Chapter 5

Thermoluminescence and Infra-red Stimulated Luminescence dating of Pedogenic Carbonates

5.1 Introduction

Calcretes are defined as terrestrial materials which consist primarily (but not exclusively) of calcium carbonate and occur in different forms from powdery to highly indurated ones (Goudie, 1983). Pedogenic carbonates occur in a variety of sedimentary sequences and soil profiles and may be present as kankar nodules, rhizoconcretions, pedotubules etc. In soil profiles, they often form several distinct horizons (e.g., calcic or petrocalcic horizons). Machette (1985) has recognised six stages of development of such carbonates depending upon the amount of calcium carbonate and gravel content present within the horizon. Generally, formation of pedogenic carbonates takes place when carbonates derived mostly from dust, rainfall, vegetation litter, shells and chemical weathering of Ca$^{2+}$ bearing minerals are leached downwards in a profile and precipitate in the lower soil horizons (Goudie, 1983). The chemical reactions involved in the dissolution and reprecipitation of calcium carbonate are:
\[ \text{CaCO}_3 + \text{H}_2\text{CO}_3 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- \]  \hfill (5.1)

\[ \text{H}_2\text{CO}_3 \rightarrow \text{CO}_2(\text{aq}) + \text{H}_2\text{O} \]  \hfill (5.2)

\[ \text{CO}_2(\text{aq}) \rightarrow \text{CO}_2(\text{g}) \]  \hfill (5.3)

where (aq) and (g) denote the aqueous and gaseous phases respectively. Carbonate precipitation occurs if there is decrease in the CO\textsubscript{2} partial pressure, evaporation, common ion effect or biological activities. Evaporation results in a rapid loss of vadose water and could lead to rapid carbonate precipitation and causing the formation of small calcite crystals. Evapotranspiration can also result in carbonate precipitation.

The basic importance of pedogenic carbonates stems from the fact that they have long been considered as important stratigraphic markers as also paleoclimatic and paleovegetational indicators. They generally form in regions of net annual moisture deficit and net annual precipitation of less than 400 mm. It has also been suggested that the presence of pedogenic carbonates implies landscape stability (Callen et al., 1983). Present estimates indicate that pedogenic carbonates cover \( \sim 20 \) million km\(^2\) or about 13\% of the total land surface (Yaalon, 1981). In Arizona, the depths of occurrence of carbonates have been related to the annual precipitation (Cooke et al., 1993). The rates of soil carbonate accumulation have also been correlated with modern mean annual precipitation (Marion et al., 1985). Pedogenic carbonates also constitute a significant part of the global carbon budget. Thus, it is essential to understand the timescales of carbon fixation as carbonates in the arid zones of the world and examine their correlation with global climatic events (Adams et al., 1990). After a brief review of the existing methods for dating carbonates, this chapter describes the new luminescence method.
to date pedogenic carbonates. Luminescence ages of carbonates from Thar Desert and their implications are also presented at the end of this chapter.

5.2 Dating of Pedogenic Carbonates: Earlier work

Radiocarbon dating of carbonates has been attempted by many workers (Godwin, 1951; Williams and Polach, 1969; 1971; Chen and Polach, 1986). Comparisons between \(^{14}\text{C}\) ages on carbonates with coexisting organic materials have generally indicated that: (a) relative ages agree suggesting that the radiocarbon ages have some stratigraphic implications; (b) arid zone carbonate ages are typically a ~ few ka older than the true carbonate age due to incorporation of ‘dead’ carbon (containing little/no \(^{14}\text{C}\)) and (c) ages on carbonates from semi-arid to humid regions are mostly younger than the age on the coexisting organics. The latter result has been attributed to post-formation contamination by atmospheric \(^{14}\text{C}\) dissolved in meteoric waters (Williams and Polach, 1969). However, Callen et al., (1983) obtained stratigraphically inconsistent \(^{14}\text{C}\) carbonate ages from Strzelecki Desert, South Australia. The ages from the rim of nodules were found to be much younger (29 ka BP) than those from the centre of the nodule (> 44 ka BP). Thus, Callen et al. (1983) suggested that \(^{14}\text{C}\) carbonate ages from arid zones are often unreliable and have little or no stratigraphic significance.

\(^{230}\text{Th—}^{234}\text{U}\) disequilibrium dating has also been attempted on pedogenic carbonates (Ku et al., 1979). However, the method needs correction for the detrital Th/U component and also assumes that after their formation, the carbonates act as closed systems in respect of exchange of thorium and uranium isotopes. Incorporation of older crust material or limestone particles can also result in erroneous ages. The Electron Spin Resonance dating method (Radtke et al., 1988) has also been used to date calcretes. However, many of the ESR ages obtained by Radtke et al., (1988) were not
consistent with the $^{230}$Th—$^{234}$U ages on the same calcrites. Also, the $g = 2.45$ ESR signal used for dating is associated with humic acids and thus might not remain stable over geological timescales. It is also not apparent whether the ESR method can be applied for ascertaining the chronology of young calcrite profiles.

Thermoluminescence (Nambi and Hedge, 1982; May and Machette, 1984) techniques have also been utilized to date calcrites but are open to criticism on various aspects: isolation of carbonate luminescence from quartz and feldspar luminescence, opacity and TL sensitivity changes on heating and diagenetic changes (Berger, 1988).

Recently, an attempt has been made to use the in situ production of $^{36}$Cl by cosmic rays for dating pedogenic carbonate nodules (Liu et al., 1994). This method at best provides model ages as it crucially depends on several factors such as the changes in the calcrite burial depth, constancy of cosmic ray fluxes through time and negligible erosion. Liu et al., (1994) reported ages from 200-700 ka for a calcrite profile from Ajo Mountains, southern Arizona. However, the leachable fraction $^{36}$Cl ages were generally larger than the carbonate fraction and the silicate residual $^{36}$Cl ages. An age inversion is also observed in the silicate residual $^{36}$Cl ages. Thus, additional dating work is necessary to test the validity of the $^{36}$Cl method for dating carbonates.

The present studies involved the development of a new luminescence dating technique for dating pedogenic carbonates, which (unlike other radiometric methods discussed above) is less susceptible to post-depositional changes and is also immune to variability of cosmic ray fluxes. This approach exploits subtle changes in the natural radiation field of a luminescent mineral after being trapped in a carbonate precipitate. Thus, the proposed method utilizes the ‘dirt’ of a nodule to date a carbonate precipitation event. In principle, the methodology should allow us to apply it to a large variety of terrestrial carbonate deposits ranging from root casts, kankar nodules and loess-dolls.
5.3 The Luminescence dating method

The proposed method is based on the same premise as used in luminescence dating of sunlight bleached sediments (Aitken, 1985). Sunlight exposure of the minerals constituting the sediment stratum during their pre-depositional transport optically bleaches the geological luminescence to a residual value \( I_0 \). On burial, a fresh acquisition of luminescence is initiated due to irradiation arising from the decay of U, Th, K in the ambient strata. This reacquisition of luminescence continues unabated till the sample is excavated and a laboratory analysis of this sample provides a signal \( I_{\text{nat}} \), such that

\[
I_{\text{nat}} = I_0 + I_d
\]  

where \( I_d \) is the TL acquired since sedimentation. In terms of equivalent radiation doses, the above equation can be functionally expressed as \( P_s = P_o + Q_s \) where \( P_s \) is the total paleodose in a sample. \( P_o \) is the initial dose corresponding to TL intensity \( I_0 \) and \( Q_s \) is the dose acquired since burial and corresponds to \( I_d \). The luminescence age equation can be written as:

\[
t_s = \frac{Q_s}{aD_{\alpha,s} + D_{\beta,s} + D_{\gamma,s} + D_{\text{cos}}}
\]  

where \( t_s \) is the age of the sedimentation episode of the host stratum (e.g., a sand dune). \( D_s \) is the total annual radiation dose whereas \( D_{\alpha,s} \), \( D_{\beta,s} \) and \( D_{\gamma,s} \) are the components of gamma dose rates provided by the decays of \(^{238}\text{U}, \ ^{232}\text{Th} \) and \(^{40}\text{K}\). \( D_{\text{cos}} \) is the cosmic ray dose rate and \( a \) is the sample dependent alpha efficiency parameter. In the case of carbonate formation, some of the mineral grains that are trapped in the carbonate matrix suffer a change in their dose rate due to dilution (or enrichment) of the radioactivity of sediment matrix by carbonate. If the dose rate experienced by a grain in a carbonated
matrix is \( D_c \), then the total paleodose \( P_c \) of a mineral grain trapped in the carbonate matrix can be expressed simply as (Fig. 5.1),

\[
P_c = P_o + Q_c
\]  

where \( Q_c \), the calcrite equivalent dose is given by the equation

\[
Q_c = (t_s - t_c)D_s + t_c D_c
\]  

Here \( t_c \) is the age of carbonate formation event. Realizing that,

\[
P_s = P_o + Q_s = P_o + t_s D_s
\]  

using equation (5.7) and equation (5.8) one obtains,

\[
t_c = \frac{P_s - P_c}{D_s - D_c}
\]  

Since both \( P_s \) and \( P_c \) have identical predepositional bleaching (i.e. \( P_o \)),

\[
P_s - P_c = Q_s - Q_c
\]  

\[
t_c = \frac{Q_s - Q_c}{(aD_{\alpha,s} + D_{\beta,s} + D_{\gamma,s} + D_{\cos,s}) - (aD_{\alpha,c} + D_{\beta,c} + D_{\gamma,c} + D_{\cos,c})}
\]  

The above equation simplifies if one considers 100–150 \( \mu \)m mineral separates which have negligible internal radioactivity. Also, the alpha dose contribution from the host matrix can be ignored by etching the outer alpha-dosed skin of the mineral. The large range
Fig. 5.1. Schematic representation of basic principles involved in luminescence dating of a carbonate. The symbols used have been explained in the text.
of gamma rays further implies that the $\gamma$ dose and cosmic ray contribution from the host matrix (< 30 cm) when compared to typical size of 1–3 cm of a carbonate nodule remains essentially unaltered even after carbonate precipitation. Setting,

$$D_{\alpha,s} = 0 = D_{\alpha,c} \quad D_{\gamma,s} = D_{\gamma,c} \quad \text{and} \quad D_{\cos,s} = D_{\cos,c} \quad (5.12)$$

the dose rate difference reduces to

$$D_s - D_c = D_{\beta,s} - D_{\beta,c} \quad (5.13)$$

Thus, only the difference in the total annual beta dose from U, Th, K in uncarbonated and carbonated mineral separates needs evaluation. The age equation in its final form can be written as,

$$t_c = \frac{Q_s - Q_c}{D_{\beta,s} - D_{\beta,c}} \quad (5.14)$$

which suggests that the dating of carbonates for mineral separates having negligible internal radioactivity (e.g. quartz) requires estimation of the differences in (i) accumulated radiation doses of mineral separates from both the carbonate matrix and the host sediment and, (ii) radioactivity content (i.e. the difference in the net annual beta dose to minerals within a host matrix and a carbonate nodule). However, for unetched K-feldspar separates, the alpha dose contribution also needs to be considered and the expression for the luminescence age becomes

$$t_c = \frac{P_s - P_c}{a(D_{\alpha,s} - D_{\alpha,c}) + (D_{\beta,s} - D_{\beta,c})} = \frac{Q_s - Q_c}{a(D_{\alpha,s} - D_{\alpha,c}) + (D_{\beta,s} - D_{\beta,c})} \quad (5.15)$$

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5.4 Methodological Aspects of the luminescence dating method

This section discusses some methodological aspects of the dating method, viz., dosimetric changes due to loss/gain of radionuclides, change in the luminescence age as a result of redissolution and reprecipitation and estimation of error in the calcrite age.

5.4.1 Dosimetric changes due to loss of $^{238}\text{U}$ and/or $^{232}\text{Th}$

The calcrite age equation can be written as

$$
\text{Age} = \frac{Q_s - Q_c}{\beta_{\text{Th,s}} + \beta_{U,s} + \beta_{K,s} - \beta_{\text{Th,c}} - \beta_{U,c} - \beta_{K,c}}
$$

(5.16)

Now if $\beta_{\text{Th,c}}$ and $\beta_{U,c}$ change to $\beta'_{\text{Th,c}}$ and $\beta'_{U,c}$ after precipitation of the nodule, the expression for the new age is given by

$$
\text{Age}' = \frac{Q_s - Q'_c}{\beta_{\text{Th,s}} + \beta_{U,s} + \beta_{K,s} - \beta'_{\text{Th,c}} - \beta'_{U,c} - \beta_{K,c}}
$$

(5.17)

Using the two equations above and assuming $Q'_c \sim Q_c$ (a reasonably good assumption since $\sim 80\%$ of the $\beta$ dose comes from K), one gets the relative change in age

$$
\frac{\Delta\text{Age}}{\text{Age}} = \frac{\text{Age} - \text{Age}'}{\text{Age}}
$$

(5.18)

given by the expression

$$
\frac{(\beta_{\text{Th,c}} + \beta_{U,c}) - (\beta'_{\text{Th,c}} + \beta'_{U,c})}{(\beta_{\text{Th,s}} + \beta_{U,s} + \beta_{K,s} - \beta_{\text{Th,c}} - \beta_{U,c} - \beta_{K,c}) + ((\beta_{\text{Th,c}} + \beta_{U,c}) - (\beta'_{\text{Th,c}} + \beta'_{U,c}))}
$$

(5.19)
Now \((\beta_{Th,s} + \beta_{U,s} + \beta_{K,s} - \beta_{Th,c} - \beta_{U,c} - \beta_{K,c})\) is the original annual beta dose difference between the host sand and the calcrete. For the calcrete sample CAL-3, this difference is 0.56 mGy/a whereas \(\beta_{Th,c}\) and \(\beta_{U,c}\) are \(\sim\) 0.086 mGy/a and 0.084 mGy/a respectively. Calculations using these values show that (i) if 50 % loss of either \(^{238}\text{U}\) or \(^{232}\text{Th}\) occurs, the change in the age will be 7 % while (ii) if 50 % loss of both \(^{238}\text{U}\) and \(^{232}\text{Th}\) occurs, the age changes by 13%.

5.4.2 The interpretation of luminescence ages for multiple carbonate precipitation events in a single profile

After the carbonate precipitation event, if redissolution and reprecipitation occurs, it is most likely that the new carbonate will form at a different depth. Assuming this to be so, we now consider two situations and the interpretation of the luminescence age in each case.

**Scenario A**

We assume that the new carbonate forms at a lower depth and incorporates only those mineral grains which were present within the adjacent host sand. Therefore, the carbonate does not contain any mineral grains present within the original carbonate. Under these circumstances, the procedure indicated in Section 5.3 can be applied to evaluate a carbonate age. The estimated carbonate age denotes the time of the new precipitation event and will be lower than the age of the earlier carbonate formation event. If such events repeatedly occur, i.e., each time the new carbonate forms at a new horizon and contains grains only from the adjacent sands, the estimated carbonate age will represent the age of the latest precipitation event.
Scenario B

If the new carbonate formed comprises of grains having different irradiation histories, i.e., grains originating from the older carbonate and from the adjacent host sand, the above approach cannot be applied to estimate the carbonate age since the paleodose \( P_c \) for carbonate minerals cannot be expressed in a unique way. Also, the resulting inhomogeneity in radioactivity within the carbonate implies that the infinite matrix assumption breaks down and the annual dose cannot be calculated in the usual manner. Additional assumptions regarding the rate of deposition and the annual dose \( D_s \) need to be made to evaluate a proper age. In such situations, the single grain dating method can perhaps be used to obtain a meaningful age.

5.4.3 Estimation of errors

If \( f \) is a function dependent on \( n \) parameters \( x_i \) each with a standard deviation \( \sigma_i \), then the variance in \( f \), \( \sigma_f^2 \) is defined as

\[
\sigma_f^2 = \sum_{i=1}^{n} \sigma_i^2 \left( \frac{\delta f}{\delta x_i} \right)^2
\]  

(5.20)

If \( \sigma_{Q_e}, \sigma_{Q_s}, \sigma_{D_e}, \sigma_{D_s}, \) and \( \sigma_{\text{Age}} \) are the standard deviations for \( Q_e, Q_s, D_e, D_s \) and the calcite age respectively then using equation (5.15) and simplifying, we get

\[
\sigma_{\text{Age}}^2 = \text{Age}^2 \left( \frac{\sigma_{D_e}^2}{(Q_s - Q_c)^2} + \frac{\sigma_{Q_s}^2}{(Q_s - Q_c)^2} + \frac{\sigma_{D_s}^2}{(D_s - D_c)^2} + \frac{\sigma_{F_c}^2}{(D_s - D_c)^2} \right)
\]  

(5.21)

Thus an evaluation of the standard deviation in age involves use of five quantities \( \sigma_{Q_e}, \sigma_{Q_s}, \sigma_{D_e}, \sigma_{D_s}, \) and the calcite age. Using equation (5.16), it can be shown that if \( Q_s - Q_c \) is \(< 5 \) Gy and \( D_s - D_c < 0.5 \) mGy/a, measurement errors of \( Q \) and \( D \) values must be
less than 5% for achieving a reasonable error limit (< 20%) on the calcrete age. Another implication of equation (3) is that the luminescence method is most suitable for dating pedogenic carbonates which have (i) formed at least a few thousand years after the sand depositional event and (ii) a large annual beta dose difference between the host sand and the carbonate (|D* - Dc| > 2 mGy/a).

5.5 Samples and procedures

5.5.1 Luminescence Measurements

For the present study, carbonates were sampled from various sites viz., Budha Pushkar, Chamu, Amarsar and Jalore in a transect across Thar Desert (Fig. 5.2). Presently, the mean annual precipitation in Chamu is ~ 300 mm. Jalore passes through the ~ 350 mm isohyet whereas Budha Pushkar and Amarsar receive ~ 450 mm and ~ 500 mm rainfall annually. For TL measurements, 105-150 μm quartz mineral separates were extracted by a sequential pretreatment of the original sand sample by HCl, H2O2 and HF. The extraction of quartz from carbonates was done by first dissolving (and discarding) the outer 0.5–1 cm of the carbonate and then fully dissolving the remaining carbonate. The residue was then treated identically as described above. The extracted quartz was tested for purity using an 880 nm infra-red stimulated luminescence system.

K-feldspar extraction was performed by treating the sample with HCl, H2O2, sieving the 75–106 μm fraction and using the density separation technique (density = 2.58 mg/cm3) with sodium polytungstate. No HF etching was done during feldspar separation due to the possibility of grain rupture and limited sample availability. Thus, alpha dose (attenuated) was also taken into account in the calculation of the annual dose for K-feldspar grains. The α-efficiency factor was assumed to be 0.15 ± 0.075 for K-feldspar grains.
Fig. 5.2. Locality map of North-west India. Pedogenic carbonate sites sampled for luminescence dating are presented in the diagram (modified after Kar, 1995). Khudala was only sampled for aeolian sands (results are discussed elsewhere).
TL measurements were done on ~ 5 mg monolayer quartz/feldspar separates deposited on stainless steel discs using a photon counting setup comprising EMI 9635QA photomultiplier tube coupled to two Schott UG11 and a Chance Pilkington HA3 filters. The UG11 filter was chosen to isolate the rapidly bleaching 325° peak (Prescott and Purvinskis, 1991). All laboratory sun-bleaching was done using natural sunlight. The TL analysis was done using the the total-bleach (bleaching time ~ 7 hrs. and ~ 30 minutes) and the R- methods (bleaching time ~ 30 minutes) generally used for sediment dating and a weighted mean of the equivalent doses was used in estimation of age. However, the weighted mean error was not used for calculating the error (σQ) in Q values since the growth curves for different bleaching methods are not independent of each other (N + β curve is common for all methods). Instead, the error in the equivalent dose (from a typical growth curve) at a certain plateau temperature was used as σQ for the samples.

IRSL dating was carried out on K-feldspar extracts. The IRSL intensities of natural and irradiated discs were normalized using 1 second shortshine glows. The optics channel comprised a EMI 9635 QA PMT coupled to corning 5-58 + 7-59 blue filters, one quartz ND-1 filter and a chance Pilkington HA-3 filter. The PMT operated in the photon counting mode was interfaced to an IBM/PC with an Ortec Accuspec multi-scaling card. Sixteen IRSL diodes (TEMT 454) with peak emission at 880 ± 80 nm (operated with a programmable constant current supply) were used for shinedown curves. Beta irradiations were performed using a 25 mCi 90Sr − 90Y beta source.

Since the K-feldspar separates from host sands and carbonates have identical predepositional bleaching histories, P* − P* = Q* − Q* and thus the additive dose method can be used in the determination of luminescence ages. In principle, the paleodoses and ages obtained using this method should have a lower error compared to partial bleach and the total bleach techniques. TL and IRSL ages on K-feldspar extracts were evaluated using equation 5.15.
The carbonate nodules kept for α-counting and γ-spectrometry were first cleaned with a brush to remove loose sandy grains and then powdered in an agate pestle. For both sands and calcretes, thick source ZnS(Ag) alpha counting was used for determining thorium and uranium concentrations and γ-ray spectrometry (NaI) was used for determining K concentration. Secular equilibrium was assumed in the calculation of annual doses.

5.5.2 X-ray Diffraction Studies

An important methodological aspect involving dating is the mobility of potassium. X-ray diffraction studies were performed to ascertain the possibility of post-formation movement of radionuclides and validity of the annual dose estimates. X-ray diffraction analysis of the samples were also carried out by Dr. V. Gogte at the Deccan College, Pune, using a RIGAKU D Max II VC XRD system, operated at 50 kV, 25 mA at scan speed of 1/sec. The peak intensities, peak positions, half widths were computed using standard software. The X-ray diffraction analysis indicated that the potassium-bearing phases are microcline, richterite, albite and muscovite. The presence of minerals such as microcline, the semi-arid nature of the region and low water exchangeable potassium (< 50 ppm) suggest that K-mobility is low, and the potassium largely remains locked up in silicate phases. Consequently the dose rate estimates can be taken as realistic. The β-range of ~ 2mm further suggests that with respect to β-doses the luminescence dating system closes over scale lengths of a few mm, an aspect that could allow examination of growth rates of carbonate nodules based on sequential leaching of grains from the core to its centre. The dominance of the beta dose from potassium (~ 83-70%) for etched quartz separates (Table 5.2a) also indicates that the effect of a possible mobility of uranium also gets substantially diluted. However, for unetched 75-106 µm K-feldspars (Table 5.2b), the contribution of potassium (~ 80-45%) towards the annual alpha and
Table 5.1: Radionuclide Data for carbonates and host sands from Thar Desert

<table>
<thead>
<tr>
<th>Location</th>
<th>Calcrete</th>
<th>$\text{Th}^*$ (µg/g)</th>
<th>$\text{U}^*$ (µg/g)</th>
<th>$\text{K}^*$ (cg/g)</th>
<th>Host Sand</th>
<th>$\text{Th}^*$ (µg/g)</th>
<th>$\text{U}^*$ (µg/g)</th>
<th>$\text{K}^*$ (cg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jalore</td>
<td>JAL-I/17C</td>
<td>1.9</td>
<td>0.50</td>
<td>0.75</td>
<td>JAL-I/17S</td>
<td>2.15</td>
<td>0.6</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>JAL-II/2C</td>
<td>1.9</td>
<td>0.55</td>
<td>1.0</td>
<td>JAL-II/2S</td>
<td>2.40</td>
<td>0.7</td>
<td>1.05</td>
</tr>
<tr>
<td>Chamu</td>
<td>TR-11C</td>
<td>5.2</td>
<td>1.5</td>
<td>0.6</td>
<td>TR-11S</td>
<td>5.7</td>
<td>1.7</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>TR-13C</td>
<td>3.7</td>
<td>1.1</td>
<td>0.8</td>
<td>TR-13S</td>
<td>5.8</td>
<td>1.7</td>
<td>1.5</td>
</tr>
<tr>
<td>Amarsar</td>
<td>TR-29C</td>
<td>4.2</td>
<td>1.2</td>
<td>0.5</td>
<td>TR-29S</td>
<td>9.7</td>
<td>2.8</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>TR-31C</td>
<td>4.6</td>
<td>1.3</td>
<td>0.7</td>
<td>TR-31S</td>
<td>10.3</td>
<td>3.0</td>
<td>1.2</td>
</tr>
<tr>
<td>Budha Pushkar</td>
<td>CAL-0</td>
<td>3.7</td>
<td>1.4</td>
<td>0.90</td>
<td>PSH 92-1</td>
<td>4.75</td>
<td>0.8</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>CAL-1</td>
<td>2.2</td>
<td>0.9</td>
<td>0.75</td>
<td>PSH 92-1</td>
<td>4.75</td>
<td>0.8</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>CAL-3</td>
<td>3.2</td>
<td>0.6</td>
<td>0.9</td>
<td>PSH 92-1</td>
<td>4.75</td>
<td>0.8</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>CAL-2</td>
<td>1.85</td>
<td>0.8</td>
<td>0.9</td>
<td>PSH 92-2</td>
<td>6.10</td>
<td>2.4</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>CAL-4</td>
<td>4.0</td>
<td>0.65</td>
<td>0.9</td>
<td>PSH 92-3</td>
<td>5.05</td>
<td>0.8</td>
<td>1.5</td>
</tr>
</tbody>
</table>

+ Error in $\text{U}$ and $\text{Th}$ concentration is typically ~10%
* Error in $\text{K}$ concentration is typically ~5%
Table 5.2a: β dose fraction from potassium to 106-150 μm quartz extracts from host sands and calcretes

<table>
<thead>
<tr>
<th>Calcrete</th>
<th>Fraction of beta dose* from potassium</th>
<th>Host sand</th>
<th>Fraction of beta dose* from potassium</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAL-0</td>
<td>0.71</td>
<td>PSH 92-1</td>
<td>0.83</td>
</tr>
<tr>
<td>CAL-1</td>
<td>0.76</td>
<td>PSH 92-1</td>
<td>0.83</td>
</tr>
<tr>
<td>CAL-2</td>
<td>0.80</td>
<td>PSH 92-1</td>
<td>0.83</td>
</tr>
<tr>
<td>CAL-3</td>
<td>0.78</td>
<td>PSH 92-2</td>
<td>0.70</td>
</tr>
<tr>
<td>CAL-4</td>
<td>0.78</td>
<td>PSH 92-3</td>
<td>0.83</td>
</tr>
</tbody>
</table>

+ Alpha dose is negligible since 106-150 μm quartz extracts were used for TL dating of these calcretes and host sands (see Section 5.3 of text)

Table 5.2b: Fraction of annual alpha and beta dose from potassium to 75-106 μm K-feldspars within host sands and calcretes

<table>
<thead>
<tr>
<th>Location</th>
<th>Calcrete</th>
<th>$\frac{\beta}{\alpha+\beta}$</th>
<th>Host sand</th>
<th>$\frac{\beta}{\alpha+\beta}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jalore</td>
<td>JAL-I17C</td>
<td>0.74</td>
<td>JAL-I17S</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>JAL-II2C</td>
<td>0.80</td>
<td>JAL-II2S</td>
<td>0.76</td>
</tr>
<tr>
<td>Chamu</td>
<td>TR-11C</td>
<td>0.46</td>
<td>TR-11S</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>TR-13C</td>
<td>0.60</td>
<td>TR-13S</td>
<td>0.65</td>
</tr>
<tr>
<td>Amarsar</td>
<td>TR-29C</td>
<td>0.46</td>
<td>TR-29S</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>TR-31C</td>
<td>0.52</td>
<td>TR-31S</td>
<td>0.46</td>
</tr>
</tbody>
</table>

* $\frac{\beta}{\alpha+\beta}$ is the fraction of the annual alpha and beta dose to 75-106 μm K-feldspars from ${}^{87}$K. Since no HF etching was performed in the extraction of K-feldspars used for TL and IRSL dating of these calcretes and sands, alpha dose (attenuated) contribution has also been taken into account in estimating this ratio.
beta dose decreases by $\sim 20\text{-}30\%$ in situations where the sand and the carbonate matrix contain higher U and Th concentrations and low potassium concentrations.

### 5.6 Results and Discussion

Table 5.1 provides radioactivity data for carbonates and host sands from the various sites. Table 5.3 provides the TL ages, carbon and oxygen isotopic values of the calcrites from Budha Pushkar, Thar Desert. Tables 5.4 and 5.5 presents luminescence data for calcrites and host sands from other sites in Thar Desert. Fig. 5.3, 5.4 and 5.5 present TL glow curves, growth curves and plateaus for quartz and feldspar extracts from host sands and calcrites. Fig. 5.6, 5.7 and 5.8 provide IRSL shinedown curves, IRSL growth curves and shinedown plateaus for K-feldspar extracts from host sands and calcrites. Fig. 5.9 presents the stratigraphy, TL ages and stable isotopic data for carbonates from Budha Pushkar, Thar Desert.

A comparison of thermoluminescence and calibrated (Stuiver and Reimer, 1993) $^{14}$C ages on carbonates from Budha Pushkar (Table 5.4) indicate that the TL ages are significantly higher compared to their radiocarbon counterparts. This is expected in view of the likelihood of post-depositional contamination of the radiocarbon samples by modern carbon. Absence of coexisting organic materials in the carbonate horizons sampled for the present studies meant that comparisons between luminescence ages of carbonates and $^{14}$C ages on coexisting organic material was not possible. However, some clues on the plausibility of luminescence ages can be found from isotopic data and the regional paleoclimatic reconstruction. Oxygen isotopic ratios of the Budha Pushkar carbonates ranging from $-4.82 \%_o$ to $-6.57 \%_o$ (relative to PDB) can be compared with the oxygen isotopic composition of $-5$ to $-6 \%_o$ (relative to SMOW) of modern meteoric waters (Sarkar et al., 1990). This suggests that the carbonates analysed were formed primarily from leaching and thus are related to monsoonal precipitation. The
Fig. 5.3 (a): TL glow curves for quartz separates from host sand, PSH 92–2. SL and SS are bleaching times of 700 and 30 minutes under natural sun.

Fig. 5.3 (b): Glow curves for quartz separates from carbonate CAL–4. SL and SS carry the same meaning as in fig. 5.3 (a)
Fig. 5.4: (a) TL total bleach growth curve for quartz separates from host sand, PSH 92–2 and (b) TL total bleach growth curve for quartz separates from carbonate CAL–4.
Fig. 5.5: (a) TL growth curve for K-feldspar extracts from host sand JAL-II/2S and (b) TL paleodose plateau for the host sand JAL-II/2S.
Fig. 5.6: IRSL shinedown curves for K-feldspar separates from the carbonate JAL–II/2C.
Fig. 5.7: (a) IRSL growth curve for K-feldspar separates from carbonate JAL-II/2C and (b) IRSL shine plateau for JAL-II/2C.
Fig. 5.8 (a): IRSL growth curve for K-feldspar extracts from host sand TR-13S.

Fig. 5.8 (b): IRSL growth curve for K-feldspar extracts from carbonate TR-13C.
Table 5.3: Thermoluminescence data, Radiocarbon ages and Stable Isotopic Values for Carbonates from Budha Pushkar

<table>
<thead>
<tr>
<th>Calcrite Sample</th>
<th>Average depth (cm)</th>
<th>Radiocarbon ages* (ka)</th>
<th>Calcrite Equivalent Dose ( Q_c )** (mGy/a)</th>
<th>Annual++ beta dose ( D_c ) (Gy)</th>
<th>Host Sand</th>
<th>Sand Equivalent Dose ( Q_s )** (mGy/a)</th>
<th>Annual++ beta dose ( D_s ) (Gy)</th>
<th>Difference ( Q_s - Q_c ) (Gy)</th>
<th>Annual beta dose difference (mGy/a)</th>
<th>Age ( T_a ) (ka)</th>
<th>Calcrite ( ^{38}O)_{PDB} (%)</th>
<th>Calcrite ( ^{13}C)_{PDB} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAL-0</td>
<td>55</td>
<td>-</td>
<td>35±1.4</td>
<td>0.99±0.09</td>
<td>PSH 92-1</td>
<td>37±0.75</td>
<td>1.40±0.13</td>
<td>2±1.6</td>
<td>0.41±0.13</td>
<td>5±3.7</td>
<td>-6.20</td>
<td>-7.74</td>
</tr>
<tr>
<td>CAL-1</td>
<td>78</td>
<td>7.38±0.20</td>
<td>36±0.86</td>
<td>0.77±0.07</td>
<td>PSH 92-1</td>
<td>37±0.75</td>
<td>1.40±0.13</td>
<td>1.0±1.1</td>
<td>0.63±0.13</td>
<td>2±1.3</td>
<td>-6.25</td>
<td>-8.57</td>
</tr>
<tr>
<td>CAL-2</td>
<td>125</td>
<td>7.22±0.20</td>
<td>50.5±2.0</td>
<td>0.88±0.08</td>
<td>PSH 92-2</td>
<td>66±1.3</td>
<td>1.68±0.15</td>
<td>15.5±2.4</td>
<td>0.80±0.15</td>
<td>19.4±5.0</td>
<td>-6.57</td>
<td>-7.84</td>
</tr>
<tr>
<td>CAL-3</td>
<td>145</td>
<td>7.22±0.20</td>
<td>50.5±2.0</td>
<td>0.88±0.08</td>
<td>PSH 92-3</td>
<td>61.6±1.2</td>
<td>1.42±0.14</td>
<td>10.3±1.8</td>
<td>0.53±0.14</td>
<td>19.4±5.0</td>
<td>-5.24</td>
<td>-7.42</td>
</tr>
</tbody>
</table>

* These samples were collected from a different location in the same dune. \(^{14}C\) ages have been calibrated using Stuiver and Reimer [20].

+ The weighted mean of these three calcrite ages is \( 17 ± 2.9 \) ka (see text)

** Estimated as a weighted mean of partial bleach analysis (bleaching time 30 min) and total bleach analysis (bleaching time 30 min. and 7 hrs.). The bleaching was done under natural sunlight and both the sand and calcrite samples were exposed simultaneously. Typical bleached fractions were ~10-18% (after 30 min. bleaching) and reduced only marginally (~few %) thereafter. This is attributed to the selection of easily bleachable quartz signal using a UG11 filter.

++ Includes beta dose contribution from U, Th and K.
Fig. 5.9: Stratigraphy, TL ages and Stable isotopic data for carbonates from Budha Pushkar, Thar Desert.
Table 5.4a: Infra-Red Stimulated Luminescence dating results for carbonates and aeolian sands from Amarsar, Thar Desert

<table>
<thead>
<tr>
<th>Calcrete</th>
<th>Depth below ambient surface (m)</th>
<th>Calcrete $P_\alpha$ Paleodose (Gy)</th>
<th>Annual beta+alpha dose $D_\alpha$ (mGy/a)</th>
<th>Host Sand</th>
<th>Sand $P_\alpha$ Paleodose (Gy)</th>
<th>Annual beta+alpha dose $D_\alpha$ (mGy/a)</th>
<th>$P_\alpha$ - $P_\alpha$ (Gy)</th>
<th>$D_\alpha$ - $D_\alpha$ (mGy/a)</th>
<th>Calcrete Age (ka)</th>
<th>Host Sand Age (ka)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TR-29C</td>
<td>1.65</td>
<td>107±3.4</td>
<td>0.84</td>
<td>TR-29S</td>
<td>128±7.7</td>
<td>1.89</td>
<td>21±1.4</td>
<td>1.05</td>
<td>20±8.2</td>
<td>42±3.4</td>
</tr>
<tr>
<td>TR-31C</td>
<td>3.10</td>
<td>196±17.6</td>
<td>1.0</td>
<td>TR-31S</td>
<td>210±14</td>
<td>2.0</td>
<td>14±1.6</td>
<td>1.0</td>
<td>&lt;36*</td>
<td>64±6.0</td>
</tr>
</tbody>
</table>

* The calcrete age of TR-31C is 14±22 ka.

Table 5.4b: Infra-Red Stimulated Luminescence dating results for carbonates and aeolian sands from Chamu, Thar Desert

<table>
<thead>
<tr>
<th>Calcrete</th>
<th>Depth below ambient surface (m)</th>
<th>Calcrete $P_\alpha$ Paleodose (Gy)</th>
<th>Annual beta+alpha dose $D_\alpha$ (mGy/a)</th>
<th>Host Sand</th>
<th>Sand $P_\alpha$ Paleodose (Gy)</th>
<th>Annual beta+alpha dose $D_\alpha$ (mGy/a)</th>
<th>$P_\alpha$ - $P_\alpha$ (Gy)</th>
<th>$D_\alpha$ - $D_\alpha$ (mGy/a)</th>
<th>Calcrete Age (ka)</th>
<th>Host Sand Age (ka)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TR-11C</td>
<td>3.0</td>
<td>164±6.2</td>
<td>1.02</td>
<td>TR-11S</td>
<td>160±7.4</td>
<td>1.66</td>
<td>&lt;9.6*</td>
<td>0.64</td>
<td>&lt;15</td>
<td>62±5.5</td>
</tr>
<tr>
<td>TR-13C</td>
<td>5.0</td>
<td>194±8.5</td>
<td>1.0</td>
<td>TR-13S</td>
<td>273±11.4</td>
<td>1.77</td>
<td>79±4.8</td>
<td>0.77</td>
<td>100±23</td>
<td>100±8.4</td>
</tr>
</tbody>
</table>

* This value represents the maximum value of the difference between the calcrete and the host sand paleodoses.
Table 5.5: Luminescence data for carbonates and aeolian sands from Jalore, Thar Desert

<table>
<thead>
<tr>
<th>Sample</th>
<th>Technique</th>
<th>Calcrete Pγ Paleodose (Gy)</th>
<th>Annual beta+alpha dose D₀ (mGy/a)</th>
<th>Host Sand</th>
<th>Technique</th>
<th>Sand Pγ Paleodose (Gy)</th>
<th>Annual beta+alpha dose D₀ (mGy/a)</th>
<th>ΔP (Gy)</th>
<th>D₀ - D₀ (mGy/a)</th>
<th>Calcrete Age (ka)</th>
<th>Host Sand Age (ka)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JAL-1/17C</td>
<td>TL</td>
<td>10.14±1.37</td>
<td>0.70</td>
<td>JAL-1/17S</td>
<td>TL</td>
<td>9.85±2.7</td>
<td>0.90</td>
<td>3.78</td>
<td>0.2</td>
<td>&lt;7.0</td>
<td>7±2.0</td>
</tr>
<tr>
<td>JAL-1/17C</td>
<td>IRSL</td>
<td>10.05±1.40</td>
<td>0.70</td>
<td>JAL-1/17S</td>
<td>IRSL</td>
<td>9.61±0.7</td>
<td>0.90</td>
<td>1.66</td>
<td>0.2</td>
<td>&lt;7.0</td>
<td>7±0.7</td>
</tr>
<tr>
<td>JAL-II/2C</td>
<td>TL</td>
<td>13.6±1.3</td>
<td>0.92</td>
<td>JAL-II/2S</td>
<td>TL</td>
<td>14.8±1.32</td>
<td>1.02</td>
<td>3.84</td>
<td>0.1</td>
<td>&lt;9.0</td>
<td>9±0.9</td>
</tr>
<tr>
<td>JAL-II/2C</td>
<td>IRSL</td>
<td>15.5±0.93</td>
<td>0.92</td>
<td>JAL-II/2S</td>
<td>IRSL</td>
<td>15.4±0.7</td>
<td>1.02</td>
<td>1.57</td>
<td>0.1</td>
<td>&lt;10.0</td>
<td>10±0.7</td>
</tr>
</tbody>
</table>

Water content (assumed) = 5% ± 1.5%
a value (feldspar) = 0.15 ± 0.075
* ΔP represents the maximum value of the difference between the host sand and the calcrete paleodoses.
Since the calcrete ages estimated by the expression ΔP/(D₀ - D₀) are higher than the host sand ages (which is physically unrealistic), only upper limits can be provided on the calcrete age. The host sand ages represent maximum age of calcrete formation.
+ The additive dose method was used for both TL and IRSL dating.
carbon isotopic values range from $-7.02$ to $-8.57\%_o$ which (Cerling, 1984) implies a contribution of 28–35 \% from C$_4$ type plants and up to 65 \% from C$_3$ type, indicating somewhat wetter conditions. Marine records from the Indian Ocean show that during the last glacial maximum (LGM) at 21.5 ka (calendar years), the monsoon circulation over the Indian subcontinent weakened significantly, resulting in marked aridity. The reestablishment of the monsoon began at around 18 ka (Van Campo, 1986) reaching its full vigour by $\sim 11$ ka. Similarly, on land, palynological studies (Singh et al., 1974) and $^{14}$C dating of the organic fraction of the sediments of a saline lake (L. Didwana) in the Thar Desert indicate hyper-arid conditions from LGM to $\sim 16$ ka. In the period 16–11 ka, the monsoon circulation reestablished itself and the annual precipitation reached twice its present value by $\sim 7$ ka. Assuming that carbonates will be only formed when precipitation is $< 400$ mm (Cooke et al., 1993), the paleomonsoonal reconstruction in Thar Desert (Bryson, 1989) suggests that during the last $\sim 20$ ka, carbonates could have only formed in Thar Desert between $\sim 17$ ka–10 ka, $\sim 6.8$–4.8 ka and $< 2.5$ ka. The luminescence age estimates thus agree well with these estimates.

For the carbonate TR–11C from Chamu, Thar Desert, only an upper age limit could be estimated due to a small difference between paleodoses $P_4$ and $P_r$. This suggests that only maximum age limits can be estimated for young carbonates (few thousand years old) which precipitate in much older host sands. Even in Jalore, only maximum ages of carbonate formation could be obtained since the differences between the calcrete and host sand paleodoses is $< 1.5$ Gy. The apparent IRSL ages (estimated by dividing the maximum value of the difference between $P_4$ and $P_r$ by the difference in annual doses $D_4$ and $D_r$) for the carbonates JAL–1/17 and JAL–H/2 are $< 8.5$ ka and $< 16$ ka and are higher than the host sand ages, $7 \pm 0.7$ and $10 \pm 0.7$. Since the calcrete cannot be formed before the deposition of the host sand, only upper limits can be provided on the luminescence ages for the carbonates JAL–1/17 and JAL–H/2, viz., $< 7 \pm 0.7$ and $< 10 \pm 0.7$ respectively. These results imply that presently, the luminescence dating
method is best suited for dating carbonates which formed a few ka after the deposition of the host matrix. For young carbonates, the host sand age will constrain the age of the carbonate.

The luminescence ages on carbonates and host sands are stratigraphically consistent and suggest that carbonate formation occurred in Thar Desert at $100 \pm 23$ ka, $17 \pm 3$ ka and $2.3 \pm 1.3$ ka ago. The $100 \pm 23$ ka event is only observed at Chamu, whereas the $2.3 \pm 1.3$ event is indicated at Budha Pushkar and Jalore. The $17 \pm 3$ ka episode is observed at Chamu, Budha Pushkar and Amarsar, a west-east transect spanning $\sim 300$ km in Thar Desert. Thus, the luminescence data provides a possibility that a major carbonate formation episode took place in Thar Desert at $\sim 17$ ka. However, these inferences are based on limited data and are only suggestive and not conclusive. Further dating work remains to be done to make a more definitive statement about the $17$ ka event.