EXPERIMENTAL DETAILS

Luminescence Dating

Luminescence dating technique relies on the fact that natural minerals such as quartz and feldspars can serve as sensitive radiation dosimeters. These minerals have a structural configuration such that they can record the environmental radiation exposure in a cumulative manner and preserve this record over long periods (i.e. geological time scales). This process is generally explained in terms of band theory of solids. In insulators (such as quartz), the valence and conduction bands are separated by a large energy gap, the forbidden band (typically 8- 10 eV). In these materials, defects in the crystals occur due to the presence of lattice imperfections, impurity atoms at various lattice and interstitial sites etc. These results in the creation of localized, metastable states- within the forbidden gap and on account of their charge configuration can trap charges (electrons and holes). Exposure of such materials to ionizing radiation, results in excitation of electrons in the valence band to the conduction band and a hole is created in the valance band. From the excited state the electron may return to the valence band to recombine with the hole, in doing so, it releases the acquired energy from radiation by heating the crystal A few charges however are trapped at the defect centers resulting in a net storage of energy. Depending on the overall charge

environment, the mean residence time of the charges in the defects sites can range from seconds to million of years and this is normally designated in terms of parameters such as trap depth and the frequency factors. The trapped charges (e.g. an electron) however can be released, when the crystal is provided external energy in the form of heat or light. The trapped charges thus released travel in the lattice and in the process recombine with the trapped hole at a suitable recombination site. The trapped hole is left in an excited state and return to its ground state via an emission of photon. In practice there are multitude of trapping centers and recombination centers. This emission of light is termed as luminescence and depending upon the stimulation source it is termed as Thermally Stimulated Luminescence or Thermoluminescence (TL) when thermal excitation is used and Optically Stimulated Luminescence (OSL) when stimulation is by light (Aitken 1985; Aitken 1997).

The primary advantage of luminescence dating of Quaternary sediments is its applicability to ubiquitous, quartz and feldspars that constitute any sediment. This fact removes the ambiguities in sample –strata correlation, as the dated samples are the strata themselves. These minerals are having a crystalline structure that makes them sensitive environmental dosimeters. For past 30 years quartz luminescence techniques have been applied to a variety of situations ranging from potteries, sediments of diverse depositional environments viz. glacial ice, volcanic ashes and carbonates/limestone (Roberts, 1997; Singhvi et al, 2001). In the case of the pottery the event dated is the kiln-firing event that thermally reset the pre-existing luminescence. In the case of sediments the event dates is the most recent sun exposure. The earliest application of TL in dating sedimentary unheated quartz was by Wintle and Huntley (1979) who demonstrated that the geological luminescence of quartz and feldspar grains reduced to a near zero value by exposure to daylight

Aitken (1985, 1998) provides a good introduction on the methodological aspects of luminescence dating. The basic premises of luminescence dating are based on the following.

(i) Natural minerals like quartz and feldspars are sensitive radiation dosimeters and can store a record of their irradiation from environmental radioactivity over geological time scales in a cumulative manner. Natural radioactivity, viz. ^{238}U, ^{232}Th and ^{40}K and cosmic ray provide a near constant source of irradiation to these minerals such that at any point the total luminescence bears a proportional relationship to the total radiation (Fig 2.1A).

(ii) Pre-depositional heating or day light exposure during the production (by weathering of rocks) and transportation of mineral grains rapidly erased the geological luminescence to a zero or near zero residual value (Fig 2.1B). On burial this stimulation ceases and a fresh acquisition begins due to irradiation from the decay of radioactivity in the new ambience. Multiple episodes of heating or daylight exposure result in the erasure of existing luminescence in each instance and consequently only the most recent deposition event is dated (Fig. 2.1C).

Age estimation

In its simplest form the age equation is

Age (yrs)=Acquired luminescence (L)/ Annual rate of luminescence acquisition (L/yrs.)

In radiation units this is expressed as

Age= Palaeodose (P)/Annual dose (D)

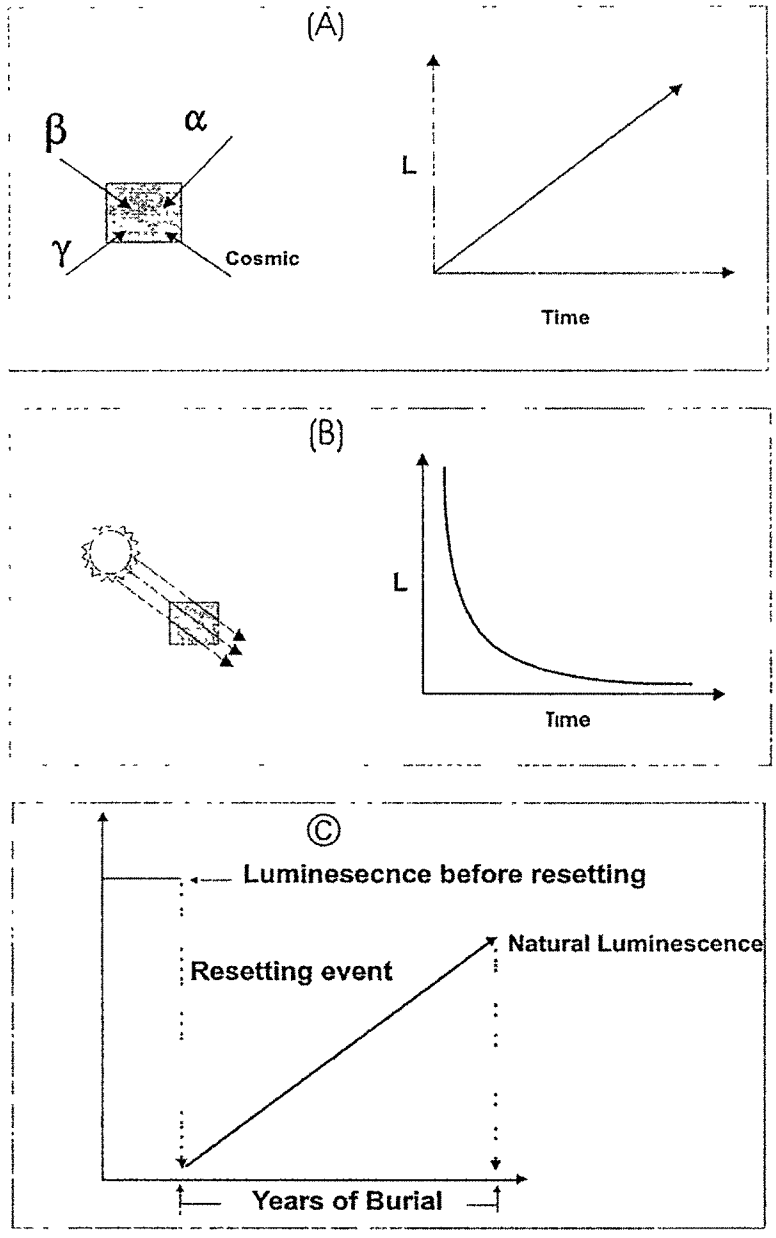


Figure-2.1. Schematic presentation of luminescence process. (A) Ionizing radiation from α, β, γ and cosmic ray bulids up luminescence signal in the sediment. (B) During transport, sediment exposed to day light that causes the bleaching of the luminescence signal to a residual value. (C) Once sediment is buried (concealed from sun light) luminescence build up takes place. In the lab we measure this event.

The palaeodose (P) is the laboratory beta dose that induces a luminescence level equal to that in the virgin sample (i.e. L). However the paleodose is unevenly distributed in

the sample matrix, as the natural radiation is a mixed field comprising alpha, beta and gamma and these has different penetration range in the crystal. In addition, on account of their higher charge and mass, the alphas interact with the mineral lattice such that they have a short trajectory over which they lose their energy. In contrast to beta and gamma rays, the short track length of alpha implies a higher ionization density over a shorter volume such that only a small fraction of these are trapped in defects that provide smaller luminescence intensity for the same amount of energy absorbed. Such a reduced effectiveness is expressed as alpha efficiency factor (*a* value) and has computed in each case.

This consideration lead to two approaches, the fine grains (size < alpha range, typically 4-11 um) and the coarse grain (size >> alpha range such that the alpha irradiated skin can be removed.). This is customary for so called fine grain (4-11 μm) dating to estimate alpha efficiency factor and is done by comparing the response of alpha to a given beta irradiation. Thus, the age equation for fine grain can be expressed as

$$\mathbf{Age= P/(}a\mathbf{D}\alpha\mathbf{+D}_\beta\mathbf{+D}_\gamma\mathbf{+D}_c\mathbf{)}$$

Where $D\alpha$, D_β and D_γ are annual dose rate from alpha , beta and gamma rays arising from the decay of ^{238}U, ^{232}Th and ^{40}K in the sample and D_c is the contribution from the cosmic rays to total dose. The computation of age requires palaeodose estimation by luminescence measurements. The annual dose is experimentally determined through elemental concentrations of radionuclides, status of the disequilibrium in the decay chains of ^{238}U and ^{232}Th and an estimate of average water content through the sample antiquity. Water in itself is devoid of radioactivity, however, it attenuates the radiation flux to the sample and hence controls the annual radiation dose A realistic estimation of water content is therefore

crucial for age determination Estimation of palaeodose relies on the estimation of the extent of pre-depositional bleaching (day light exposure) and the long-term stability of the luminescence signal.

Aeolian sediments are ideal for the luminescence dating technique, as aeolian sediment largely transport by process of saltation and suspension. This allows adequate opportunity for re-setting of the luminescence signal prior to burial. However, mineral grains transported by rivers can experience a wide variety of light exposure conditions before deposition. Bleaching will depend primarily on the characteristics of the water, the water depth, turbidity and distance of transportation. Furthermore, different grain size are likely to have different histories of light exposure, with fine grains being carried nearer to the top of the water surface and coarse grains being moved by saltation or traction close to the river bed. Some grains will be deposited in mid channel bars hence the surface grains would be exposed to direct sun light. Thus any particular grain will have had an unknown light exposure history before deposition (Fuller et al., 1994). In the recent times with the development of single aliquot and single grain dating is able to circumvent the problem arising out of incomplete or heterogeneous bleaching of fluvial sediments (Duller, 1996, Murray and Wintle, 2000b).

Optical Dating

In the initial application of luminescence to sediments, thermoluminescence was used. It was observed, while the initial thermoluminescence signal reduced rapidly with sun exposure, the beaching became slower with increasing time such that it asymptotically reached a finite residual value beyond which further bleaching was not possible. Thus, modern samples of known zero age, yielded a finite signal that had to be subtracted during

the analysis. This was because an optical process was being probed by a thermal stimulus. Huntley et al., (1985) demonstrated that it was possible to obtain luminescence on optical excitation using a green light. This innovation led to many possibilities and advantages. These included, the prospects of probing only the optically excitable signal (thereby avoiding the need to estimate the residual signal), prospects of multiple read outs due to the fact that stimulation could be pulsed, avoidance of interference from black body irradiation etc. On the other hand, as the energies of optical stimulation are high, it implies that all trapped charges can be emptied out simultaneously and unlike TL where higher temperature implied higher stability, there are no obvious means to assess the stability except for the preheating of a sample. Initial articles by Huntley, et al. (1985), Godfrey-Smith, (1988) and Aitken (1998) provide a good summary of the development and the physic aspect of the method.

Similarly, studies on feldspar with stimulation by different wavelengths demonstrated that K-rich alluminosilicates could be used for luminescence dating. This was possible due to resonance effect such that IR stimulation by 880 nm raised the electron to an excited state close to the conduction band from where the electron could reach by thermal energy (Hutt and Tchonka, 1988). Since IR stimulation is done at 880 nm, it implies that the luminescence observation could be conducted on a wider range of visible wavelengths compared to the 514.5 nm stimulation, which restricts viewing to UV-blue region only.

Pretreatment procedures

Chemical pretreatment is prerequisite before the luminescence measurement. In the present study, the samples were sequentially treated with 1N HCl in order to remove the carbonates followed by 30% hydrogen peroxide to remove the organic contaminants. Subsequent to this the treatment was governed by the choice of the grain size that in turn was

determined by the mean grain size of the sediment. In case of coarse grains, samples were sieved for different size fraction and usually 105-150 μm fraction is isolated. The required size fraction was subjected to the removal of magnetic fraction using isodynamic separator. Quartz and feldspar mineral separates were then isolated using Na-polytungstate (ρ= 2.58 g/cm^{-3}). The alpha irradiated skin of quartz mineral were etched for 80 minutes in 40% HF with magnetic stirring and followed by a treatment with 12N HCl for 30 minutes. Etching of K-feldspar was not attempted because of the possibility of uneven etching due to the presence of cleavage and fractures (Srivastava et al., 2001) It is envisaged that the non-etching would offset the dose rate estimates by ~5% The purity of Quartz grains was checked by the infra-red stimulated luminescence and such etched quartz grains were mounted as monolayer on stainless steel discs using Silkospray^{TM}. In view of the facts that Quartz grain can occasionally have feldspar micro-inclusions that could contaminate the Quartz BGSL signal. In order to get the clean Quartz signal, all aliquots were pre-bleached by 880 nm Infra-Red (IR) light at 100°C (Jain and Singhvi, 2001) with a reasonable assumption that 100°C IR stimulation does not adversely affect quartz BGSL.

In the fine grain technique (using 4-11 μm), after HCl and H_2O_2 treatments the samples were deflocculated in 0.01N sodium oxalate solution to remove particle <4 μm (clays) and washed. This reaction could take up to few days and multiple deflocculatiom was often needed. Following this, the sample was suspended in acetone column and the required grain size was separated using appropriate Stoke's settling times of typically 1.5 and 15 min. The separated fraction was resuspended in acetone and equal volumes were precipitated and deposited on to 9.65 mm aluminum discs for eventual drying up at ~50^{0}C (Singhvi et al., 2001)

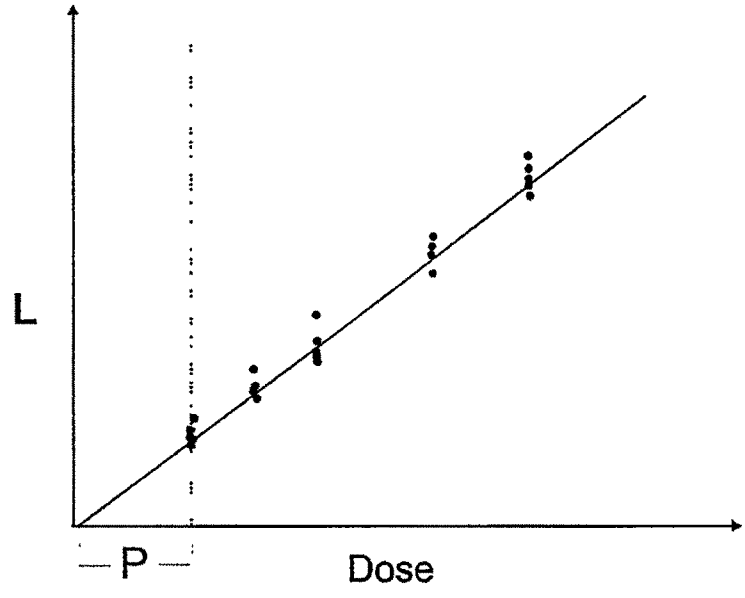
In the present study paloedose estimate was made using multiple aliquot additive dose (MAAD) method for Quartz and feldspar grains and Single aliquot regeneration (SAR) and Single aliquot additive dose (SAAD) methods for quartz samples only.

Multiple Aliquot Additive Dose (MAAD) Procedure

In MAAD procedure, identical discs with their natural luminescence are given incremental beta dose and luminescence vs applied dose growth curve is plotted. Extrapolation of this curve to zero or residual luminescence (in the case of sediments) provides the paleodose In the present study, a minimum of 6 discs per dose points are taken and irradiation going up to six times to anticipated paleodose were given (Felix and Singhvi, 1997) to achieve an optimum precision. The palaeodose was obtained by extrapolating the signal value to zero taking due cognizance of the mathematical function of the luminescence vs. dose growth curve (Fig. 2.2).

The MAAD procedure has the advantage that it eliminates any adverse effects due to sensitivity change by laboratory irradiation, bleaching or heating. However, the draw back is that palaeodose is obtained by extrapolation outside the experimental data points, and the value critically depends on mathematical function used (linear, exponential or polynomial). In addition, the use of such a large population of grains 1-5 mg (equivalent to ~4000 grains of 100 micron) in each disc. Though it has the sanctity of a statistically rigorous analysis, it also leads to an averaging of the signals from bleached and unbleached grains leading to an overestimation (Olley et al., 1999). Other difficulties that accrue with MAAD include the effects due to highly variable sensitivity of individual grains within aliquot. This implies dominance of brighter grains that may not be the best grains always.

Use of MAAD also implies that the individual discs are identical sensu-stricto. To achieve this, various normalization methods are used. These include the weight normalization; second glow normalization and the short shine normalization (Jain et al., 2003) In the present study short shine normalization was used (0.3-second illumination is given to each disc and the photon output is considered equivalent to the amount of the sample). In case of quartz this may be equivalent to the number of bright grains. This procedure is followed for coarse grained quartz and feldspar and fine grained feldspar.



L- Luminescence P- Palaeodose

Figure-2.2. In MAAD procedure, identical discs with their natural luminescence are given incremental beta dose and Luminescence vs. applied dose growth curve is plotted. Extrapolation of the curve to zero or residual luminescence (in the case of sediments) provides the paleodose (P).

Single Aliquot Regeneration (SAR) procedure

In SAR method, estimation of paleodose is made on a single aliquot by recording its natural luminescence and then reconstructing a regenerated luminescence verses dose growth

curve through a cycle of increasing irradiation preheat and measurement (Fig. 2.3). The intensity of the natural sample is then read on this curve to obtain a palaeodose. This forms the basis of SAR protocol (Murray and Wintle, 2000b) Recording paleodoses on many such aliquots and appropriately treating the data provide statistical rigour. The procedure involves measurement of natural OSL after irradiation and preheats. This changes the sensitivity of the samples and is monitored at each stage via the response of 110 ^{0}C peak to a fixed test dose. (Murray and Roberts, 1998). The natural and regenerative OSL measurements are carried out at 125 ^{0}C in order to keep the 110 ^{0}C trap empty during the OSL stimulation (Murray and Wintle, 1998). An improved single-aliquot regenerative-dose protocol of Murray and Wintle, (2000) is given below.

Step	Treatment[a]	Observed[d]
1	Give dose D_1	-
2	Preheat[b] (160-300 °C for 10 s)	-
3	Stimulate[c] for 100 s at 125 °C	*Li*
4	Give test dose D_t	-
5	Heat[b] to 160 °C	-
6	Stimulation for 100 s at 125 °C	*Ti*
7	Return to 1	-

[a]For the natural sample , I= 0, and D_0= 0 Gy

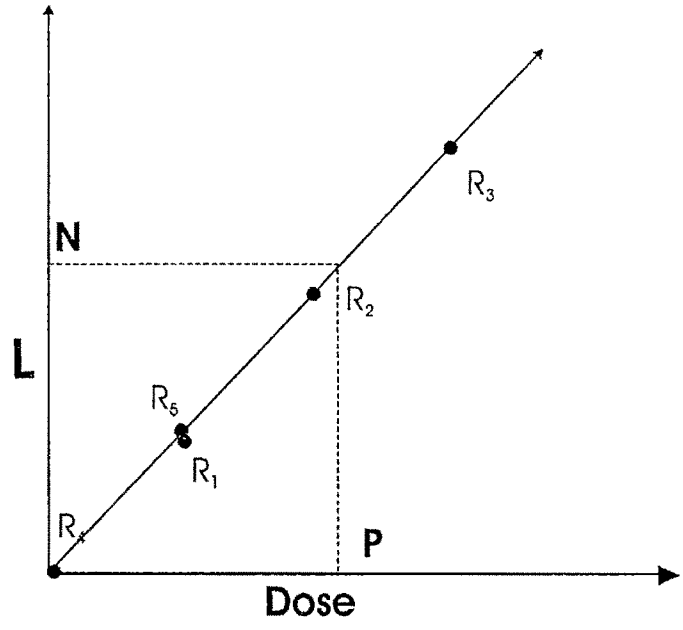
[b]Aliquot cooled to <60 °C after heating. In step 5, the TL signal from the test dose can be observed, but it is not made use of in routine applications.

[c]Stimulation time is dependent on the stimulation light intensity.

[d]*Li* and *Ti* are derived from the initial OSL signal (0.3 or 0.8 s) minus a background estimated from the last part of the stimulation curve.

Ste-7 first regeneration dose followed by step-1 to step-6 and can be continued for repeated regeneration doses. In the procedure test dose is kept constant so that any change in

sensitivity can be corrected for provided relationship between test-dose signal and the regenerated OSL is linear, and the intercept of this relationship must be small compared to the measured OSL signal (Murray and Wintle, 2000) In routine application including the present work, five regeneration dose responses are recorded. The first three are to constrain the natural signal and are planned in a following manner. $R_1<N\sim R_2>R_3$ The fourth regeneration (R_4) is zero to monitor the recuperation that may arise due to thermal transfer



L- Luminescence, P- Palaeodose, N- Natural

Figure-2.3. Single aliquot regeneration growth curve. A sequence of regenerative doses (R_1, R_2, R_3 -------) are given after the natural (N) and palaeodose (P) is interpolated on the regenerated growth curve.

from optically insensitive traps which are partly drained by the 240^{0}C preheat. Although 160^{0}C preheat (cut heat) is given after each test dose, however, it may not be sufficient enough to empty the thermally shallow but light-insensitive traps. OSL traps eventually retrap these traps during 240^{0}C. The fifth regeneration dose (R_5) is equal to the first (R_1) and the ratio R_5/R_1 enabling in examining the reproducibility of the signal hence provide a mean to further check the change in sample sensitivity during the cycles of measurements (Murray

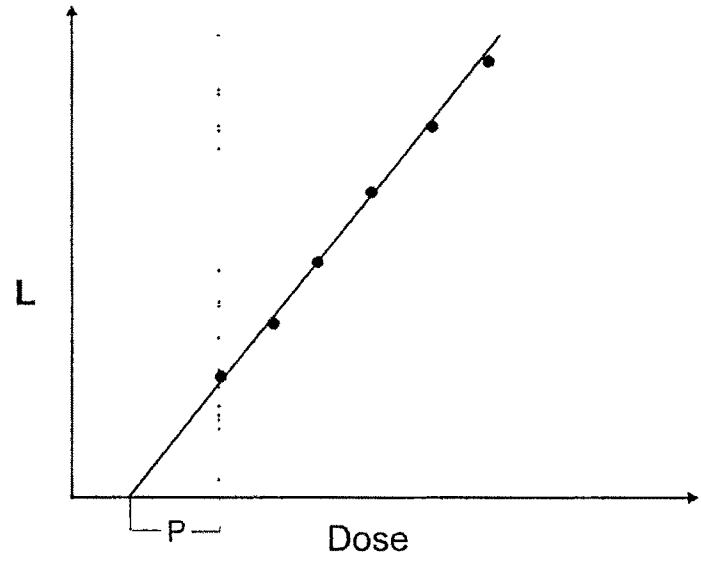
and Wintle, 2000) This procedure is followed for coarse grain quartz samples that are analyzed using SAR protocol.

In single aliquot regeneration technique, only those equivalent doses were taken for analyses in which recycling ratio lies between 0.95 to 1.1 and minimum equivalent dose plus two-sigma error were considered is the computation of ages.

Single Aliquot Additive Dose (SAAD) procedure

In this procedure pulsed excitation of short duration is carried out on a sample with incremental irradiation and preheats using the protocol devised for feldspar by Duller (1994). Samples were mounted on 1cm-diameter aluminum discs using mask around 4 mm in diameter. The measurements were carried out in Riso reader with BGSL stimulation from 300-watt halogen lamp filtered with a GG-420 and BGSL signal was monitored through a U-340 and interference filter Typically for each sample, 6-8 aliquots were measured (Fig. 2 4). A preheat of 220 ^{0}C for 2 minute with simultaneous IR stimulation (Jain and Singhvi, 2001) in order to remove any possible contamination of the quartz BGSL by feldspar BGSL and to conform to the recommendation of Murray et al., (1997) that a preheat at 200 ^{0}C remove the unstable signal from young samples. The BGSL signal was measured at 125 ^{0}C for 0.2 s for the naturally L- acquired BGSL and after each of the samples, seven cycles of additional laboratory doses (8, 16, 32, 64, 82, 82, 82 Gy). Two additional aliquots from each sample were used to correct the signal lost due to repeat preheating and measurements. The performance of this correction procedure was monitored using the last three measurements cycles, all of which had the same laboratory dose. If the said procedure is working correctly then the corrected BGSL signals from the last three cycles having the same laboratory dose

should have similar corrected BGSL signal. Using this procedure four scroll plain samples were analyzed by Mark D. Bateman at Department of Geography, Sheffield University, UK



L- Luminescence, P- Palaeodose

Figure- 2.4. Figure showing the SAAD growth curve reconstructed giving incremental irradtiation, preheat and and illumination. Similar to MAAD, the palaeo dose is extrapolated on the X-axis.

The SAR method has advantage over SAAD and MAAD in the sense that

(i) SAR does not require normalization of the luminescence out put that is crucial for MAAD

(ii) Corrects for sensitivity changes (this does not occur in SAAD to an extent)

(iii) The equivalent dose determination is done by interpolation rather than extrapolation as in case of MAAD and SAAD methods.

(iv) Single aliquot provides multiple equivalent doses for a single sample. This offers the possibility of using small samples or single grains, thereby identifying aliquots with most bleached grains or most bleached aliquots.

This is important in case of fluvial samples where uncertainty about homogeneous bleaching is always high.

In the present study, samples were analyzed by multiple aliquot additive dose and single aliquot regeneration techniques and four scroll plain samples were additionally analyzed by single aliquot additive dose technique. This allowed to examine the variability in predepositional bleaching if any, especially with the samples of fluvial origin

Luminescence and Radioactivity measurements

BGSL and IRSL measurements of coarse grain quartz and feldspar were carried out on Riso TA-DA-15 reader with IRSL illumination using infrared diodes and a filtered halogen lamp was used for BGSL. Some of the later measurements of SAR were done using the blue LEDS. For IRSL, detection optics comprised 7-59 and BG-39 filters coupled to an EMI 9635 QA photomultiplier tube, whereas for BGSL, the optics comprised 2 ×U340 and BG-39 filters Beta irradiation were made using a 40mCi ^{90}Sr /^{90}Y beta source. The growth curve regression used the software supplied with the Riso system. Fine grain feldspar measurements using MAAD protocol were carried out in a Daybreak 1150 automated TL system with illumination using TEMT 484 infrared diodes and a detection optics comprising Corning 7-59, Schott BG-39 and Neutral Density 2.0 filters, coupled to EMI 9653QA photomultiplier tube.

Anomalous fading

IRSL signal is dominated by fine grain feldspar that may exhibit anomalous fading (athermal- rapid loss of stored signal from deeper traps at ambient temperature). An estimated loss of 2 to 10% in luminescence signal per decade due to fading has been

observed (Huntley and Lamothe, 2001) suggesting that IRSL ages could be underestimated. In order to check this, six samples were measured for anomalous fading through a measurement sequence of optical bleaching, beta irradiation, storage in dark for 3 months, read out and comparison of similar samples with similar cycle but with out waiting The luminescence yield of irradiated + stored sample was compared with an identically irradiated sample measured soon after irradiation. The ratio of the two gives the fading ratio and was typically ~1.

Preheats

An important part of the protocol in luminescence dating is elimination of unstable signal over the time scale being addressed. Pre-heating the aliquots before illumination and after the laboratory irradiation does this. The objective is to remove the unstable shine component in OSL dating and to achieve a charge distribution similar to that of a natural sample. This is done either heating the aliquots at lower temperature and extending the time or increasing the temperature and reducing the time

Various pre-heat temperatures have been suggested such as 160° for 16 hours (Stokes, 1992), 240 ^{0}C for 1 minute (Franklin et al., 1995), 220 ^{0}C for 5 minutes (Rhodes, 1998). We have used 240 ^{0}C for 1 minute pre-heat that removes the 280 ^{0}C peak with negligible effect on the 325 ^{0}C peak (Franklin et al., 1995). Since majority of the OSL signal comes from the optical release of charges from the trap responsible for the 325 ^{0}C peak (Spooner, 1994, Wintle and Murray, 1997) in quartz. Where as in feldspar it has been suggested that no single pre-heat procedure could ever be successful and that different pre-heating procedures should be tried until a palaeodose plateau is obtained (Berger and Anderson, 1994) It was found that

a preheat temperature of 220 ^{0}C for 1 minute gives a stable plateau for both fine and coarse grain feldspar that has been adopted in the present study.

Dose rate estimation

The dose rate estimation relied on ZnS (Ag) thick source alpha counting for elemental concentration of Uranium, Thorium. Potassium concentration was estimated using NaI (TI) gamma ray spectrometry Radioactive equilibrium was assumed in the decay series. Though this may not always hold true for fluvial sediments, a nearly 50% contribution to the dose by potassium provides some cushion against gross errors in the interpretations based on this assumption. Conversion of elemental concentration to dose was done via the conversion factors given in Aitken (1998).

Error estimation

Estimation of error is based on Aitken (1985). Two types of errors are associated with luminescence dating (i) the random error in plaeodose, a-value and annual dose computation and (ii) systematic errors arising due to uncertainty in alpha and beta source, alpha and potassium counting (calibration). Besides this parameters used in converting uranium and thorium content to annual dose rate and uncertainty in water content estimation also adds into the errors.

Radiocarbon Dating

Three isotopes of carbon occur in nature: the stable isotope ^{12}C (abundance 98.89%) and ^{13}C (1.11%) and radioactive isotope called the radiocarbon (^{14}C) abundance- 10^{-10} %. Radiocarbon is continuously produced in the upper atmosphere through interaction between

cosmic ray produced neutrons and nitrogen nuclei. Once produced, it gets oxidized and enters into the global carbon cycle through photosynthesis

Cosmic ray intensity has not changed much in the past hence the ^{14}C production and decay (half life, 5730 years) process builds up a steady state concentration of ^{14}C in the atmosphere. Living organism exchange carbon from the atmosphere and are labeled with a constant value of ^{14}C concentration. However, once the exchange process is terminated, the accumulated ^{14}C decays with its characteristic half life of 5730 years. An expression that relates radioactivity in the dead carbon containing material with its living counter part is expressed as;

$$A = A_0 \square^{-\square t}$$

Where A = residual ^{14}C activity in the dead material

A_0 = steady state ^{14}C activity in living counter part

t = time elapsed since death

Initial ^{14}C activity (A_0) can be found by measuring the ^{14}C activity in a 1890's wood sample (pre industrial). At times NBS-I oxalic acid that has ^{14}C activity 95% of the 1890 wood sample is also used.

The above expression explicitly assumes that in all parts, the initial ^{14}C activity of the living material was A_0 However, the modern studies have shown that this assumption is not true and ^{14}C concentration in the atmosphere was modulated by the earth's magnetic field, solar activity, sunspot cycles etc. The variability in ^{14}C production through time is corrected by calibrating the radiocarbon ages with that of the independent age estimates such as tree ring and varve chronology.

Experimental Procedures

There are three source of organic matter that contributes to the lake sediments.

(i) the aquatic plants that grow in the lake itself (autochthonous)

(ii) the terrestrial plants from the lake catchment (alchthonous) and

(iii) organic material transported along with the aeolian dust.

Out of these the aquatic and land derived organic carbon constitute major part.

About 500 gm of the bulk lake sediment was treated with conc. HCl to remove the detrital and secondary (precipitated) carbonates. The samples were then combusted at 800°C with medical oxygen in a quartz tube to get CO_2 Pure carbon dioxide was extracted using various freezing and cooling cycles and then finally collected in traps cooled at liquid nitrogen temperature. CO_2 was converted into acetylene by reacting CO_2 at a controlled rate with pure lithium metal melted in a specially designed reaction chamber kept at 550°C (Polach and Stipp 1967, Tamers 1975). About 6 gm of lithium was taken for CO_2 equivalent to 1gm carbon. The reaction product was lithium carbide (Li_2C_2) which was cooled at room temperature and then hydrolyzed using distilled water to produce C_2H_2 along with traces of gases and water vapour. Double distilled ground water is used at this stage so that there is no interference from tritium activity. The gas was dried using moisture traps at -100°C. Two traps filled with glass beads coated with NaOH and H_3PO_4 and a third one filled with sodalime are used to remove trace gases in order to get 99.99% pure acetylene.

Finally the acetylene was absorbed and is polymerized into benzene using a catalyst V_2O_5 pellets (Polach et al., 1972) and recovered by heating the catalyst at 110°C followed by condensing the benzene vapor at liquid nitrogen temperature The overall chemical yield is between 90 - 94%. Old coal (a laboratory batch labeled as Anthracite-II) was used as a background standard, OXALIC ACID-I (Olsson 1970) and OXALIC ACID-II (Stuiver 1983, U.S. National Bureau of Standards) were used as the modern carbon standards.

The radioactivity was measured using a standard liquid scintillation counter An organic scintillator (Butyl-PBD) was mixed (0.015 g per ml) with the sample benzene prior to decay measurements. ^{14}C decays were counted in a low background Teflon vial in the ultra low background detector "LKB-QUANTULUS ". The overall procedure is standardized to 1 ml of benzene volume (Yadava and Ramesh, 1999). The counting interval was set to 85-min duration and 30 repeat measurements were made to check the data for statistical fluctuations. The average background for 1 ml of benzene was 0.30±0.03cpm and the modern reference standard (NBS Oxalic acid-I) was 9.36±0.13cpm ml^{-1} of benzene over a period of a year with an overall precision of 1.5%. The laboratory-dating limit was estimated to be 40 kyr

CLIMATE PROXIES

Mineral Magnetic

Mineral magnetism deals with the transport, deposition and transformation of magnetic grains by the environmental condition and geomorphic process Environmental magnetism encompasses diverse fields such as climatology, ecology, geomorphology, land-use studies, limnology, meteorology, oceanography, sedimentology and soil sciences and provides a relatively rapid, simple and non-destructive tool for climate reconstruction (Oldfield, 1991, Verosub and Roberts, 1995). In the present study following climatic sensitive parameters were used.

Magnetic susceptibility: It is a measure of concentration of ferromagnetic or ferrimagnetic grains in the sample and is expressed as either volume specific (κ) or mass specific (χ). It is measured with an inductance bridge that produces weak alternating fields of high frequency. Volume specific susceptibility is a dimension less quantity where as mass susceptibility is expressed as 10^{-8} m^3kg^{-1}in SI unit

Frequency dependent susceptibility: It is a measure of the concentration of ultra fine magnetic grains (~100 ^{0}A) (superparamagnetic grains) and is measured using the same inductance bridge at high (4.7 kHZ) and low (0.47 kHZ) frequency It is expressed as volume (κ_{fd}) or mass (χ_{fd}) or simply as a percentage (χ_{fd} %) determined by dividing χ_{fd} x 100 by χ

'S' ratio: It is the magnetomineralogical S-ratio and is a quantitative measure of degree of saturation where "S" is the absolute value of the Isothermal Remnant Magnetization (IRM) remaining after exposure to a reverse field of 300 mT divided by the SIRM acquired at 1.5 T (Verosub and Roberts, 1995)

The magnetic susceptibility was measured with a Geofyzica Brno KLY-2 Kappabridge while IRM was carried out using a MMPM9 Pulse Magnetzer and a 2G three axis SQUID Cryogenic Magnetometer at the Palaeomagnetic Laboratory, University of Tuebingen, Germany by N. Basavaiah.

Geochemical parameters

Due to their resistance to chemical alteration, elements like Al, Fe, Ti and Si are used as reliable climate proxies in lake deposits. In view of this, lake sediments from higher central Himalaya have been analyzed for major elements using X-ray fluorescence spectrometry (XRF). The samples were processed in Siemens Sequential X-ray spectrometer (SRS-3000) equipped with Rh end window X-ray tube at Wadia Institute of Himalayan Geology, Dehra Dun. The sample pellets were prepared by pressing the powdered sample under a pressure of 16 ton made. A few drops of polyvinyl alcohol were added to the sample powder to serve as a binding agent The analytical accuracy was 5% and precision in terms of maximum observed standard deviation on repeated measurement was 2% (Saini et al , 1998).

Organic carbon estimation in dunes

Studies in Thar Desert have shown that dunes are poor in organic carbon due to sparse vegetation, eroded topography of sand dunes and lack of sufficient moisture (Bhandari, 1988). However, variability in organic carbon concentration between stabilized (vegetated) and unstabilized (without vegetation) dunes are observed (Dhir, 1977). Thus suggest, that organic carbon concentration in a vertical sequence of a stabilized dune can be used as a potential proxy for reconstructing past vegetation/moisture condition. This prompted estimation of the organic carbon concentration in chronologically constrained fossil dunes.

Luminescence dated dune samples from the desert margin were analyzed in Fisons NA1500 elemental analyzer. The samples were treated with 10% Acetic acid (to remove the carbonate), followed by rigorous washing with double distilled water. Following this, samples were oven dried at 60 ^{0}C. Nearly 10-15 mg of homogenized sample was taken in aluminum cups, sealed and put into a combustion tube through an auto-sampler for carbon and nitrogen analyses. A four-point calibration sequence was made using a Deer River Shale reference standard containing 2.53% carbon and 0.12% nitrogen. The analytical precision for measurement of carbon was estimated to be ~ 4% while for nitrogen it was estimated at ~ 6%.