The internal dose is calculated by considering infinite matrix assumption with proper use of the '*a*' value (i.e. alpha effectiveness (Aitken, 1985a; Aitken and Bowman, 1975; Banerjee et al., 2001)). In the present program, *a* value of 0.1 was used for rock surfaces.

$$\dot{D}_{\alpha} = a\dot{D}_{\alpha \text{ internal}} \tag{4.22}$$

However, the value can be changed depending upon the exact measurements for the sample matrix.

In case of γ gamma rays, the range is ~30 cm that is much higher than the thickness of the sample (which is ~1 mm), so there is negligible attenuation of gamma dose inside the natural sample. In computation of gamma dose rate the geometrical size of the surface is important. The geometrical size decides the computation of the gamma dose rate. In the program for dose rate computation extremum situation where the dimension of the rock is much higher than the gamma range was considered. Thus for a small point on the surface from where the sample for analysis need to be used, the dose rate contribution from the external and the internal region is half of the infinite matrix assumption i.e.

$$\dot{D}_{\gamma} = (0.5)\dot{D}_{\gamma \text{ internal}} + (0.5)\dot{D}_{\gamma \text{ external}}$$
(4.23)

Similar equation can be used for estimating they dose rate of U, Th and K.



Figure 4.6:Variation of β dose contribution inside the surface from two regions having different U, Th and K concentration. In this t is the thickness of the surface sample to be used, O is the dose evaluation point at some time. R_m is the range of β (ref: Aitken, 1985c).

Computation of β dose rates to the surface is complex as the β range is comparable to its thickness resulting in a gradient in the β dose rate at the surface. The total β dose rate comprises contribution by the external and internal matrix including the self-dose of grains /regions being analyzed. In the present work dose is computed as the average β dose deposited inside the surface of a given thickness from the two region of different radionuclide concentration. Fig. 4.6 shows the β dose contribution from the two regions. Considering the dimension of the surface is much larger than the β range the dose rate from the external region just at the surface is 50% of the dose rate from infinite matrix assumption. This dose rate at the surface attenuates with depth inside the sample (β dose contribution of region-1 in region-2 as shown in Fig. 4.6). Aitken, 1985b gives the estimate of the attenuation of dose as the function of depth for U, Th series in aluminium absorbers and suggests that the dose attenuates exponentially with attenuation coefficients of 1.54 mm⁻¹ and 1.78 mm⁻¹ in aluminium (density~2.7 gm/cm³) absorbers for U and Th respectively. Using these coefficients and the fact that they are inversely proportional to the density of the material, the attenuation coefficient for rock was estimated. For granitic rocks having density of ~2.657 gm/cm³, the attenuation coefficients are 1.51mm⁻ and 1.75 mm⁻¹respectively. The attenuation of coefficient for the ⁴⁰K was

estimated using Monte Carlo simulations using the methodology discussed in the Chapter 3 sections 3.2.1 and 3.3.1.1 and the attenuation coefficient was computed to be 2.97 mm⁻¹. The final average dose rate to a sample of thickness z due to external region was computed as

$$\dot{D}_{\beta ext} = (0.5) \dot{D}_{\beta ext \text{ infinite}} \frac{1}{z-d} \int_{d}^{z} e^{-\mu t} dt$$
(4.24)

Here, $\dot{D}_{\beta extinfinte}$ is the infinite matrix external β dose rate, *t* is the thickness of sample slice to be used *d* is the thickness of layer removed and μ is the attenuation coefficient. The above equation was used to estimate the contribution of external β dose rate for each of the individual radionuclide.

The other region contributing to the dose rate is the internal region. In this case, to the first approximation, change in the geometry of the contributing range sphere is responsible for dose variation in the sample. As the dose evaluation point moves from interior towards the surface, the volume of the region contributing to the dose decreases and at the surface only a hemispherical region of the interior region, with a radius equal to range of β particle deposits dose and hence the dose rate at the surface due to interior region is halved. In the deeper regions the dose evaluation point is surrounded by the similar matrix, so infinite matrix assumption is valid. Therefore, while estimating the dose rate to the sample slice of thickness *z* the fraction of infinite dose deposited at dose evaluation point will be similar to the volume fraction of the contributing region. Fig. 4.6 shows the geometry involved. At point O (Fig. 4.6) near the surface spherical "cap" like volume, will not contribute to the dose and only remaining region as shown will be contributing. The volume of the "cap" is given by

$$V_{cap} = \frac{1}{3}\pi x^2 (3R - x)$$
(4.25)

Where *R* is the range, x = R - z', where *z*' is the distance of dose evaluation point O from surface. Therefore, the fraction of volume contributing to the dose is given by

$$f_{v} = \frac{V - V_{cap}}{V}$$

$$= \frac{\frac{4}{3}\pi R^{3} - \frac{1}{3}\pi x^{2} (3R - x)}{\frac{4}{3}\pi R^{3}}$$

$$= \frac{4R^{3} - x^{2} (3R - x)}{4R^{3}}$$

$$= \frac{4R^{3} - (R - z')^{2} (2R + z')}{4R^{3}}$$
(4.26)

The average dose rate due to internal region can be given by

$$\dot{D}_{\beta int} = \dot{D}_{\beta int \, \text{infinte}} \frac{1}{z-d} \left| \int_{d}^{z} f_{\nu}(z') dz' \right|$$
(4.27)

and the average β dose rate to the sample can be given as

$$\dot{D}_{\beta} = \dot{D}_{\beta \text{ int}} + \dot{D}_{\beta \text{ ext}} \tag{4.28}$$

This is to be evaluated for each of the U, Th and K separately and then summed up to get the dose value. The program written in the Matlab can be used to evaluate this dose rate using the concentration of U, Th and K for internal and external regions, the thickness and the density of the sample. The dose rate estimated is not corrected for the water and if water is present in the external soil matrix, then the external dose rates for α , β and γ need to be corrected using water correction factors (Aitken, 1985c).

4.3.2 Laboratory Dose Rate

Laboratory irradiation for the regeneration of luminescence signal in the sample is done using a 90 Sr- 90 Y beta source with maximum β energy of 2.28 MeV. As the sample thickness is comparable to maximum β range, there is attenuation of beta dose and henceregenerated luminescence with depth. This necessitates estimation of laboratory dose rate that folds in the depth dependence of beta dose and is done using the average dose. The dose depth profile of the β source was taken from the (Wintle and Aitken, 1977), and normalized w.r.t. first dose point. Fig. 4.7 shows the 90 Sr- 90 Y beta dose profile inside the quartz. An empirical functional form of type

$$y = 0.3418 + (5.2)\sqrt{\frac{0.39625}{x}}J_1\left(\frac{2\sqrt{0.39625x}}{0.124}\right)e^{\left(\frac{-(x+0.39625)}{0.124}\right)}$$
(4.29)



Figure 4.7:Beta dose profile for ⁹⁰Sr source in quartz from Wintle and Aitken, (1977)

describes this curve. In this J_1 is the modified Bessel function of first kind. The average dose rate for the sample integrated over entire thickness to get the average laboratory dose rate as

$$\dot{D}_{av.Lab} = \dot{D}_{fine} \frac{1}{z - d} \int_{d}^{z} f_{sr}(z') dz'$$
(4.30)

Where \dot{D}_{fine} is the laboratory dose rate for the fine grain, which gives the dose at the surface of the sample, which attenuates with depth and quantity in the integral gives the integral of relative dose rate a function of depth.

Preceding subsections describes the effect of transparency and the dose rate evaluation and lay out the procedure to take due cognizance of these effects. In the following, the development of a 2D spatially resolved system is described.

4.4 Spatially Resolved Luminescence (SRL) Measurements

The effort in this approach is in-situ measurement of luminescence from individual grains embedded in a sample matrix. This can be done either by stimulating the relevant region with pointed laser beam and detecting the luminescence emitted using a photon multiplier tube (PMT) (Bailiff and Mikhailik, 2003) or by using an imaging system. The imaging system can be either a photographic plate (Hashimoto et al., 1986), Imaging photon detector (IPD: McFee, 1995) or Charge Coupled Device (CCD: Baril, 2004; Duller et al., 1997; Greilich et al., 2005). In imaging system, the entire surface is stimulated and luminescence emitted is imaged on to a position sensitive detector (Fig. 4.8). The luminescence signal is captured in form of time-integrated images and can be used for further analysis.

Development of Electron Multiplying CCD (EMCCD) based system was successfully attempted as a part of this thesis and is described below

4.4.1 The Schematic of the System

Fig. 4.9 shows the block diagram of the system that comprises,

- a. instrumentation related to stimulation system, user interface for its control
- b. design of optical arrangement for imaging the luminescence on to the EMCCD
- c. data acquisition involving EMCCD control andimage acquisition and

d. dataprocessing, which includes image registration and analysis of the acquired image for final D_e estimation.

In this system, the sample can be stimulated either by heat or by light in a controlled and prescribed manner. A LabVIEW based program serves as interfacing software to manage the functioning of the controller. The luminescence emitted by the sample is imaged on to the EMCCD maintaining 1:1 ratio. The luminescence signal is captured by EMCCD as 2D grayscale time integrated images. A timer pulse is used to synchronize the actions of EMCCD with the stimulation system. The captured images are then processed in the image processing programs that were written in Matlab to give the spatially resolved dose estimates. The following sections discuss each of the unit in some detail.

4.4.2 Stimulation Unit

In this system, we can stimulate the sample both thermally and optically The stimulation unit is stabilized using feedback control. The Heating unit (Fig. 4.10) consists of a nichrome heater plate with resistive heating and a feedback control. The system enablesheating of sample up to 500°C temperature in a programmed manner at variable rates varying from 0 to 10°C/s. The temperature is monitored by a K-type Chromel-Alumel thermocouple (spark welded at the bottom of heater plate). The thermocouple has a sensitivity of ~41 μ V/°C. The temperature measurements using thermocouple were compensated using an ice point compensation chip to correct for the variations in the ambient temperature. The system provides reproducible and stable temperature profile with error in temperature being ≤±1% of the target temperature. The graph in Fig. 4.10 shows the performance of the heating system.The measured temperature closely follows the driving signal and the error in the temperature is nearly zero.



Figure 4.8:Spatially resolved luminescence using imaging method



Figure 4.9:Block diagram of the system for spatially resolved luminescence



Figure 4.10:Heating unit with nichrome heater plate





The light stimulation unit consists of two types of light emitting diodes: Blue (NSPB-500S) and an Infrared diode (HSDL-4230). The blue diodes have a peak intensity of ~470 nm with FWHM of ~15 nm, the forward angle of ~15° and has maximum power dissipation of 120 mW. The IR diodes have emission at 875±17 nm, power dissipation of 260 mW and the forward angle of 17°. Fig. 4.11b,d gives the emission spectrum of Blue and IR diodes respectively. The intensity of the diodes can be, 1) varied from 0-100% of the total power, and 2) ramped at variable rates linearly. A cluster of 30 diodes each of Blue and IR arranged on circular ring structures (Fig. 4.11a,c) appropriately located at an angle such that these together provide a uniform intensity at the location of a sample on the heater position. The diodes are housed in the aluminium holder, which also acts as a heat sink and maintains diode at room temperature ensuring that their emission wavelength does not change. The intensity of the diodes is continuously controlled using a photodiode and any change or difference in the intensity from programmed intensity is compensated by means of feedback loop.

4.4.3 Interfacing

The stimulating unit is programmable and the parameters are set in the interfacing software built in LabVIEW (Fig. 4.12). Several options of stimulations are possible such as simultaneous thermal and optical stimulation, stage heating, ramping of optical signal, reheating for black body radiation etc. Parameters like stimulation temperature, heating rate and heating duration can be set for thermoluminescence readout and for OSL the software selection provides for choice of stimulation: constant wave or ramped with preset rate. The selected parameters for the stimulation are saved in the sequence file and the program is executed such that the data can be accessed in real time (Fig. 4.12). The system has the built in feature that inform on the status of each of the parameters in real time.

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Figure 4.12:Interfacing software developed in LabVIEW

4.4.4 Optical Arrangement

The luminescence emitted is imaged on to EMCCD camera by means using a 1:1 Imaging optics, which was a challenging task as the photon counts are generally low. Although the current generation EMCCD cameras are capable of single photon efficiency, however, as the signal duration in luminescence dating studies are small, signal integration over a long time period is not possible. Thus maintaining a good S/N ratio along with a faithful optical imaging area is prerequisite. To collect sufficient light, the solid angle of the objective lens should be as large as possible with the optical aberrations at the minimal levels. Ideally for a perfect optical system all the parallel rays after passing through a lens should converge at a single point, however real optics is never perfect and such rays do not converge to a single point resulting in the aberrations bothChromatic and monochromatic aberrations.



Figure 4.13: Chromatic aberrations of the lens

Chromatic aberrations (Fig. 4.13) arise because of the wavelength dependence of the optical components results in focusing of different wavelength at different focal points and therefore deteriorate the image quality. These aberrations are minimized by using a combination of lenses with similar refractive index but with opposite signs. Achromatic doublet lenses are generally used to minimize chromatic aberrations. The other type of aberration is monochromatic aberration and arises because of geometrical imperfections (Fig. 4.14) of the optical components. These can be

- 1. Spherical Aberration
- 2. Comatic Aberration
- 3. Astigmatism
- 4. Field Curvature and
- 5. Distortions

In order to understand and quantify aberrations several theories were proposed. The monochromatic aberrations mainly arise due to surface deformities and results as a consequence of assumption that $\sin(\theta) \sim \theta$, which is not the case. The paraxial behavior can be explained using first order theory, however the deviation from this theory is explained by considering the next order terms. This order includes the terms of $\sin(\theta) \sim \theta + \theta^3/6$, which are third order termsand can be used to predict aberrations.



Figure 4.14:a) and b) Spherical aberrations in different lens configurations. Small refraction angle configuration (b) has less SA aberration c) Comatic aberration d) Astigmatism e) Field curvature f) Distortions

Based on theoretical estimation using Fermat's principal it is known that aberrations can be minimized by careful selection of the lens system. Most of geometrical aberrations can be reduce by choosing lens or combination of lenses, such that refraction angle (θ) is minimum. A combination of lenses having different signs but similar magnitude of refractive index can help in minimizing chromatic aberrations.

Conjugate Ratio (object/image)	Plano-Convex	Bi-Convex	Achromatic Doublet	Cylindrical Plano-Convex
Infinite	Better	Good	Best	Better
10:1	Better	Good	Best	Better
5:1	Better (pair)	Better	Best (pair)	Good
1:1	Better (pair)	Better	Best (pair)	Good

Table 4.1:Qualitative comparison of the image quality obtained with different lens combination for different lenses

For our system, several possible lens combinations were tried out in order to obtain a faithful image. Table 4.1 shows the qualitative comparison of different lenses for different object to image ratio. It was found that a pair of achromatic doublet lens in conjugate mode provides the best option for our system. Consequently, a pair of achromatic doublet lens (Fig. 4.15b) having 50 mm diameter and 61.2 mm back focal length, withtransmission in 400-700 nm for detection in blue region was chosen. For UV imaging, a separate pair of fused silica lenses with UV transmission is needed.

Fig. 4.15a shows the ray diagram of the optical arrangement. In this, the two achromatic doublet lenses are placed in the conjugate mode such that the planeside of the first lens is towards the sample. This is to minimize the spherical aberrations. The first lens converts the rays of light into parallel beam, which is then reflected by a mirror placed at an angle of 45° towards second lens. The second lens then focuses these parallel rays of light on to the chip of EMCCD camera. The optical glass filters placed in between the second lens and EMCCD helps in analyzing a particular band of the luminescence. All these optical

components are housed inside a finely designed mechanical arrangement (Fig. 4.15c). This mechanical arrangement offers flexibility in holding the optical components, fine focusing of the optics to obtain a sharp image, flexibility in easy sample loading and changing, flexibility in changing of the optical glass filters and provides a path for luminescence light, shielding it from room light or stray light.

4.4.5 Data Acquisition

The luminescence imaged by optics is acquired by the EMCCD camera (Fig. 4.16, Andor iXON DU-897 back illuminated EMCCD camera with UVB coating). Fig. 4.16 shows the response of the EMCCD camera with a peak efficiency of 95% at about 550 nm, ~80% in blue region (450 nm) and 35% in UV region (380 nm). It has a pixel array of 512×512 with16 µm×16 µm each resulting in a chip size of 8.2 mm×8.2 mm and can function in both frame transfer and conventional mode. At full resolution, it has a maximum frame rate of 35 frames per second. It has single photon counting efficiency and cango up to a gain of 1000 inelectron multiplying (EM) mode. In EM mode the signal intensity is increased by impact ionization which is similar to PMT and readout noise is <1e per pixel. In addition to EM gain there is conventional gain, which can further enhance the signal intensity. The internal Peltier cooler cools the EMCCD chip up to -100°C thus reducing the thermal noise. The integration area can be increased by binning the pixels together. This is however at the expense of resolution but with improved S/N ratio. The images can be acquired for different times with different readout rates (maximum of 10 MHz, up to a 16-bit dynamic range) and can be accumulated for fixed time period or can also be recorded as a kinetic time series, thus recording the variation of the signal intensity with the time. The data acquisition can be initiated both by internal and external triggering. In external triggering, the data acquisition can follow an external clock and can acquire data depending upon the set parameters after receiving the external pulse.

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c)

a)



Figure 4.15:a) Ray diagram of the optical arrangement b) Achromatic doublet lenses used c) Mechanical housing for optical components



Figure 4.16: Andor iXON DU-897 EMCCD camera and its response curve

4.4.6 Measurement Procedure

Fig. 4.17a, b shows the whole process. First of all focusing is done, then parameters are set in the interfacing software and sample is stimulated. The luminescence is thus recorded as a time series in form of images by the EMCCD camera. Fig. 4.17a shows one such image acquired when a quartz sample is heated linearly with time. This image corresponds to 110°C peak of quartz and the graph shows the variation of intensity of images in the time series with corresponding heater plate temperature. This is the typical glow curve of the quartz.Similarly the Fig. 4.17b shows the focusing and the luminescence image and time variation of image intensity when a feldspar samples is stimulated with IR LED. The graph shows the typical IRSL decay curve of the feldspar. The intensities of image pixels correspond to the intensity of the luminescence signal emitted by that particular area of the sample.

4.4.7 Data Processing (Image Processing)

As the luminescence signal is proportional to the dose, so by analyzing the intensity of individual pixel dose acquired by a region can be estimated. In order to estimate the dose from luminescence images, images are to be processed and this is done in two steps.

4.4.7.1 Processing in Andor Solis

The first hand image processing is done in the Andor Solis (version 4.12.30003.0) software provided by EMCCD Company for data acquisition. In this software two important functions are performed. First one is to integrate the signal intensity of images for particular time duration. The images in this time duration could be the images corresponding to TL peak of the sample in case of TL measurements or it could fast component of luminescence signal in case of OSL/IRSL measurement. Additionally a constant background in the images needs to be subtracted. Finally the processed images are saved as *.fits file. These *.fits file are then processed in the five programs written in the Matlab to get the pixel wise or region wise dose value. Following is the description of the functioning of these programs.

4.4.7.2 Matlab Analysis Programs

A total of five programs were developed for the image processing and data analysis. These are described below.

4.4.7.2.1 Read out: The first program

The first program is an image-reading program. The *.fits files generated in Andor Solis for different doses are imported as two-dimensional arrays. During background subtraction in Andor Solis, some of the pixel values become negative; this is because of randomness of the background values. As negative values have no meaning and lead to erroneous results during calculations so they need to be set to 0. This program checks entire array of all the images for negative values and then sets these values to zero. These are the images, which are to be further processed for D_e estimations.

In addition to this, there is a provision of importing additional set of *.fits images which corresponds to main images. This second set of images is used for alignment of the images in Matlab program during subsequent analysis. These



Figure 4.17:a) Glimpse of image acquired after focusing and the corresponding TL curve. The image shown is of 110°C TL peak of quartz, b) Glimpse of image for infra red stimulation.

could be the images of the sample recorded after measurement with a faint LED light source seen by the camera through the disc, or the images corresponding to bright peaks (like 110°C peak of quartz). Such frames enable alignment of positions in each frame. The main images can also be used for the alignment provided the discs have sufficient number of bright grains to be used as marker for alignment. In that case, second set of images is not required.

4.4.7.2.2 Image Alignment: the second program

In the measurement sequence, the natural luminescence of sample is first recorded and then regeneration laboratory dose is given in an irradiator to regenerate the luminescence signal. The sample is then again placed in the



Figure 4.18:Selection of the control points in the second program to align the regeneration dose images w.r.t. natural luminescence base image.

sample position in imaging system and recorded. However, while repositioning the sample the same position cannot be regained and the sample gets displaced or rotated w.r.t. initial measurement and thus the corresponding images of luminescence measurements get shifted w.r.t. each other. In order to estimate the D_e correctly the images corresponding to different doses are aligned up to single pixel accuracy. This process is called image registration. The image registration is done by a program where the images are aligned w.r.t. a base image (in this case the natural luminescence signal image is considered to be the base image and all other images are match aligned with this image) by means of a set of the control points (Fig. 4.18). The control points are a set of the identifiable features in the two images, which are to be aligned. These control points are selected manually in the control point selection toolbox of the Matlab. The selected control points of two images are then used to form a transformation matrix. This transformation matrix operates on the array of the image corresponding to regenerative dose and aligns it with the base image. The requirement of number of control points needed for defining transformation is ≥ 2 but generally, ~10 control points are selected to give an optimum alignment.

Quite often, the main images used for dose evaluation do not have sufficient number of distinct identifiable features to be used as control points. In such cases, second set of images imported in first program can be used for selecting the control points and then defining the transformation matrix. The transformation matrix is then operated on the main images as usual in order to align them in accordance with the natural base images.

4.4.7.2.3 Fine Alignment: The third program

This program further improves on the alignment to achieve single pixel accuracy in the alignment. This is done by cross correlating the intensity of pixel around the control points. In this a region of11×11pixels is defined around each selected control point in the input and the base image and then correlation between the values at each pixel in the regions is calculated. The position with highest correlation is selected and used as a new optimal control point. In this methodology, the maximum difference of the 4 pixel is allowed from the original control point. If the difference is more than 4 then the original input points are provided as output without any modifications. After this, a new transformation matrix is defined using optimal control points obtained after correlation. This matrix then operates on the images corresponding to regenerative dose to give the images aligned up to single pixel accuracy with the base image. Fig. 4.19a

shows the unaligned images after processing in first program and Fig. 4.19b gives the corresponding aligned images after processing in second program and third program.

4.4.7.2.4 Dose Evaluation: The Fourth and Fifth Programs

These programs are used for the dose evaluation. The fourth program is used to estimate the pixel wise dose and the fifth program is used to estimate the region wise dose values. In this, the value of luminescence signals corresponding to each region (or pixel) of images for different dose values and dose values are used as input and a growth curve of saturating exponential form as given below is fitted

$$y = a \left[1 - e^{-\frac{x+c}{b}} \right]$$
(4.31)

Here *a*, *b*, *c*are the fitting parameters, *y* is value of luminescence signal intensity and x is the dose value. The values of a, b, and c are estimated by minimizing the chi-square value. Finally, dose value corresponding to each region (or pixel) is tabulated and stored along with the fitting parameters in form of array.

4.4.8 System performance

4.4.8.1 Dose Recovery Test

In order to test the system dose recovery tests were performed. In this a known dose was given and recovered using regeneration method. Fig. 4.19 shows one such example for quartz. In this, D_e of 28.4 Gy was given and treated as unknown dose. Then the unknown dose was recovered by TL regeneration method by giving incremental beta doses and recording corresponding luminescence image. These images were then processed by the methodology described in previous section. They were corrected for the background, aligned using set of control points and using correlation function and finally region specific dose values are evaluated.Fig. 4.19c shows the nature of growth curve





c)

Figure 4.19:a) Luminescence images corresponding to a known given dose and the regeneration dose. b) Corresponding aligned images after processing in second and third program. c)regeneration growth curve for the region marked in (b) and estimated dose value.

and the corresponding dose value for the grain marked in Fig. 4.19b. Fig. 4.20a shows the histogram of doses scaled with given doses. Most of the recovered doses are within $\pm 10\%$ of given dose as shown by the band signifying the limits and all the values are within $\pm 20\%$ limits. Similar measurements were performed for TL regeneration method and IRSL regeneration method of feldspar. Fig. 4.20b and c shows the respective results.

4.4.8.2 Case Study

Feldspar: As a case study, a sample RYK-1mG1 from a site Rayeka along the banks of R. Mahi was used and coarse grain (90-150 µm) feldspar fraction from this was separated using standard protocol. This sample was previously analyzed by OSL of quartz. The De's for quartz using PMT system were treated as independent control. The feldspar fraction was then mounted on a stainless steel disc using silicon oil and measured using EMCCD system and De's were determined from different ROIs. Fig. 4.21 shows the results. It can be seen that the range of the doses obtained from different ROIs using EMCCD camera (Fig. 4.21a) are similar to doses obtained using single aliquots SAR ages on quartz. with the exception of one dose value (Fig. 4.21b). The average dose from feldspar ROIs (excluding the single high dose) was 147±27 Gy and the corresponding dose rate for feldspar was 1.95 Gy/ka. These gave an age of 75.6±15 ka. On the other hand, the average dose value for the quartz is 140±5 Gy and dose rate is 1.853 Gy/ka, which gives an age of 75.6±8 ka. Thus, the age obtained using ROI matches exactly with the dose obtained using quartz confirming that system is working perfectly and can be used for measurement of the natural samples.

Quartz: The system was also tested for the natural sample of quartz VP-04-08 which is fluvial sample from the Vijapur region along the banks of River Sabarmati in western India. The coarse grain (90-150 μ m) quartz sample was separated using standard protocol and D_e measurements were done in EMCCD system using TL regeneration method. The images were then processed and D_ewere determined for different ROI. Fig. 4.21c shows the result.

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Figure 4.20:a) Histogram showing the ratio of the estimated and given dose value for TL regeneration. b) Histogram showing the ratio of the estimated and given dose value for IRSL regeneration.Shaded area shows the ±10% range of given dose



Figure 4.21:a) Histogram showing the dose values and age results for feldspar sample RYK-1mG1 from Rayeka region estimated in EMCCD system. b) Histogram showing the dose values and age results for same sample estimated using PMT based Risoe TL/OSL system. c) Histogram showing the dose values and age results for quartz sample VP-04-08 from Vijapur. The results are compared with 5 discs estimate of PMT based Risoe TL/OSL system.

Using this we obtained an average dose of 252.6±15 Gy. The dose rate of the sample is 2.34±0.2 Gy/ka giving an age of 107±11 ka. In order to compare it with the PMT based system 5 discs of same sample were measured using the TL regeneration method in RisøTL/OSL reader and an average dose of 287±5 Gy was obtained giving an age of 123±10 ka. These ages are to extent similar considering that error limits are high and more discs in the PMT based system are needed to give the correct picture of distribution. In this case, also it can be inferred that EMCCD based system, the software and the computational schemes were working as expected and could be used routinely.

4.5 Summary and Discussions

In this work, an instrument for spatially resolved luminescence studies was developed including all the instrumentation and software programming. Methodological studies were conducted to test the functionality of the system. The system worked well for two control samples and the results provide confidence in its routines usage, in several possible applications in luminescence chronometry and dosimetry techniques.

Computations related transparency and dose rates carried out to set the stage for a rigorous basis for surface dating technique. The results shows that low transparency material can be suitable for surface dating, but S/N ratio can be the limiting factors. Contrastingly, the high transparency materials can be used provided their thickness is less than beta range, thickness and transparency remains constant during the measurements.

Development EMCCD of based spatially resolved luminescence measurement system and image analysis software were prepared and tested. These required mathematical calculations, Monte Carlo simulations, experimentation, instrumentation and programming. The system was designed and tested in house along with all the electronics, optical arrangement and programming for analysis. The system is capable of doing both spatially resolved TL and OSL measurement and completely tested for the TL and IRSL stimulation using dose recovery tests for standard samples. The system is also

tested for finding the age of natural samples using TL regeneration technique. However, system is yet to be tested for BLSL and OSL of natural quartz samples. In case of IRSL the luminescence signal for natural sample was a low and the power of the light stimulation source needs to be increased in order to get the detectable signal. Therefore, the existing diodes may have to be replaced by the laser diodes for giving the sufficient light for stimulation.

Chapter-5

Dose Distribution: Improvement in Measurement Protocol

5.1 Introduction

Single aliquot regeneration protocol is increasingly used for the estimation of D_e of quartz. The protocol involves multiple measurements on the same aliquot using regeneration method. The natural OSL is first measured and then an OSL vs. dose growth curve is constructed by with due correction for changes in the sensitivity that occur during measurements. Murray and Roberts, (1998);

Murray and Wintle, (2000) developed the SAR protocol for D_e estimation (Fig. 5.1).



Figure 5.1:SAR protocol suggested by Murray and Wintle, (2000)

The D_e is calculated for each aliquot by repeated regenerative procedure involving the measurement of the natural OSL (L_0) (cycle n = 0, irradiation = 0 Gy) by exposing the aliquot to an optical stimulation preceded by a pre-heat (Fig. 5.1) to isolate the most stable signal. This is done by generating a D_e vs. preheat plot and generally a plateau is seen in the region 200-280°C. Typical preheat durations are 10-60s. The OSL signal is subsequently regenerated by a series of irradiation (D_n) –preheat–optical stimulation (L_n) cycles (typically n = 5).

Three additional steps following each natural and regeneration OSL measurements are used to correct for possible changes in the luminescence sensitivity of an aliquot during preheat and read out at each stage. These is done by addition of a small (e.g. few Gy) test dose, a cut heat TL readout to 160°C (to remove unstable signal), and an optical stimulation to detect the OSL resulting from the test dose (T_n). Murray and Roberts, (1998) show that the intensity of

TL/OSL measured after T_n is correlated with the luminescence intensity of preceding regeneration signal, so that T_n provides a way to correct for the sensitivity changes during the repeated measurement as

$$L_{n(corr.)} = \frac{L_n}{T_n}$$
(5.1)

In addition to this, two tests namely, repetition of the one of regeneration dose and measurement of signal without giving any dose (i.e. zero dose) are done to check for the reliability of sensitivity corrections and thermal transfer (charge transfer from deeper traps as discussed in chapter 1). Finally, the background and sensitivity corrected OSL intensities, are plotted as a function of laboratory beta dose to construct a regeneration growth curve and the D_e values are estimated by interpolating the intensity of natural signal on the regenerated growth curve.



Figure 5.2:Growth curve of one of the natural sample.In this natural point lie way above the growth curve of the sample.

Wintle and Murray, (2006) summarize the present status of the SAR procedure. SAR regeneration technique assumes that any changes in sensitivity during preheating-optical stimulation-irradiation cycles can be monitored and corrected by evaluating either OSL or 110°C TL responses to test doses

administered following each preheat and optical stimulation cycle (Murray and Wintle, 2000). This protocol provides a high precision (<5%) in D_e estimates by using large number of aliquots and then treating them as independent measurements. Analysis of the D_e distribution also helps in isolating the most bleached fraction. While on someoccasions the SAR ages have been in reasonable agreement with independent age controls (e. g., Hansen et al., 1999; Murray and Mejdahl, 1999; Strickertsson and Murray, 1999), there have also beeninstances of disagreement (Long et al., 2011) and samples with anomalously high natural OSL intensity that lies significantly beyond the saturation intensity of the regenerated luminescence vs. dose growth curve (Fig. 5.2). Such instances provide indication that the natural OSL and the regeneration curves may not be measured with the same OSL sensitivity. In the present thesis, we examined the magnitude of sensitivity change and developed a protocol for the same for routine use.

5.2 The Samples

Samples used in this study were collected from a variety of depositional environments viz., 1)aeolian sands(Thar Desert and Australia),2) fluvial environments in different regions (flash floods, floodplains and slack water deposits) from river Alaknanda (Himalaya) and Narmada (Central India), from Namibia, Bangladesh and Vietnam) and from 3) lacustrine environments (Thar Desert). The use of conventional SAR protocol indicated all the samples were well behaved with recycling ratios of 1.0 ± 0.1 , and dose recovery within $\pm 10\%$ of given dose. The details of some of these samples and measurement procedure followed are described in Jaiswal, (2005); Nagar, (2007); Singhvi et al., (2011).

5.3 Sensitivity Changes during Measurements

A critical assumption in the SAR procedure is that any change in the luminescence sensitivity of the sample can be corrected using test dose OSL/TL. Earlier studies indicate that OSL / 110°C TL responses to test doses measured

subsequent to regenerative cycles are sufficient to quantify sensitivity changes during construction of the regenerated growth curve. It is implicitly assumed that preheat and the OSL measurement of the natural OSL signal does not alter the luminescence sensitivity of the sample. However, based on 110°C TL and OSL sensitivity correlations, previous studies have documented changes in the natural OSL sensitivity during pre-heating and optical stimulation of natural samples (Stokes, 1994a; Stokes, 1994b). In a SAR protocol, the 110°C TL or OSL measurements do not track the sensitivity before preheat and natural OSL measurement and only the post regeneration sensitivity is tracked. Consequently for the samples where the sensitivity changes occur during the natural OSL readout, the application of the standard SAR procedure as used now, could be systematically inaccurate (higher or lower). Thus, there is a need to monitor sensitivity changes during measurement of natural signal itself.

In order to quantify the sensitivity changes during natural measurements, sensitivity changes during repeated OSL readout and heating cycles was examined in detail. Both OSL only and TL (450°C) only cycles were first examined, which is then followed by combined OSL and preheat cycle (as in standard SAR protocol).

5.3.1 Sensitivity Changes in OSL Measurement Cycle

Thesensitivity changes during repeated TL/OSL and irradiation, was monitored using the intensity of 110°C TL peak from a fixed test dose at each stage. Fig. 5.3 gives the experimental protocol. In this, a test dose (TD) of ~30 Gy was given after each step and the 110°C peak was recorded with a fixedinterval between the irradiation and read out (to ensure that signal loss due to thermal decay of 110°C was identical for all samples). Each read out was done up to 160°C, to ensure complete erasure of the peak. The sequence was repeated several times for a given regeneration dose and for OSL recording for 1000s.



Figure 5.3: Steps followed for the monitoring the sensitivity changes during repeated dosing, heating and OSL(1000 s) or TL(450°C). In this x=0 for natural sample and x=1–n for laboratory dose

Fig. 5.4 shows the variation of sensitivity with number of cycles. In this, the 110° C TL peak signal is normalized with respect to 110° C TL peak (TL₂) following first TD.

The sensitivity changed with each step in a cyclic manner and overall the sensitivity increased. The change was aliquot dependent and the change between TL_1 and TL_3 ranged from 1 to up to 1.3 or more. In general, for regeneration doses the sensitivity after an OSL readout washigher thanbefore OSL read out, suggestingpossibility of photo- transfer of charges from deeper traps to OSL traps (similar to that reported byBailiff et al., 1977). The change in sensitivity during natural OSL measurement is seen (Fig. 5.4). The sensitivity changes significantly from TL_2 to TL_3 (up to 20%). This indicates that the test dose OSL signal is recorded at sensitivity different from the natural OSL signal

(in this case the sensitivity decreases, so TD signal is recorded at lower sensitivity). Therefore, this cannot be used for correcting sensitivity of the natural



Figure 5.4: Sensitivity variation during repeated OSL(1000 s) measurement cycles, sensitivity is monitored by means of 110°C TL peak. The sensitivity is normalized with respect to 110°C TL peak for natural samples obtained by giving a TD

OSL. However, as the sensitivity changes during the regeneration cycle is cyclic and proportional for regeneration and TD signal, so TD signal can be used to correct for sensitivity changes in regeneration signal (cycle no. 3 onwards). The resulting growth curve however correspond to a sensitivity that is different from the natural sensitivity. The interpolation of natural signal on such regenerated curve constructed using a different sensitivity, leads to systematic errors and, a correction is needed.

5.3.2 Sensitivity Changes during Heating

This measurement used a similar protocol described above, except that the OSL (1000s) step was replaced with TL (450°C) read out (Fig. 5.3). Fig. 5.5 shows the variation of sensitivity of 110°C TL peak with the repeated cycles of irradiation and TL measurements. The values in graph are normalized to TL_2 ,

which is the sensitivity of natural samples. Following inferences can be drawn from the Fig. 5.5.



Figure 5.5: Sensitivity variations during repeated TL(450°C) measurement cycles.

- a) Similar to OSL measurements, the sensitivity changes are also cyclic and show an overall increase.
- b) The sensitivity before a TL (450°C) readout is lower (Fig. 5.5) than the sensitivity after TL (450°C) suggesting thermal transfer during the TL (450°C) readout.

5.3.3 Combined Preheat–OSL Cycle

Fig. 5.6 shows the modified SAR protocol that monitors the sensitivity changes during the measurement of natural OSL. To monitor the sensitivity change during preheat and the measurement of natural OSL (i.e. the OSL signal in the samples as received), a test dose (TD1) was given before preheat (240°C, 10s) and its TL_a in the temperature range Room Temperature (RT) –200°C was recorded. Similarly another test dose TD2 is given after a preheat (240°C, 10s) and corresponding TL_b (RT-200°C) was recorded. Natural OSL was then read

and a third test dose TD3 was given and TL₃ (RT-200°C) was recorded. The standard SAR protocol was then carried out. In view of the addition of beta dose prior to the read out of natural OSL, the dose (TD1+TD2) is to be subtracted from the palaeodose estimated by the NSC-SAR protocol.To avoid complicating effects of either low temperature trap population during laboratory irradiation or photo-transfer to low (<300°C) temperature traps during optical stimulation anthermal cleaning stepof200°C @ 2°C/s was included prior to the test dose irradiation after OSL. The later part of the SAR protocol remained unchanged. This procedure permitted us to construct a SAR growth curve and monitor sensitivity changes at each stage of its construction using integrated TL from 90–120°C and in view of its linear relation with OSL sensitivity (Murray and Roberts, 1998; Murray et al., 1997; Murray and Wintle, 2000; Stokes, 1994a; Stokes, 1994b; Wintle and Murray, 1999). The linear relationship was confirmed for each of the samples (Fig. 5.7).

The experimental procedure in Fig. 5.6 permitted,

- Estimation ofthechanges in the sensitivity of each aliquot due to preheating and optical stimulation during measurement of the 'natural' OSL signal
- 2. Observation of sequential changes in sensitivity during measurement of both the natural and regenerated OSL and
- 3. Assessment of the reproducibility of observed sensitivity changes by comparing results for aliquots from a number of samples.
- 4. Examination of the net effect of change in natural sensitivity on D_e by introducing a correction factor, which can be used to correct for the D_e for changes due to sensitivity changes.

Table 5.1 shows the experimental results. The experimental results discussed above suggest significant sensitivity changes during measurement of the natural OSL signal. We therefore suggest a routine use of a modified natural sensitivity corrected SAR (NSC-SAR) procedure (Fig. 5.6). This procedure includes in it the correction for the sensitivity changes during the read out and preheat of natural OSL and is analogues to Stokes, (1994b).



Figure 5.6: Modified NSC-SAR protocol used to correct for the sensitivity changes occurring during the measurement of natural signal.

Table-5.1: Equivalent dose (D_e) values before and after NCF correction and their percent change

		De	0/ shares				
Sample	Without o	correction	After co	orrection	70 change		
	Least 10 %	Mean	Least 10 %	Mean	Least 10%	Mean	
MHK-07-01	29.7±0.5	46.0±0.2	25.7±0.6	38.7±0.2	13.6	16	
MHK-07-02	26.8±0.2	51.4±0.09	23.9±0.2	47.8±0.1	10.9	7	
MHK-07-03	47.7±0.5	72.5±0.2	41.6±0.8	54.3±0.4	12.7	25.1	
MHK-07-04	61.3±1.1	86.9±0.4	50.6±1.0	76.1±0.5	17.5	12.4	
MHK-07-05	66.1±0.4	80.3±0.2	58.5±0.4	69.7±0.2	11.5	13.2	
MHK-07-06	27.0±0.2	35.7±0.1	26.3±0.2	32.1±0.1	2.5	10.2	
MHK-07-07	36.5±0.3	43.1±0.1	32.4±0.2	36.9±0.1	11.2	14.2	
MHK-09-09	50.9±1.0	57.6±0.6	34.3±1.3	41.3±0.7	32.7	28.2	
MHK-12-09	60.9±1.2	69.4±0.8	38.7±0.9	43.7±0.5	36.4	37	
MHK-13-09	67.1±2.5	82.2±1.4	40.4±1.7	50.3±0.8	38.8	39.8	
MHK-15-09	75.2±1.9	85.7±1.2	47.6±1.1	51.0±0.8	36.7	44.4	
R16-TL3-OXF	9.3±0.3	13.1±0.2	7.4±0.4	10.5±0.2	20.4	19.8	
R16-TL6	20.2±0.5	25.1±0.3	14.9±0.7	22.9±0.5 26.		8.8	
R16-TL7	11.4±1.2	17.9±0.6	8.2±0.9	2±0.9 12.9±0.5 2 ⁻		27.7	
TRMT-T	1.4±0.3	3.3±0.2	2.8±0.3	4.2±0.2	104.2	28	
TRMT-B	4.4±0.4	9.0±0.3	3.0±0.6	8.9±0.3	1	31.4	
820/2*	-	17.2±1.1	-	16.7±1.5	-	3	

833/3* - 19.8±1.2 - 24.9±1.7 - 802/2* - 6.2±0.4 - 5.6±0.8 - 827/1* - 13.4±1.1 - 13.1±1.0 - BJ-1* 9.7±1.8 25.7±1.2 7.8±1.6 20.2±1.2 20	9.7
802/2* - 6.2±0.4 - 5.6±0.8 - 827/1* - 13.4±1.1 - 13.1±1.0 - BJ-1* 9.7±1.8 25.7±1.2 7.8±1.6 20.2±1.2 20	9.7
827/1* - 13.4±1.1 - 13.1±1.0 - BJ-1* 9.7±1.8 25.7±1.2 7.8±1.6 20.2±1.2 20	2.2
BJ-1* 9.7±1.8 25.7±1.2 7.8±1.6 20.2±1.2 20	
	21
BJ-2* 9.4±0.5 17.5±0.7 8.0±1.0 15.7±0.6 16	10
BJ-5* 14.1±1.0 22.2±0.9 13.7±0.7 21.3±7.3 3	4
NB-1* 34.0±0.2 58±14 31.6±1.8 56.2±1.7 7	3
NB-3* 10.1±0.7 23.0±2.0 8.3±1.8 19.1±1.0 18	17
9-4* 2.2±0.3 2.8±1.5 0.80±0.03 1.20±.0.03 63	57
BNG-1* 3.2±0.3 5.6±1.6 2.3±0.7 5.3±1.7 28	5
VPN-5* 12.1±0.7 32.0±3.0 10.2±1.8 31.1±1.0 15	3
4-11-3* 0.10±0.01 0.80±0.20 0.10±0.01 0.75±0.2 -	6
OTS-1* 19.4±5 30.4±9.2 18.2±0.6 28.2±9.7 7.8	6.6
OTS-2* 3.4±0.5 5.7±1.6 2.9±0.4 4.9±1.5 16.3	17.2
OTS-3* 18.2±0.5 27.3±7.0 13.4±0.4 21.9±5.5 24.7	35.8
OTS-4* 8.5±2.8 27±14 6.2±2.0 19.8±9.2 36.4	37.1
OTS-5* 1.7±0.1 2.3±0.6 1.4±0.1 2.1±0.5 9.5	21.4
RW-1* 10.2±1.8 24±12 8.2±2.0 21±13 16.2	24.4
RW-1* 10.2±1.8 24±12 8.2±2.0 21±13 16.2 RW-2* 3.3±0.5 7.8±4.0 2.7±0.5 7.2±3.2 8.3	24.4 22.2
RW-1* 10.2±1.8 24±12 8.2±2.0 21±13 16.2 RW-2* 3.3±0.5 7.8±4.0 2.7±0.5 7.2±3.2 8.3 RW-3* 3.8±1.5 12.1±5.1 3.0±1.0 9.2±4.0 31.5	24.4 22.2 31.0

MVW-10*	1.0±0.2	3.0±1.4	0.8±0.2	2.7±1.3	11.1	12.5
MVW-11*	28.6±4.1	40.4±8.0	22.6±3.5	32.1±6.5	26	26
MVW-13*	10.3±1.6	25±10	8.4±1.1	20.0±7.2	25.5	22.6

*These samples were analyzed by Dr. Manoj Jaiswal and Dr. Y. C. Nagar

The modified SAR procedure invariably reduces the scatter in the palaeodose distribution suggesting that some of the dispersion in the palaeodose arises due to sensitivity changes and not due to poor bleaching or the heterogeneity of radiation field. A number of the samples were analyzed using this modified NSC-SAR protocol.Apart from the samples analyzed for present work, some of the samples were also analyzed in the work by Dr. Y.C. Nagar and Dr. Manoj Jaiswal, which are also tabulated with present results to give a complete picture of the protocol.



Figure 5.7: Correlation between TL and OSL

5.4 NSC-SAR Protocol: Results

5.4.1 Changes in 90–120°C TL Sensitivity during Experimental Procedure

A wide range of behavior was observed in the samples, (Fig. 5.8, Table 5.2). Differences were seen even for aliquots of same sample. Thus, while for some aliquots no significant change in the sensitivity during the measurement of the natural OSL was seen, majority of aliquots exhibited sensitivity change either during pre-heating and/or optical stimulation. Table 5.2 shows that the sensitivity can either increase or decrease during the read out of the natural OSL and for a majority of the samples, the ratio of the TD TL intensity after and before OSL (TD3/TD1) was <1, indicating that during the readout of natural OSL, generally the sensitivity decreases. However, as shown in Table 5.2 in some of the cases there is no change in sensitivity during natural OSL measurement and the ratio is ~1. There are few cases where OSL sensitivity during natural measurement increases.

Similar behavior for the sensitivity changes during the preheat measurements were observed and in this case also, the ratio of sensitivities could be either <1, =1 or >1. Such sensitivity changes have important implications for assumptions used in SAR protocol and as discussed later, can cause systematic offsets in ages. Sensitivity changes that occur during the regeneration cycles (steps 8-13, 15-20, 22-27, and 29-34) also exhibit considerable sample-to-sample and aliquot-to-aliquot variability (Fig. 5.8).

The change between the natural and regenerated sensitivity was further examined by comparing the relationship of the 90–120°C TL and OSL sensitivities for natural and regenerated signals (Fig. 5.7). The OSL and 90–120°C TL sensitivities following regenerative cycles exhibit statistically significant linear correlation with regression lines that in most cases passes through or close to the origin. While the relationship between OSL and the 90–120°C TL sensitivity in some cases were well defined by the same best fit lines (e.g. Figs. 5.7), a majority of aliquots produced 'natural' OSL vs. TL

sensitivity relationships that were not in agreement with the regeneration cyclebased best fit linesThese trends closely match the trends of lower (below the best-fit line) and higher (above the best-fit line) 90–120°C TL sensitivity in the course of measurement of the natural OSL (Table 5.2). The best-fit regression equations were used to derive a 'predicted' OSL sensitivity following measurement of the natural by solving the equation for each of the given values of 90–120°C TL sensitivity. In most cases the ratio closely mimicked the overall change in the 90–120°C TL sensitivity during measurement of the natural OSL.

These observations suggest that in some cases the TD OSL sensitivity measured following readout of the natural OSL may not be a realistic measure of the sensitivity of the natural signal. Therefore the use of a 'Natural Correction Factor' (NCF), which is the ratio of the 90–120°C TL sensitivity obtained initially (TL_a for TD1) and after the natural OSL measurement (TL_c for TD3), becomes necessary (Fig. 5.6). We propose that natural OSL signals are corrected by this factor, so that

$$L_{nat,corr} = \left(\frac{L_{nat}}{T_{nat}}\right) \times \frac{1}{\text{NCF}}$$
(5.2)

where NCF is the ratio:

$$NCF = \frac{TL_1}{TL_3}$$
(5.3)

under the proviso that the test doses are the same. Table 5.2, summarizes the sensitivity changes for a representative set of samples from diverse depositional environmentsThis procedure can be easily folded in with the standard SAR procedure of Murray and Wintle, (2000) and makes it more robust by adequately correcting for sensitivity changes that occur during the SAR regeneration cycles.



*Courtesy Dr. Y.C. Nagar and Dr. Manoj Jaiswal

Figure 5.8: Sensitivity variations during SAR measurement.

Comula	D i	Post PH / Pre PH	Post OSL / Pre OSL	Overall	Natural	TL	ı factor	
Sample	s c			Change	factor	D _{e(corr})	D _{e(unco} rr)	D _{e(corr)} / D _{e(uncorr)}
MHK-07-	1	0.84 ± 0.01	0.81 ± 0.01	$\textbf{0.69}\pm\textbf{0.01}$	0.676±0.007	1.48± 0.01	51.1± 1.1	0.66 ± 0.04
01	2	0.85 ± 0.01	0.94 ± 0.01	$\textbf{0.80}\pm\textbf{0.01}$	0.800±0.009	1.25± 0.01	37.6± 1.3	0.90 ± 0.05
МНК-07-	1	0.850±0.003	0.918±0.003	0.78 ± 0.001	0.781±0.003	1.281 ±0.00 5	62.2± 0.8	0.90 ± 0.02
02	2	0.842±0.003	0.934±0.003	0.80 ± 0.001	0.787±0.003	1.271 ±0.00 5	76.9± 1.3	0.85 ± 0.02
MHK-07-	1	0.70±0.01	0.89±0.01	0.62 ± 0.01	0.620±0.005	1.61± 0.01	91.8± 1.9	0.75 ± 0.04
03	2	0.70±0.01	0.95±0.01	$\textbf{0.67}\pm\textbf{0.01}$	0.665±0.005	1.50± 0.01	56.8± 1.3	0.85 ± 0.04
MHK-07-	1	0.88±0.01	0.94±0.01	$\textbf{0.83}\pm\textbf{0.01}$	0.834±0.006	1.20± 0.01	81.8± 1.6	0.91 ± 0.04
04	2	0.86±0.01	0.96±0.01	$\textbf{0.83}\pm\textbf{0.01}$	0.824±0.008	1.21± 0.01	67.6± 2.0	0.96 ± 0.05
MHK-07-	1	0.858±0.004	0.870±0.005	$\textbf{0.75} \pm \textbf{0.004}$	0.746±0.004	1.34± 0.01	97.0± 1.2	0.77 ± 0.02
05	2	0.830±0.004	0.886±0.005	$\textbf{0.74} \pm \textbf{0.004}$	0.735±0.004	1.36± 0.01	95.7± 1.4	0.80 ± 0.02
MHK-07-	1	0.829±0.004	0.913±0.005	0.76 ± 0.004	0.757±0.004	1.32± 0.01	35.9± 0.2	0.87 ± 0.01
06	2	0.807±0.004	0.94±0.01	$\textbf{0.76} \pm \textbf{0.002}$	0.757±0.004	1.32± 0.01	33.5± 0.4	0.90 ± 0.02
MHK-07-	1	0.784±0.004	0.894±0.005	0.70 ± 0.004	0.702±0.004	1.43± 0.01	42.2± 0.4	0.86 ± 0.01
07	2	0.773±0.003	0.933±0.004	$\textbf{0.72}\pm\textbf{0.002}$	0.721±0.003	1.39± 0.01	49.1± 0.5	0.88± 0.02
MHK-09-	1	0.962±0.005	0.879±0.004	0.845±0.004	0.845±0.004	1.18±	49.8±	0.70 ±
09	2	0.959±0.004	0.906±0.004	0.869±0.004	0.869±0.004	1.15±	51.6±	0.74

Table 5.2: Variation of the preheat and OSL sensitivity factors and ratio of corresponding doses with and without use of correction factors

						0.01	3.8	±0.02
MHK-12- 09	1 2	0.903±0.004 0.851±0.004	0.882±0.004 0.852±0.005	0.797±0.003 0.725±0.004	0.797±0.003 0.725±0.004	1.26± 0.01 1.38±	79.2± 8.9 74.9±	0.54 ± 0.02 0.53 ±
						0.01	7.1	0.02
MHK-13-	1	0.927±0.005	0.870±0.005	0.807±0.004	0.807±0.004	1.24± 0.01	102.4 ±13.3	0.52 ± 0.01
09	2	0.92±0.01	0.85±0.01	0.776±0.001	0.776±0.005	1.29± 0.01	107.0 ±14.6	0.47 ± 0.02
MHK-15-	1	0.87±0.01	0.89±0.01	0.776±0.001	0.776±0.005	1.29± 0.01	86.7± 7.1	0.58 ± 0.01
09	2	0.89±0.01	0.90±0.01	0.801±0.001	0.796±0.005	1.26± 0.01	107.6 ±8.2	0.60 ± 0.01
R16-TL3-	1	1.065±0.002	0.822±0.002	$\textbf{0.87} \pm \textbf{0.002}$	0.876±0.002	1.142 ±0.00 3	7.1±1. 0	0.55 ± 0.05
OXF	2	1.120±0.003	0.824±0.002	$\textbf{0.92}\pm\textbf{0.002}$	0.923±0.003	1.084	15.1±	0.82±
						±0.00 3	1.4	0.01
R16-TL7	1	1.02±0.01	0.88±0.01	$\textbf{0.90} \pm \textbf{0.001}$	0.905±0.007	1.11± 0.01	50±16	0.71 ± 0.07
	2	1.08±0.01	0.86±0.01	$\textbf{0.93} \pm \textbf{0.001}$	0.929±0.008	1.08± 0.01	26.0± 4.0	0.86 ± 0.09
TRMT-T	1	1.225±0.002	0.864±0.002	1.06 ± 0.002	1.058±0.002	0.945 ±0.00 2	11.3± 1.5	1.2 ± 0.2
	2	1.239±0.003	0.881±0.002	1.09 ± 0.002	1.092±0.002	0.916 ±0.00 2	5.6±1. 2	1.8 ± 0.3
TRMT-B	1	1.121±0.003	0.942±0.003	1.06 ± 0.003	1.057±0.003	0.946 ±0.00 3	8.6±1. 4	1.24 ± 0.2
	2	1.054±0.003	0.901±0.003	$\textbf{0.94} \pm \textbf{0.003}$	0.950±0.003	1.052 ±0.00 4	14.0± 1.7	0.86 ± 0.02
	1	0.85 ± 0.01	0.97 ± 0.01	0.82 ± 0.01	1.22 ± 0.01	16.6± 0.4	22.7 ± 0.4	0.73 ± 0.02
R16 -TL6	2	$\textbf{0.80}\pm\textbf{0.01}$	$\textbf{0.87}\pm\textbf{0.01}$	$\textbf{0.70}\pm\textbf{0.01}$	1.44 ± 0.01	10.5 ± 0.3	19.5 ± 0.3	0.54 ± 0.02
820/2*	1	1.02 ± 0.02	1.02 ± 0.02	1.02 ± 0.02	0.98 ± 0.01	18.1± 0.7	17.3 ± 0.7	1.05 ± 0.06

	2	$\textbf{0.95}\pm\textbf{0.01}$	$\textbf{0.97}\pm\textbf{0.01}$	$\textbf{0.93}\pm\textbf{0.01}$	1.08 ± 0.01	15.2 ± 0.3	17.2 ± 0.3	0.88± 0.02
833/3*	1	1.05 ± 0.05	1.21 ± 0.05	1.27 ± 0.04	$\textbf{0.79} \pm \textbf{0.02}$	27.9 ± 1.7	19.2 ± 1.5	1.45 ± 0.14
000,0	2	1.08 ± 0.05	$\textbf{0.97} \pm \textbf{0.04}$	1.05 ± 0.03	$\textbf{0.95}\pm\textbf{0.03}$	20.5 ± 1.4	20.5 ± 1.4	1.07 ± 0.10
902/2*	1	$\textbf{0.99} \pm \textbf{0.01}$	$\textbf{0.99} \pm \textbf{0.01}$	0.97 ± 0.01	1.03 ± 0.01	5.0± 0.1	5.0± 0.1	0.92 ± 0.03
802/2	2	0.97 ± 0.01	$\textbf{0.99} \pm \textbf{0.01}$	0.95 ± 0.01	1.05 ± 0.01	7.4± 0.1	7.4 ± 0.1	0.91± 0.02
017/1*	1	$\textbf{0.96} \pm \textbf{0.01}$	$\textbf{1.01}\pm\textbf{0.01}$	$\textbf{0.97} \pm \textbf{0.01}$	$\textbf{1.03}\pm\textbf{0.01}$	15.8± 0.2	15.8± 0.2	0.96 ± 0.02
827/1	2	1.00 ± 0.01	$\textbf{1.01}\pm\textbf{0.01}$	1.01 ± 0.01	$\textbf{0.99} \pm \textbf{0.01}$	11.0± 0.2	11.0± 0.2	1.02 ± 0.02
BL1*	1	$\textbf{0.97}\pm\textbf{0.01}$	1.10 ± 0.05	1.07 ± 0.04	1.10 ± 0.02	5.2± 0.2	6.7 ± 0.3	0.78 ± 0.04
01-1	2	$\textbf{0.81}\pm\textbf{0.01}$	1.02 ± 0.02	$\textbf{0.83}\pm\textbf{0.02}$	$\textbf{1.10}\pm\textbf{0.02}$	5.3± 0.2	6.7 ± 0.4	0.78 ± 0.05
DI 2*	1	0.97 ± 0.01	1.10 ± 0.05	1.00 ± 0.04	1.10 ± 0.02	12.9± 1.1	15.7 ± 1.7	0.82 ± 0.01
UJ-2	2	$\textbf{0.81}\pm\textbf{0.01}$	1.02 ± 0.02	$\textbf{0.83}\pm\textbf{0.02}$	1.12 ± 0.02	16.7± 0.9	17.6± 1.2	0.95 ± 0.01
BJ-5*	1	$\textbf{0.92}\pm\textbf{0.01}$	$\textbf{0.97} \pm \textbf{0.02}$	$\textbf{0.90}\pm\textbf{0.02}$	$\textbf{1.10}\pm\textbf{0.02}$	13.0± 0.8	13.0± 1.7	1.00± 0.01
	2	0.94 ± 0.01	1.06 ± 0.05	1.00 ± 0.04	1.10 ± 0.02	14.0± 0.8	13.8± 1.1	$\begin{array}{c} \textbf{1.01} \pm \\ \textbf{0.01} \end{array}$
NB-1*	1	0.96 ± 0.01	$\textbf{0.94} \pm \textbf{0.01}$	0.90 ± 0.02	$\textbf{0.97} \pm \textbf{0.01}$	25.4± 2.1	28.6± 2.7	0.89 ± 0.11
	2	$\textbf{0.86} \pm \textbf{0.01}$	$\textbf{0.88} \pm \textbf{0.01}$	$\textbf{0.76} \pm \textbf{0.01}$	$\textbf{1.01} \pm \textbf{0.01}$	27.4 ± 2.2	31.5 ± 2.8	0.87± 0.10
NB-3*	1	$\textbf{0.97} \pm \textbf{0.01}$	0.98 ± 0.01	0.95 ± 0.01	1.10 ± 0.01	4.8± 1.1	5.4 ± 1.3	0.89 ± 0.07
	2	1.00 ± 0.01	0.96 ± 0.01	0.96 ± 0.01	$\textbf{1.10}\pm\textbf{0.01}$	7.8± 1.2	8.1± 1.6	0.96 ± 0.03
<u>۵-11-3*</u>	1	$\textbf{0.98}\pm\textbf{0.01}$	$\textbf{0.99} \pm \textbf{0.01}$	$\textbf{0.97}\pm\textbf{0.01}$	$\textbf{1.01}\pm\textbf{0.01}$	0.10± 0.01	0. 14 ± 0.01	0.71± 0.09
- 11-2	2	1.05 ± 0.05	0.99 ± 0.01	1.03 ± 0.04	0.95 ± 0.01	0.10± 0.01	0.13. ±0.01	0.77 ± 0.10
9-4*	1	$\textbf{0.96} \pm \textbf{0.01}$	1.16 ± 0.05	1.11 ± 0.05	$\textbf{1.16}\pm\textbf{0.04}$	0.80	2.1	0.38

	2	1.05 ± 0.05	1.05 ± 0.01	1.10 ± 0.05	1.12 ± 0.05	+0.03	+0.02	+0.01
						$0.76 \pm$	1.8. ±	$0.42 \pm$
						0.02	0.02	0.01
	1	0.92 ± 0.01	0.99 ± 0.01	0.91 ± 0.01	0.92 ± 0.01			
VPN-5*								
	2	$\textbf{0.89} \pm \textbf{0.01}$	$\textbf{0.96} \pm \textbf{0.01}$	$\textbf{0.85} \pm \textbf{0.01}$	$\textbf{0.90} \pm \textbf{0.01}$			
						$0.80\pm$	$2.1\pm$	$0.38\pm$
	1	$\textbf{0.77} \pm \textbf{0.01}$	1.55 ± 0.06	$\textbf{1.20}\pm\textbf{0.05}$	$\textbf{0.80} \pm \textbf{0.01}$	0.03	0.02	0.01
BNG-1*								
	2	$\textbf{0.76} \pm \textbf{0.01}$	1.61 ± 0.01	$\textbf{1.20}\pm\textbf{0.01}$	$\textbf{0.76} \pm \textbf{0.01}$	$0.76 \pm$	1.8. ±	$0.42 \pm$
						0.02	0.02	0.01
						33.0 ±	35.0 ±	0.94 ±
MVW-	1	0.61 ± 0.01	0.97 ± 0.02	0.60 ± 0.01	1.06 ± 0.02	4.4	4.7	0.01
11*	2	0.62 0.01	4.07 0.02	0.00	1 10 1 0 05	27.0	22.2	0.04
	2	0.62 ± 0.01	1.07 ± 0.02	0.66 ± 0.01	1.19 ± 0.05	27.9±	33.2. ⊥ 2.1	0.84 ±
						2.6	± 3.1	0.01
						12 0 ⊥	154	0.08 ±
	1	1 18 + 0 05	0.88 ± 0.01	1 03 + 0 05	1.02 ± 0.02	15.0 ⊥ 0 0	15.4 ⊥ 1.8	0.96 ⊥
MVW-	Т	1.18 ± 0.05	0.08 ± 0.01	1.03 ± 0.03	1.02 ± 0.02	0.9	1.0	0.01
13*	2	1.01 ± 0.01	0.83 ± 0.01	0.83 ± 0.01	1.17 ± 0.05	36.9+	43.5.	0.86 +
		101 - 0101	0.00 - 0.01	0.00 - 0.01	111/ _ 0100	1.4	+ 1.6	0.01
						25.7±	29.8±	0.86 ±
	1	0.67 ± 0.01	0.70 ± 0.01	0.50 ± 0.01	1.29 ± 0.04	1.1	1.2	0.01
RW-1*								
	2	$\textbf{0.79} \pm \textbf{0.01}$	$\textbf{0.73} \pm \textbf{0.01}$	0.60 ± 0.01	$\textbf{1.27} \pm \textbf{0.05}$	16.3 \pm	$21.1\pm$	0.77 ±
						0.7	0.9	0.01
						$19.8\pm$	$24.2\pm$	$0.82\pm$
	1	$\textbf{1.22}\pm\textbf{0.01}$	$\textbf{0.68} \pm \textbf{0.01}$	$\textbf{0.83}\pm\textbf{0.01}$	$\textbf{1.22}\pm\textbf{0.03}$	1.9	2.3	0.01
RW-4*								
	2	$\textbf{1.13}\pm\textbf{0.01}$	0.55 ± 0.01	0.62 ± 0.01	1.26 ± 0.05	16.2 \pm	$20.4 \pm$	$0.79 \pm$
						1.0	1.3	0.01
ļ								
				0.50		21.4 ±	30.5 ±	0.70 ±
070 4*	1	0.89 ± 0.01	0.63 ± 0.01	0.56 ± 0.01	1.08 ± 0.03	1.0	1.4	0.01
015-1*	2	0.00 + 0.01			0.07 ± 0.01	22 4 ⊥	<u>эгг</u> +	0 00 ±
	2	0.88 ± 0.01	0.58 ± 0.01	0.51 ± 0.01	0.97 ± 0.01	22.4 ±	25.5 ±	0.88 ±
						1.2	1.4	0.01
						32+	36+	0 89 +
	1	0.98 ± 0.01	0.89 + 0.01	0.87 + 0.01	1.12 ± 0.05	0.2	0.3	0.03
OTS-5*		0.00 ± 0.01	0.00 ± 0.01	0.07 ± 0.01	1.12 ± 0.05	0.2	0.0	0.00
	2	0.98 ± 0.01	0.94 ± 0.01	0.92 ± 0.01	1.11 ± 0.04	2.1±	2.3 ±	$0.91\pm$
						0.2	0.2	0.06

*These samples were analyzed by Dr. Manoj Jaiswal and Dr. Y. C. Nagar

A cautionary suggestion here is to use test doses of >10Gy to minimize differences in the supra-linearity of individual grains. This approach suggested above is based on the observations of good correlation between the 90–120°C TL and OSL during regeneration cycles (Fig. 5.7).



Figure 5.9: Comparison of SAR dose values with NCF corrected dose values.

Fig. 5.9 gives comparison of D_e with and without corrections factors, which shows that with a few exceptions, most samples have SAR ages that have systematic offset. While it is difficult to compare these results against robust ages (if there are any!), the fact that in all cases the scatter in palaeodoses reduced (Fig. 5.10) irrespective of the diverse depositional environments and variability in individual aliquots suggests that the correction procedure works well. Fig. 5.11 (and Table 5.2) shows that there can be significant differences in the D_e values, if uncorrected for the sensitivity changes. These changes can be either on positive or negative side of actual D_e values. The routine use of NSC-SAR protocol provides way to correctly estimate the dose values. The dose distribution obtained is much more compact and robust than the uncorrected dose distribution (Fig. 5.10).



Figure 5.10: Comparison of histogram obtained usingSAR with NSC-SAR protocol.

5.5 Discussion

The development of SAR based D_e determination procedure has been one of the most exciting research initiatives in luminescence dating. However, we had some concerns over the lack of measurement of the natural sensitivity prior to measurement of the natural OSL, and considered this a gray area for the SAR procedures. The present study affirms that significant sensitivity changes during readout of the natural OSL occur for most samples. The change is variable in magnitude and direction from one aliquot-to-aliquot and implicitly from grain to grain, given that only a few grains contribute to the OSL. We employed 90-120°C TL sensitivity as a surrogate for sensitivity change during the read out of natural OSL.Importantly, it was seen that these changes are dissimilar to those, which occur during regeneration measurements. In the absence of such a correction, systematic errors in any D_e estimate using conventional SAR are to be expected. This in itself may serve as a useful criterion to identify and /or reject potentially problematic samples.



Figure 5.11: Comparison of SAR and NCF corrected equivalent doses

The proposal is to employ a correction factor to correct for possible sensitivity change of the natural aliquot. This strategy effectively adjusts the sensitivity of the natural OSL measurement to match the linear OSL 90–120°C TL relationship observed during the regeneration cycles. Table 5.1 shows the data set comparing the D_e estimated using of the natural correction factor (*NCF*). These dose values are significantly different from estimates made using conventional SAR.

The latest version of the SAR protocol is termed the standard SAR (Murray and Wintle, 2000; Wintle and Murray, 2006), represents a refined approach to the SAR method as first proposed (Murray and Roberts, 1998). For samples that do not exhibit sensitivity changes during the natural OSL measurement, such procedure will provide accurate, high precision D_e estimates. We consider it

prudent to bracket the natural OSL signal measurement with test doses and to observe the 90–120°C TL and to measure this TL during the low temperature pre-heating following all subsequent test doses. Such an approach simultaneously would

- 1. allow a check of sensitivity changes during measurement of natural OSL,
- provide a test of the relationship between 90–120°C TL and OSL sensitivity (which in itself is a test of the appropriateness of the post natural measurement OSL sensitivity e.g., Fig. 5.7), and
- provide an alternative means of regenerated growth curve normalization (which in many cases may provide improved counting statistics and corresponding improved growth curve forms e.g., Fig. 5.9).
- 4. Our study also demonstrates the importance for systematic studies that quantifies the nature of natural sensitization effects, establishes their relationship to pre-heat and optical stimulation procedures. We have examined a significant set of samples but we need more research into this aspect.

An important outcome of this study is the caution in the use of single grain data as done in an automated single grain reader. This is because; the sensitivity of an individual grain cannot be measured easily. It is not yet clear if the brighter grains suffer lesser sensitivity changes but this needs to be probed at a single grain level to decide on the prospects of using single grain ages. These are non trivial measurements on account of low photon yield in TL and OSL of single grains. However, a systematic effort is needed. Limited studies that we carried out did not indicate any relationship between sensitivity and sensitivity change.

5.6 Conclusions

1. Sensitivity changes due to pre-heating and optical stimulation during measurement of natural OSL are omnipresent.

- 2. The amplitude of such changes may be significant (\pm 40%) and could result in large (~50%) systematic errors in standard SAR D_e determinations.
- Use of 90–120°C TL measurements following repeated applications of a test dose provides a means of testing for changes in natural OSL sensitivity
- 4. Additionally, comparison of the relationship between OSL and TL responses to a test dose following measurement of natural OSL and those measured following each regeneration cycle, can provide an independent measurement of the appropriateness of the post natural OSL sensitivity correction.
- 5. We propose the use of a modified SAR procedure (NSC-SAR) that corrects for any changes in sensitivity occurring during the natural measurement cycle. The procedure has no effect on samples that do not exhibit changes in sensitivity during the measurement of natural OSL however, in some cases there may be a shift in the estimated D_e of up to 60%.
- 6. The extent and significance of these effects requires detailed investigation, as it may ultimately serve as a SAR acceptance/rejection criteria for quartz samples.

Chapter-6

Summary and Future Outlook

6.1 Summary: Present Understanding

The present thesis investigated the amplitude and style of distribution of radiation doses in nature due to natural radioactivity and their causes. The distribution in doses occurs at microscopic level and macroscopic levels due to different ranges of ionizing radiations (α , β and γ) and heterogeneous distribution of radioactivity at a grain level. The ranges of these radiations scale in ratio 1:100:10,000 respectively, and this difference in their ranges results in distribution in doses. The present thesis tried to quantify this distribution to make the dose estimation more rigorous and explore the new possibilities, which can

help extend thedating limits and the precision of luminescence dating. In this detailed study it was seen that there are several factors responsible for the distribution in doses and their quantification provides a basis for improved age calculations, i.e. :

- 1. Generally, considerable distribution is found in palaeodoses obtained from well bleached $\sim 100 \mu m$ size single grains of the quartz. During this study using Monte Carlo simulations and the mathematical model developed by Mayya et al., (2006), it was found a significant amount of distribution in the doses results from the fluctuation of K-feldspar grains around quartz grains. K-feldspar contain⁴⁰K, which is one of the major contributors to the β -dose, and the range of these particles is comparable to inter-grain distances. As different feldspar, grains are located at different distance so each feldspar grain will deposit unequal doses in the quartz grains and fluctuations in configuration of feldspar grains around guartz grains result in different dose deposition. In this thesis, the nature of distribution and the minimum dose rate (δ) value was estimated as a function of concentration of K. In addition to this, estimation of dose distribution was done for different porosity and water content and it was seen that for higher porosity the dose distribution function shifts towards higher dose side. A new value of δ for different combinations was obtained that allows the estimation of age even for poorly bleached samples.
- 2. The distribution of doses at single grain level due to heterogeneity in β dose results in distribution in doses for single aliquots formed by several such single grains (~100). This distribution in the single aliquots doses was estimated by means of Monte Carlo simulations. The simulations allowed measurement of several useful parameters like determination of the number of the discs to be used for analysis and the resultant accuracy, maximum possible error and dispersion in doses because of β dose heterogeneity. These parameters help improve the accuracy in age determination. The maximum possible error and spread in the palaeodoses defines a limit in the precision of ages in luminescence dating, and the ratio of maximum to minimum dose value helps identify

the samples having distribution because of β dose heterogeneity from the samples having other causes of dose distribution. This then helps deciding the kind of model (FMM, MAM, CAM etc.) that could be used for age estimation. This work also suggest that mean of the dose distribution provides reliable dose estimate if β heterogeneity is the sole cause of distribution.

3. The dating range of guartz is limited by the fact that the luminescence signal of quartz saturates around ~250Gy. This saturation of luminescence signal along with the dose rate of sediment matrix decides the limit of the dating. In this work the efforts were made to date the interior of a ~Sub-centimeter size quartz grains. The interior of such large grains provide the opportunity to date older sample hence extending the dating limits of luminescence dating. In this work, Monte Carlo simulations were used to find the beta dose profile inside the large size quartz and it was found that the contribution of beta dose from the sediment from all the sources reduces to negligible level at depths of ~2mm. This implies that a central core inside the grains of Diameter>4mm would always exist, that would receive dose only because of gamma radiation. For this region thedose rate is a third of the dose rate in a sediment matrix. As the dose rate in the interior is lower, the luminescence signal saturates later in time and samples 3-4 times older than normal luminescence age limit can be dated.

Transparency and the bleachability experiments suggest that such large size quartz grains can be bleached by ~3 hrs of natural daylight. Thus, a carefully selected sample can be used to date older samples. A well-defined procedure is suggested for sample preparation and measurements. Experimental verification proved the proposed hypothesis and one of the sample having an age >200ka was dated using the methodology provided.

4. A major limitation of luminescence dating has been the need for specific minerals of definite grain sizes for dating. Many times, it is difficult to separate the minerals or the proper grain sizes. This limitation can be

overcome by insitu measurements, i.e. analyzing the grain without separating them from the matrix. This can be done using surface dating technique, which involves measurement of luminescence signal corresponding to small region on the surface and analyzing that small region to estimate the dose values. However, the major issues for such studies were related to transparency of materials to be used, the dose rate estimation and measurement of spatially resolved luminescence signal. The calculations suggest that the issue of transparency can be taken care of by using the transparent material with limitation that its thickness should be smaller than the maximum β range and transparency and thickness should remain constant during the measurements. A programin Matlabenablesthe estimation of the natural dose rate and laboratory dose rate in terms of average dose deposited in a given thickness of sample. For estimating the natural dose rate, the radioactive concentration of the two regions should be known.

For spatially resolved luminescence measurements, an EMCCD based imaging system was designed and tested. All the units of this system (including heating and light stimulating unit, interfacing software, synchronous image acquisition, Optical arrangement and data processing software) were developed in-house. The luminescence is recorded as time series images whose intensity varies in accordance with the stimulating mode. The images acquired are processed in the programs written in Matlab to find out the D_e value. These programs read the image, align the images up to single pixel accuracy and finally evaluate pixel specific or region specific dose values. The system has been tested for dose recovery test and could successfully recover the doses within ±10% of the given dose for TL of both quartz and feldspar and IRSL of feldspar.. The system can now be used for routine measurement of the natural samples.

5. The SAR protocol is widely used protocol to measure the palaeodose, D_e. This protocol estimates the D_e with continuous monitoring of the sensitivity during the measurements with the help of signal corresponding

to small test dose (TD). However, in the SAR protocol there was so far no provision of the correction for the sensitivity changes occurring during the measurement of the natural luminescence of the samples. Sensitivity monitoring experiments suggested that significant sensitivity changes occurred during the measurement of natural OSL. This sensitivity change during the measurement of natural OSL can result in a change in dose value up to 40% and the direction and amplitude of this change can be either way, i.e. it can decrease or increase. This affects De measurements. The change is not uniform and varies from disc to disc and sample to sample. In this thesis a methodology to correct for these sensitivity changes was developed and was termed as natural sensitivity corrected SAR (NSC-SAR) protocol. This protocol includes measurement of TD TL signal before and after the natural signal measurement and the ratio of these two is used to correct for the changes in thesensitivity. The application of this protocol provides improved results, the scatter in the doses reduces significantly and the dose distribution becomes much more compact.

6.2 Future Outlook

Present thesis offers newer possibilities in the development of experimental techniques and for newer geological applications. Some of the new possibilities that could merit further studies are as follows,

 The distribution in doses resulting from spatial fluctuation of the beta sources needs experimentally quantification. In the theoretical development of beta dose heterogeneity model, one of the critical assumptions was that the concentration of K should be low and that the effect get diluted for higher concentrations of K. This needs further quantification in respect of the increasing potassium and corresponding dilution of heterogeneous component.

- It will also be interesting to combine the theory of coldspots (Jacobs et al., 2008) with the theory of K-feldspar hotspots to give a unified theory, which can accommodate all the possible dose distributions in natural environment for well-bleached sediments.
- 3. The dose deposited in the grains is a function of the radioactivity ranges and the size of the grains. This implies that, the rate at which the dose is deposited in the grains of variable sizes is different. Hence, for a sample of given age, the different size of the grains in the same sample will have different doses. A plot of dose as a function of dose rate (for different sizes) will give an isochron in which the slope gives the age of the sample and this method can also be tried with the added advantage that external environmental parameters such as heterogeneity of matrix and water content and their effects can be minimized.

$$D = Age \times \dot{D} \tag{6.1}$$

- 4. Dating of large grains offers new prospects in dating the fluvial deposits or dating of the terraces. The river lain gravels having ~cm size quartz and which are older (~200-400ka) and undatable by normal luminescence methodology or any other technique can be dated. This will fill in much needed void in Quaternary Geology in terms of dating of the processes and climatic events in 100-1000ka range.
- 5. The work on large grains also offers prospects for dating lithic implements in archeology. Given that at time early man heated rock for making them amenable to mechanical working, as also that these rocks remained in day light during their use it is possible now to use a slice of these to date such implements. The exploitation of beta dose gradient additionally offers prospects of directly dating the lower Paleolithic, which at present is poorly dated in the Indian context.
- 6. An important element that can be developed is the non destructive dating of tools by adopting the present EMCCD system with confocal optics. This

is an uncharted area and will be worthwhile to explore this aspect and use confocal microscopic methods in luminescence dating.

- 7. While measuring the luminescence signal of large size quartz grains it was found that the sensitivity of the large size quartz grains was several orders of magnitude lower than the associated grains of size 90-150 µm. The sensitivity of the grains decreases as a function of increasing diameter. Such a large variation in the sensitivity with the size can be used to identify the causes of sensitivity variations in case of quartz and also use sensitivity change as a surrogate for time. As this has been a long-standing question in case of the luminescence technique.
- 8. Spatially resolved luminescence system developed can be further tuned in respect of its optical and technical attributes. Future improvements would include, optics for UV detection, removal of reflecting surfaces to reduce the loss of signal, and improvements of light collection using parabolic reflector around the samples and by a combination of convex and concave mirrors, which has high reflection efficiency. It can thus improve upon S/N ratio significantly.
- 9. Further development of the system can be done by transforming the system to a spatially resolved spectrometer, which will be capable of doing measurements in different wavelength regions. This development will make the instrument only one of its kind making such measurements.
- 10. The development of surface dating technique will help in many areas of geological applications. In addition, as it can date the specific regions of the surface hence it is capable of dating different geological events by dating of rock. It can be used to find terrestrial age of meteorites. It can date glacial moraines to study the dynamics of glaciers through time. It can be used to date the secondary growth of the minerals like in case of gypsum, or find out the rate of the carbonate nodule formation by dating the quartz inclusions in the carbonate nodules and hence can be used to find the rate of carbonate formation. These ideas need to be explored to identify the potential areas of refinements for routine application of surfaces
- 11. The capability of the system to detect luminescence coming from different regions can be helpful for documenting the variation in the intensity of the individual grains or regions while heating or recording OSL. It will be helpful in finding the spatial distribution of the quartz and feldspars on the surfaces. Earlier such measurements were though possible but time consuming as for recording TL, each grain need to be recorded individually and then compared, similar is the case with OSL. On the other hand in present system individual measurement is not needed, and the properties of different region or grains can be studied in a single run. This aspect needs to be formally established
- 12. The imaging capability of this system can be used to find out the uniformity of the phosphor development procedure, by analyzing the luminescence signal from different regions of a phosphor.

List of Publications

- Extending the maximum age achievable in the luminescence dating of sediments using large quartz grains: A feasibility study., N. Chauhan, S. Anand, T. Palani Selvam, Y. S. Mayya and A. K. Singhvi, *Radiation Measurements* 44: 629-33
- 2. Dispersion in SAR paleodoses due to spatial heterogeneity of natural beta dose.N. Chauhan and A. K. Singhvi, *Geochronometria* 38(3):190-198
- Changes in Natural OSL Sensitivity during single aliquot regeneration procedures and their implications for equivalent dose determination., A.K. Singhvi, N. Chauhan, Y.C. Nagar and M. Jaiswal, *Geochronometria* 38(3):231-241
- A ~200 ka record of climatic change and dune activity in the Thar Desert, India.A. K. Singhvi, M. A. J. Williams, S.N. Rajaguru, V.N. Misra, S. Chawla , S. Stokes, N. Chauhan, T. Francis, R.K. Ganjoo and G.S. Humphreys.*Quat. Sci. Rev.*: 29:3095-3105
- A survey of some new approaches in extending the maximum age limit and accuracy of luminescence application to archeological chronometry., A.K. Singhvi, N. Chauhan and R.H. Biswas, *Mediterranean Archeology and Archaeometry* 2010(4)

Under preparation

- 1. Single grain natural beta dose distribution in sediments: effect of beta straggling and density of soil. N. Chauhan, S. Anand, D.P. Shinde, Y.S. Mayya and A.K. Singhvi, (Under Preparation)
- 2. Development of system for spatially resolved luminescence measurements., N. Chauhan, P. Adhyaru, H. Waghela and A. K. Singhvi, (Under Preparation)
- 3. Termite mounds may persist for millennia S.T. Garnett, G. Ainsworth, N. Chauhan, D. L. Garnett, J. Korb, L. Prior, A.K. Singhvi, A.M. Schmidt, R. Wasson, K.K. Zander, (Under Preparation)
- 4. The role of India in Early Modern Human Dispersals : Implications of the earliest Microlithic blade technology (outside Africa), at Mehtakheri, Madhya Pradesh, India., Sheila Mishra, N. Chauhan, A. K. Singhvi, (Under Preparation)
- 5. Magnetic separation of quartz and feldspar: implication towards increasing the sensitivity of Quartz., Y.C. Nagar, N. Chauhan, N. Porat and A.K. Singhvi (Under Preparation)

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