APPENDIX E

Experimental Procedures For Luminescence Dating

The principles of luminescence dating have already been discussed in Chapter 4 (section 4.1). In this appendix, are described, the experimental procedures followed for sample collection, estimation of equivalent dose (ED) and dose rate.

E.1 Sample collection

It has already been mentioned earlier (appendix A) that core sections selected for luminescence dating were wrapped in aluminium foil and stored in airtight polythene bags as soon as they were raised. The core length varied from 5-20 cm and was 5 cm in diameter. Owing to the time lag between sample raising and it's covering, the outer skin of the core had been exposed to light. However subsequent processing of sample was done under subdued red light after removing the outer l cm skin of the core sample and cutting 2 cm off from the ends of the core. The skin was discarded to avoid any possibility of contamination. The end portions were used for alpha counting (to determine U and Th contents), Gamma spectrometry (U/Th series disequilibrium checking), AAS (K content estimation) and water content estimations. Only the central unexposed portion was taken for equivalent dose estimation.

E.2 Laboratory procedures for determination of ED

The methods for estimation of ED have been discussed in Chapter 4 (Section 4.1.2). For the construction of growth curves, aliquots/discs of the same sample must be given different treatments. The procedures for preparation of aliquots are described below. The entire process was done under subdued red light illumination.

E.2.1 Sample preparation

Selection of grain size and mineral phase: For the purpose of dating, finer fraction (4-11µ) comprising of silt was preferred since they are likely to have been in suspension longer and more likely to have been bleached during transport. The silts comprised about 10-30% in Horizon-2 and also constitute a significant fraction in Horizon-3. For a few samples, in Horizon-2, coarse grained dating of feldspars was also attempted. This method was not generally applied since very little feldspar was found in the sand sized fraction. Feldspar mineral phase was generally preferred since they saturate at larger doses and are more useful for dating older sediments. The infra red stimulated luminescence (IRSL) dating was used for obtaining the ages of samples in the present study. For a few samples, Thermoluminescence (TL) dating using partial bleach method was also attempted.

Sample pre-treatment: Samples were sequentially treated with 1N HCl to remove the carbonates, 30% v/v hydrogen peroxide to remove the organic matter and 0.01N sodium oxalate solution to deflocculate the sample. All the treatments were continued till the reactions were over and sample was washed with distilled water in between the steps.

Preparation of discs: For convenience of handling, aliquots of sample were prepared by depositing the separated size onto 1cm diameter aluminium/steel discs. These discs had been cleaned earlier using emery paper to ensure uniform distribution of sample on its surface. Both the fine grain and the mineral inclusion technique were used.

Fine-grain technique: In this technique, (Zimmerman, 1971) the samples were suspended in a 6cm column of acetone. The 4-11m size fraction was separated using Stoke's settling in acetone. One and a half minutes time was required for the >11µm size fraction to settle. To separate <4µ size, again a settling time of 15 minutes was given and the overlying filtrate removed. The material settled at the base of test tube was the required 4-11µ size fraction. Different aliquots of the sample were prepared by re-suspending the sample in either acetone or alcohol and pipetting on to aluminium discs. These discs were dried in the oven at 45°C. In view of difficulties of separation of required mineral phases, e.g. quartz or feldspar, at this size, specific optical windows (by use of suitable filters) were used to discriminate against and/or select emissions of a particular mineral phase (Debenham and Walton, 1983).

Coarse grain technique: This technique was developed initially for studying 90-125μm quartz inclusions (Fleming, 1970) and is also called as the mineral inclusion technique. This technique has been extended to study the large K-feldspar inclusions too (Mejdahl and Winther-Nielson, 1983). After sample treatment, the coarser size fraction was dried and sieved to obtain the required size (95-150μm) fraction. The magnetic minerals were then removed using a hand magnet followed by isodynamic separation using a Franz magnetic separator. Since, in both quartz and feldspar, only the outer ~20μm skin was exposed to α radiation, it was removed by an appropriate HF acid etch. The two mineral phases were separated using heavy liquid (sodium polytungstate) density separation (d>2.65 to float quartz and 2.58<d<2.65 to isolate the K-feldspar).

Even though the process for preparation of discs was same, there were small differences in sensitivities between discs either due to variation in the sample amount or due to differing luminescence sensitivities of the grains which caused a scatter in the luminescence output. For this purpose, sample normalisation, described below, is done. In the present study only short shine normalisation was used but the other methods are mentioned for the sake of completeness.

E.2.2 Sample normalisation

Short shine normalisation: This relies on the fact that it is possible to measure the initial OSL signal of a sample without significantly reducing the geological optical signal. Each aliquot, prior to any treatment, was given 0.5 seconds of IR stimulation. This signal was subsequently used for normalisation.

Weight normalisation: This is used for mineral inclusion method and involves dividing the luminescence signal of each aliquot by the weight of the sample present in that aliquot. Implicit in the use of this method is the assumption that the luminescence characteristics of grains in the aliquot are similar. However, this may not be strictly true and in some cases when the luminescence characteristics are dominated by a small number of bright grains, weight normalisation is not very successful.

Zero glow normalisation: Zero glow normalisation was first suggested by Aitken and Bussel (1979). It takes advantage of the fact that due to the short lifetime of the 110°C peak, it is absent in all the natural samples. Each aliquot was given a test dose that is small compared to it's palaeodose and the intensity of the 110°C peak measured. This TL is a measure of the overall sample response of the aliquot as influenced by differences in weight, spreading and proportions of the bright grains present. Because of it's short lifetime, the peak is liable to decay significantly within a few minutes and hence a standardised schedule for irradiation and recording has to be adopted.

E.2.3. Sample treatment

The samples treatment consisted of irradiations (β and α) for estimation of ED, and pre heat.

Irradiation: Beta irradiations were given on an automated time controlled fifteen seater irradiator (Littlemore Inc.) using a 25 mCi ^{90}Sr/^{90}Y β source. The dose rate was 2.2 Gy/min for fine grains. Alpha irradiations were made on a manually timed, evacuated six seater irradiation system using an ^{241}Am source (Singhvi and Aitken, 1978) of strength 220 μCi.

Pre Heat : Just prior to recording (TL or OSL), all samples were pre-heated at 160° C for 6 hours to remove unstable part of the signal. The system consisted of a heavy brass block fixed in a temperature controlled furnace. The block has small slit in which the sample aliquots were placed on a copper plate and inserted.

E.2.4 Calculation of 'a' value

The α efficiency factor 'a' was calculated using the formula,

$$a = \beta\ (Gy)/(13*S*y)$$

where, β is the dose that gives the TL intensity equal to that given by y (minutes) of α exposure from an ^{241}Am source of strength 'S' (given in μm^{-2} min^{-1}) (Aitken and Bowman, 1975).

Since in this study chiefly IRSL method of dating has been used, the 'a' value was also obtained from the IR stimulation of α and β irradiated samples. The natural luminescence was zeroed using IR long shine (5 min) and also by long sun bleach. The alpha efficiency factor was determined for sample N-127 by both, long sun and IR regeneration, methods and found to be the same within 1σ. For other samples subsequently, sun regenerated IR growth curves were constructed for both α and β doses and the 'a' value calculated. The estimated 'a' values are given in Table 4.1.

E.2.5. Anomalous fading test

In the present case, the primary provenance is dominated by metamorphic and volcanic rocks. Since IRSL dating was done on the feldspars, there was a possibility of samples exhibiting anomalous fading. All the samples were checked for anomalous fading. Two sample aliquots were given 20min beta exposure and the TL recorded immediately along with another set of two aliquots which had been identically irradiated 3 months previously. This was considered as optimum test since it has been found that the samples which show fading in the IRSL signal also show fading in TL (Spooner, 1993).

E.2.6 Luminescence measurement

OSL measurements: OSL system comprising a rotatable sample holder with a capacity of 16 discs was used. The IR source consisted of 14 GaAs

LED's arranged in series which emit light at 880±80 nm. The source was operated using a programmable constant current DC supply. The detector consisted of a bialkali photomultiplier tube (9635QA) connected to a photon counting system, the output of which was recorded through EG&G 4096 channel ACE-MCS card coupled to an IBM/PC-486. The signal was filtered using Corning 5-58(blue pass)+7-59(violet pass) and Chance Pilkington HA3 (IR rejecting) combination. The background was typically 150 cps as compared to the sample signal of a few thousand cps.

TL measurements: These were made on an automated TL system (Daybreak). The system comprised of a heating arrangement and the emissions were detected using a PMT tube (EMI 9635 QA) through UG11 (ultraviolet pass) +HA3 filters. Since in case of NaI the samples were very bright, Neutral Density (ND) filters of different transmission powers were additionally used. All the measurements were carried out in pure Nitrogen atmosphere and a heating rate of 5°C/s was used.

E.3 Laboratory procedure for measurement of dose rate

The dose rate is a measure of the environmental radioactivity of the sediment over a period of time. Nearly all the dose rate is provided by uranium, thorium decay series and potassium-40. The following procedures were used for dose rate estimation.

AAS: ^{40}K was estimated using by Atomic Absorption Spectrometry (AAS). Samples were digested by sequential treatment of HF, $HClO_4$, HNO_3 and HCl. The solutions were then diluted to bring them to the linear portion of the absorbence curve. The absorption spectra were recorded on the Perkin-Elmer 305 atomic absorption spectrometer.

α counting: U and Th were measured using thick source alpha counting. The samples were crushed, and spread onto a ZnS(Ag) scintillator. All the measurements were made using an alpha counter (Daybreak 582). The counting system was calibrated using standard sand 105A with 10.2 ppm U, as described by Aitken (1985). Typical background rates were ~0.2 counts/ks for a counting area of 13.85 cm ^{2}.

γ spectrometry: To determine disequilibrium, if any, in the decay chains of U and Th gamma spectrometry was carried out. Samples were sealed in plastic vials using araldite and stored for a period of 2-3 weeks to allow the radon to build up. Subsequently high energy gamma counting using a p type Ge(Li) well type detector with a multi channel analyser was done. The standard used for calibration had U=5.69 ppm., Th=14.5 ppm and K=2.63%. The amount of ^{235}U was determined using gamma counting of the sealed sample and that of U computed by comparison with the standard; U was also calculated by counting a post ^{222}Radon daughter, ^{214}Bi. A discrepancy in the U concentration as determined by both these methods will be indicative of disequilibrium. Similarly, the concentration of ^{232}Th was determined by counting two of it's post ^{220}Rn daughters - ^{208}Tl, ^{212}Pb and one pre ^{220}Rn daughter ^{228}Ac, and comparing with the standard which is in equilibrium. The amount of ^{40}K was also computed by gamma spectrometry. The values show agreement with that obtained from AAS.

E.4 Water content estimation

About 30gm of sample was weighed and kept in oven to dry at 60°C in order to determine 'as found' water content. The results are given in Table 4.1. For the purpose of determining the saturation water content, a chunk of sample was oven dried and tightly wrapped in aluminium foil to ensure no free space for water. Over a period of few days, distilled water was added from a dropper to the sample. Once this amount was absorbed, water was added again. This continued till the sample was saturated and a thin film of water stayed on the surface - this was carefully removed. The difference in weights before and after addition of water gave an estimate of the saturation water content.

E.5 Data analysis

The OSL intensity was normalised with respect to short shine and the growth curve constructed by fitting a polynomial or a saturating exponential curve to the data. The ED was obtained from the intersection of the additive growth curve with the x- axis for different IR exposure times (Chapter 4, Section 4.1.2). The weighted average of ED values over the plateau was used.

The 'a' value was computed by constructing both β and α regeneration growth curves and using the equation (Section E.2.4) given by Aitken and Bowman (1975).

The dose rate was calculated from the relative contributions of α, β, and γs from U, Th and K using standard tables (Aitken, 1985). A correction to account for the higher stopping power of water for α, β, γ as compared to air is applied (Zimmerman, 1971). An average of 'as found' and saturation water content was used for dose rate calculations.

The luminescence age was subsequently calculated using equation 4.3. The errors on age were computed according to the procedures discussed in Aitken (1985). The reported ages represent the calculated mean of the age over the plateau. The quoted error on age is the minimum measured error over the age plateau. The results are given in Table 4.1.