METHODOLOGICAL ASPECTS OF RADIATION DOSIMETRY OF NATURAL RADIATION ENVIRONMENT USING LUMINESCENCE TECHNIQUES: NEW MINERALS AND APPLICATIONS

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METHODOLOGICAL ASPECTS OF RADIATION DOSIMETRY OF NATURAL RADIATION ENVIRONMENT USING LUMINESCENCE TECHNIQUES: NEW MINERALS AND APPLICATIONS

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DECLARATION

This is to certify that the contents of this thesis entitled "Methodological Aspects of Radiation Dosimetry of Natural Radiation Environment Using Luminescence Techniques: New Minerals and Applications" comprise original research work of the candidate and have at no time been submitted for any other degree or diploma.

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Guide:

Prof. Shyam Lal Physical Research Laboratory Ahmedabad- 380 009, Gujarat, India **Dedicated to**

My

(Late) elder sister, Seema

<u>Abstract</u>

Radiation dosimetry is the quantitative measurement of energy absorbed by matter on exposure to ionization radiation. Environmental dosimetry deals with measurement of dose received by matter from natural radiation environment arising from decay of naturally occurring radionuclides, viz. uranium, thorium and potassium with minor contribution from cosmic rays. During the past three decades, environmental dosimetry using natural minerals such as quartz and feldspars have provided a useful geochronological tool to the extent that it now occupies centre stage in the studies related to recent earth history. The dose absorbed by these minerals can be measured using Luminescence and Electron Spin Resonance (ESR) techniques.

In nature, gypsum occurs as a chemical precipitate from desiccating brines. Generally, gypsum forms through two possible pathways, 1) through direct precipitation from the brine or, 2) through precipitation from pyrites using sulfur produced by microbial activity. It is known that during periods of climatic stress, lakes dry up and in the process of drying up the residual water gets increasingly enriched in salts which eventually precipitate out. The precipitation occurs in the sequence, halite (NaCl)-glauberite $(Na_2Ca(SO_4)_2)$ -anhydrite $(CaSO_4)$ and gypsum (CaSO₄.2H₂O) is end product. Geologists therefore take gypsum as a climatic event marker and in desertic environments gypsum occurrences suggest phases of extreme aridity. Depending on local chemical, hydrologic conditions and rates of desiccation, gypsum occurs in various forms ranging from diffused powdery precipitate (microcrystalline to cryptocrystalline) to well formed crystals of several cm. sizes (the desert roses). In some situation the gypsum thus formed, suffers physical weathering and gets transported as gypsum sand. So far the chronometry of gypsum deposits has only been marginally attempted except by using geological evidences and occasionally attempted using ESR. This is partly due to absence of organic material that could be radiocarbon dated. Similarly, low radioactivity content of the material makes it difficult to apply methods such as uranium series disequilibrium techniques.

The present study examined the methodological aspects of the application of the Luminescence and Electron Spin Resonance techniques. This involved the examination of gypsum as Luminescence and ESR radiation dosimeter, i.e. its radiation response, the long term stability of the signals and development of protocols for dating that are independent of presence or absence of water of hydration. Both the direct (using gypsum itself) and indirect (using the quartz from its sedimentary context) methods were examined.

Luminescence dating is a radiation damage technique for numerical chronometry of geological samples ranging from 10a to \sim 1Ma (a = annum or year). The technique is based on the measurement of trapped charges in natural minerals produced by natural radiation. Most commonly used minerals are quartz and feldspar that occur in most geological settings. Given that as a first approximation the radiation flux of ambient radioactivity is constant through time, the total numbers of trapped charges are proportional to the elapsed time since the burial of sediment.

Electron Spin Resonance (ESR) or Electron Paramagnetic Resonance (EPR) is a nondestructive method that measures the concentration of paramagnetic species in a sample. ESR dating is based on measurement of the concentration of radiation induced paramagnetic centres. The concentration of these centres in a given sample provides a measure of the total radiation dose to which the sample was exposed. ESR spectroscopy deals with the microwave absorption among the magnetic field split Zeeman states of the lowest electronic state of paramagnetic ions in the sample. The EPR spectrum is obtained by monitoring the microwave absorption at a fixed frequency, as a function of magnetic field. This yields both the information about the electronic structure and the concentration of the paramagnetic ions.

In the present study the samples were analyzed from two locations, viz. i)Thar Desert, where the gypsum occurred as a stratified context in relict lake sequences, and ii)White Sands, New Mexico, USA, where the gypsum occurs as wind transported sand.

The study comprised the following:

- 1. Characterization of the material using techniques such as X-ray diffraction, Fourier Transform Infrared Spectroscopy (FT-IR), Thermogravimetry (TG) and Differential Thermal Analysis (DTA),
- 2. Luminescence characterization of gypsum including study of the kinetics of Thermoluminescence (TL) emission.
- 3. Extraction and dating of the quartz associated with gypsum,
- 4. Methodological aspects of ESR of gypsum and their radiation response,
- 5. Application to dating of gypsum occurrences in the Thar Desert, India and White Sands, USA.
- 6. ESR based inferences on the formation path ways and formation environment of the gypsum

Being sparingly soluble in water, gypsum once formed remains mostly unaltered and this fact ensures that their analysis provides an age of a geologically closed system. Gypsum occurs in three phases, viz. gypsum anhydrite (CaSO₄), hemihydrite (CaSO₄.¹/₂H₂O) and gypsum (CaSO₄.2H₂O). Gypsum loses its water on heating and this aspect has implication in developing any technique that has a thermal treatment component. Thermogravimetry and Differential Thermal Analysis confirmed that samples were CaSO₄.2H₂O. FT-IR spectrometry and X-ray diffraction (XRD) revealed that the White Sands samples were pure Gypsum whereas in the Thar Desert Gypsum additionally contained calcite and Hannebachite (CaSO₃.½H₂O). The presence of Hannebachite increased the yield of SO₃⁻⁻ that could be detected by ESR of gamma irradiated samples. In the present study it was seen that the natural Gypsum is sensitive to radiation. The ESR studies indicated the presence of five centres viz. SO₃⁻⁻ (G₁), SO₄⁻⁻ (G₂), SO₂⁻⁻ (C) and O₃⁻⁻ (LS). Out of these the centre O₃⁻⁻ was light sensitive. Out of these five centres, SO₃⁻⁻, SO₄⁻⁻ and O₃⁻⁻ were sensitive to radiation and were used for ESR dating, ESR of SO₄⁻⁻ and SO₃⁻⁻ gives the most recent precipitation event while the ESR of O₃⁻⁻ gives the age of most recent sun exposure. ESR ages based on using SO₄⁻⁻ and light sensitive signal are in consistent with control BLSL optical ages on traces of quartz associated with gypsum sand. The comparison between ESR and TL paves a way to put an estimate on the alpha efficiency factor (a–value) and it also provide the prospects of ascertaining the life time of SO₄⁻⁻ signal.

In this first ever application to date gypsum occurrences using Luminescence dating technique in Thar Desert, the SAR ages of the quartz extracted from the sand horizons, overlying and underlying of gypsum horizons, range from 14 ka to <2 ka and enabled following inferences, 1) overall more humid condition during 14 ka – 6ka (infrequent gypsum layer) and 2) aridity in the region since 6 ka (frequent gypsum layer). Most near surface gypsum occurrences belong to this category.

The present study gives the first detailed geochronology of the White Sands, New Mexico, USA. The SAR De's spanned a range from 2.2 ka to7.3 ka. The ages are consistent with C^{14} age of 7000 years B.P obtained from a basal clay layer that underlies the bedded gypsum, and correspond to the onset of a regional arid event at 7ka.

In the present study gypsum from two locations gave contrasting ESR spectra. One is a clear gypsum spectrum and the other a spectrum masked by Mn²⁺ signal. This implied that two gypsum formed in different environments, one is in oxic and other is anoxic. This was resolved with the help of FT-IR which indicated that Thar samples had additional contamination of hannebachite (CaSO₃.¹/₂H₂O) suggest that Thar gypsum formed bacterial sulfer reduction (BSR) under a reducing environment at the time of formation of gypsum. White Sands samples on the other hand show the simple calcium-sulphate precipitation.

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Chapter 1

Introduction

1.1 Introduction

Radiation dosimetry is concerned with the measurement of the energy deposited in matter by ionizing radiation. The absorbed dose is measured in Gray (1Gy = 1 Joule/kg). The environmental dose received by the matter in natural environment arises due to radiation associated with decay of naturally occurring radionuclide viz. ²³⁸U, ²³²Th, ⁴⁰K, ⁸⁷Rb and cosmic rays. The accumulated radiation dose can be measured using methods such as, Thermally Stimulated Luminescence (TSL or Thermoluminescence; TL), Optically Stimulated Luminescence (OSL) or the Electron Spin Resonance (ESR).

Naturally occurring mineral, gypsum (CaSO₄.2H₂O) is an evaporite and serves as a climate event marker of enhanced aridity. It occurs widely in varied contexts, such as an authegenic precipitate and as wind blown sand. All warm deserts of the world have gypsum deposits (Goudie and Pye, 1983), but due to the lack of secured, routinely applicable numerical dating method to determine their ages, these occurrences have not been exploited fully for paleoclimatology. Climate, water level, temperature etc., control the formation and preservation of gypsum. Study of gypsum helps in understanding the linkage between mineralogy and groundwater chemistry of playas/interdunal depressions. In nature, gypsum can form through two pathways, i) a direct precipitation of gypsum and ii) through, the sulfur produced by microbial activity.

In the present thesis, possible use of gypsum (CaSO₄.2H₂O) and anhydrite (CaSO₄) for radiation dosimetry and geochronology was examined using luminescence and ESR methods and was aimed to develop a routinely applicable reliable dating method for gypsum using Optically Stimulated Luminescence (OSL) and Electron Spin Resonance (ESR) techniques. Methodological aspects and their application to gypsum deposits were examined in detail, and protocols thus developed were applied to samples collected from playa gypsum in Thar Desert, Rajasthan, India and gypsum sand from White Sands, New Mexico, USA.

1.2 Evaporite deposits and their significance

Evaporites are minerals that form by the evaporation of the surface water particularly in coastal (lagoons) and lacustrine (playas) environments with mean annual precipitation of ~ 200 mm and high seasonality. In India and parts of North America gypsum occurs in areas with marginally higher mean annual rainfall and high potential evapotranspiration (Watson, 1983). The types of minerals formed in these environments depend mainly on the ionic composition of the brines (dissolved cations), the concentration of ions and the relative humidity (climate). Factors that control evaporite deposits are (i) climate (ii) water budget, (iii) high temperatures and (iv) active winds (Warren, 1999). A deficit in water budget means that evaporation exceeds inflow. The inflow is modulated by (i) precipitation (river discharge and groundwater) and (ii) seawater ingression (lagoons). Water thus accumulated in shallow basins evaporates due to high temperature and dry winds leading to the precipitation of salts including gypsum. Generally, the presence of thick evaporite beds suggests dry and warm climate of extended duration.

1.2.1 Gypsum

Gypsum is the most common sulphate mineral on earth. Besides its climatic significance, it also has a large commercial value as building material (plaster of paris) and in agriculture (neutralizes sodic soils). Gypsum can occur as primary precipitate formed through the evaporation from brine at surface, shallow–subsurface or as secondary deposits, transported by wind.

During dry climatic conditions, evaporation of shallow lakes (playa) causes enrichment of salt in the residual water. As the evaporation progresses, precipitation of salt occurs. The sequence of salt precipitation begins with the Halite (NaCl), followed by Glauberite (Na₂Ca(SO₄)₂), Anhydrite (CaSO₄). Gypsum (CaSO₄.2H₂O) precipitates last (Alpers et al., 2000). This would imply that gypsum precipitation occurs under extremely dry conditions. It occurs in various forms such as diffused powdery precipitate (microcrystalline to cryptocrystalline) to well formed crystals of several centimeters in size (the desert roses). The crystallinity of the cryptocrystalline texture can only be seen microscopically in thin sections by transmitted polarized light. Powdery gypsum is the variety of gypsum consisting dirt and sand, and known as gypsite. The textural variability is modulated by surrounding lithology, hydrological conditions and the rates of desiccation. Under certain climatic condition, precipitated gypsum can be physically weathered (broken down) and transported as sand by the prevailing winds to form gypsum dunes.

In nature gypsum appears both as crystalline aggregates and massive crust. Colorless and transparent varieties of crystalline gypsum are also known as satin spar, alabaster, or selenite. It dehydrates when heated up to about 150°C and transforms into hemihydrates (CaSO₄.¹/₂H₂O). Further heating to about 220°C transforms it into anhydrite (CaSO₄). Gypsum forms a double sheet structure in which two sheets of sulphate are bound together by calcium and are connected with the next layer by weak hydrogen bond due to the presence of water molecules. In aqueous medium, gypsum is sparingly soluble

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(solubility ~ 2.6 g dm⁻³ at 25°C and 1 atmosphere pressure). Presence of salts that have common ions such as, calcium bicarbonate and sodium sulphate, decrease the solubility while others increases its solubility (Alpers et al., 2000).

In relict lacustrine successions, rhythmic occurrence of gypsum punctuated by lacustrine sediment indicates fluctuating lake hydrology. Thus, based on stratigraphic record it is possible to reconstruct the cyclic fluctuation in climate between dry-to-wet. However, in order to ascertain the timing of such fluctuations, it is important to have the chronology of gypsum and the associated sediments. So far, owing to the difficulties involved in a direct dating of gypsum, the precise timing of changes in the lake hydrology remained undetermined. Some attempts were made in Namib Desert to ascertain the timing of gypsum crust formation by radiocarbon dating of material incorporated in gypsum crust provided estimates on gypsum formation during 36 ka to 26 ka BP (Watson, 1988). Similarly, in southern Tunisia, the presence of archeological artifacts corresponding to Mousterian typology embedded in gypsum crust, assigned an age of 28 ka (Page, 1972). In both the cases, since materials used for dating were in their secondary context, it can be argued that the above age estimate is towards the higher side then the actual age. Similarly, in the Prungle lake of southern Australia, indirect age estimate using the stratigraphic record and radiocarbon ages, two major episodes of laminated gypsum and lunette formation was bracketed to 25 ka - 17.5 ka and 17.5 ka - 16 ka BP (Magee, 1991). In general absence of organic material and low radioactivity content makes it difficult to apply radiocarbon and uranium series disequilibrium techniques.

Ikeya (1978) was the first to suggest that gypsum can be dated by ESR technique. He used the G_2 center at g = 2.008 for dating the gypsum from a dry cave deposit at Mammoth Cave National park, Kentucky, USA. Nambi (1982) suggested that gypsum can be dated by Thermoluminescence (TL) and ESR, and attempted dating of samples from India (Rann of Kutchchh) and Italy. For ESR dating he used the center G_1 at g = 2.0040 and obtained age ranging from 41 to 47 ka in Indian context. For TL dating he used the 350°C TL peak and obtained the age ranging from 63 to 71 ka for Indian sample, and an age estimate of 2.8 Ma for Italian sample. Similar attempt was made by Ikeda and Ikeya (1992) using ESR on precipitated gypsum collected from the San Andreas Fault. Using the center G_2 at g = 2.008, ESR ages were ranging between

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0.26-0.30 ka. Recently Mathew et al., (2004) employed the G₂ center to date the fibrous gypsum that formed along the fault plane in Kutchchh region of western India. The ages ranged from 70 to 300 ka.

However in the above studies, details regarding the sample integrity (phase transformation) in case of TL (due to heating) and center identification used for dating in case of ESR were not discussed. In absence of these data, validity of the ages can not be ascertained.

The present thesis attempted to develop a method for numerical chronometry of gypsum using both direct dating (ESR on gypsum) and indirect dating (OSL on quartz extracts) and applied in Thar Desert of Rajasthan, western India and the White Sands in New Mexico, USA, where some age controls were available.

1.3 Methods for chronometry of evaporites

Several dating approaches have been attempted for the chronology of evaporite deposits. These include e.g. ESR dating, ²³⁰Th/²³⁴U and ³⁶Cl, and luminescence dating methods. In this section a brief appraisal of these techniques is attempted.

1.3.1 U-series isochron dating

The most commonly-used methods for dating geological formations involve radioactive decay. The isotopes of uranium (235 U, 238 U) are radioactive and decay to lead isotope, through a series of alpha, beta and gamma decays. Radiometric dating is possible because of the fact that decay of a radioactive parent to its daughter takes place at a fixed half-life. 235 Uranium, for instance, has a half life of 7.04 x 10⁸ years. Based on decay of these radionuclide, the fundamental equation for determining the age of terrestrial and extraterrestrial material and minerals can be written as,

$$D = D_0 + P(e^{\lambda t} - 1)$$
(1.1)

Where, D_0 is the initial number of daughter atom, D is the total number of daughter atom at present time; P is the number of parent atom and λ is the decay constant.

This equation can be solved for time t, by measuring the value of D and P, provided that decay constant λ of parent is known. This equation represents the straight line of the form,

$$y = mx + c \tag{1.2}$$

Where, m is the slope and c is the intercept on the y-axis.

The measured values of D and P define this straight line, with the slope of $e^{\lambda t - 1}$. This line is called isochron because all the data points that lie on the line correspond to same age, since the slope of the straight line is constant (Faure and Mensing, 2005).

Isochron dating technique falls into the radiometric dating technique and can be applied to crystallization and metamorphism events. Isochron dating assumes that the source of the rock or rocks contained unknown amounts of both radiogenic and nonradiogenic isotopes of daughter element, along with some amount of the parent nuclide. Thus, at the time of crystallization, the ratio of the concentration of the radiogenic isotope of the daughter element to that of the non-radiogenic isotope is some value independent of the concentration of the parent.

Using the isochron method Luo and Ku (1991) and Philips et al., (1993) dated the evaporatic sequence of western Qaidam Basin, China. In their approach to date evaporite, Lou and Kou (1991) assumed that (i) 230 Th/ 234 U = 0 at their time of formation (t = 0), (ii) samples have been closed to U and Th isotopic exchange since their formation and (iii) mineral do not contains 232 Th and 230 Th when formed and they determined the age by using equation,

$$\frac{{}^{230}Th}{{}^{232}Th} = \left(\frac{{}^{230}Th}{{}^{232}Th}\right)_{0} e^{(-\lambda_{0}t)} + \frac{{}^{234}U}{{}^{232}Th} \left[\frac{{}^{238}U}{{}^{234}U} \left(1 - e^{(-\lambda_{0}t)}\right) + \left(1 - \frac{{}^{238}U}{{}^{234}U}\right) \left(\frac{\lambda_{0}}{\lambda_{0} - \lambda_{4}}\right) \left(1 - e^{-(\lambda_{0} - \lambda_{4})t}\right) \right]$$
(1.3)

Where, λ 's are the decay constant (subscripts 0 and 4 represents ²³⁰Th and ²³⁴U respectively).

1.3.2 Cosmogenic radionuclide method (³⁶Cl)

Every object of the earth is continuously exposed to cosmic ray radiations, which are primarily protons. These secondary particles, produced by the nuclear spallation reaction (reaction of primary cosmic rays with the molecules of N_2 and O_2 in upper atmosphere), reach the earth surface. These secondary cosmic ray particles produce the cosmogenic radionuclide (e.g., ³⁶Cl) when strike to the earth and interact with soil/rock (Lal, 1991).

$${}^{40}Ca(n,2n3p) \, {}^{36}Cl$$

$${}^{39}K(\mu^{-},p2n) \, {}^{36}Cl$$

$${}^{40}Ca(\mu^{-},\alpha) \, {}^{36}Cl$$

$${}^{35}Cl(n,\mu) \, {}^{36}Cl$$

$${}^{39}K(n,\alpha) \, {}^{36}Cl \qquad (1.4)$$

Depending upon the production rate and half-lives of the radionuclide they can be used as geochronometer, provided that the production rate of these nuclides could be accurately determined. ³⁶Cl is generated in the atmosphere by the spallation of argon-36 with cosmic ray protons, and in soil and rock by neutron activation of ³⁵Cl. This needs understanding of the changes in (i) the irradiation geometry and (ii) the cosmic ray flux through time. ³⁶Cl has a half life of 301 ka, and produced both in the atmosphere and at earth surface. ³⁶Cl decays by emitting a beta particle and electron capture, most of the decays (98%) are by beta-particle emission. The potential application of ³⁶Cl to hydrologic studies was given by Nishiizumi et al., (1989) and Davis et al., (2001).

In the context of dating of evaporites, ³⁶Cl method was used by Philips et al., (1993). In their study they calculated the ages of halite by measured the ³⁶Cl/Cl values (with an assumed initial ratio of ³⁶Cl/Cl) and the equations proposed by Jannik et al., (1991),

$$R_d = \frac{R_i}{\lambda_{36}\Delta t} \left(1 - e^{-\lambda_{36}\Delta t} \right) \tag{1.5}$$

Where, R_d is the ³⁶Cl/Cl ratio at the time of halite deposition, R_i is the ³⁶Cl/Cl ratio of the chloride in water flowing into the lake and Δt (=t₀-t_d) is the time difference between the dry lake and the deposition of halite.

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1.4 Luminescence dating

1.4.1 Basic principles

Luminescence is the emission of light from an insulator/semiconductor when heated or exposed to light, followed by a prior absorption of energy (radiation). Luminescence can be classified in two parts, i) fluorescence and ii) phosphorescence.

1. Fluorescence

A molecule in an excited state can lose its energy and return to its ground state in a variety of pathways. One of the pathways is fluorescence, where the resultant emission (fluorescence radiation) is of lower energy (frequency) than that of the absorbed radiation. Fluorescence emission takes place nearly simultaneously with the absorption of light and ceases with the cessation of stimulation and generally corresponds to a direct transition (Fig. 1.1). The life time of the excited state in this phenomenon ranges from few picoseconds to milliseconds.

2. Phosphorescence

The difference between the phosphorescence and fluorescence is the time delay between stimulation and emission of light. In phosphorescence, the transition from excited state to ground state involves a meta-stable state which corresponds to a charge trapped at a lattice defect. The trapped charge resides in meta-stable states until energy greater than the energy gap between the excited state and meta-stable state (trap-depth) is provided. Depending upon the life time of the meta-stable state phosphorescence can be further classified in two groups. In first case, the trap depth is smaller than the lattice vibration energy, such that electron can be excited without any external stimulation. In another case the mean life time of the trapped charge in metastable state can range from 10^{-4} s– 10^{9} years.



Figure 1.1 (a) Fluorescence phenomenon, arrows shows the direct transition of electron from excited state (e) to ground state (g), and (b) phosphorescence phenomenon, m, designates the metastatble state.

Thermoluminescence (TL) and Optically Stimulated Luminescence (OSL) belong to this category and can be understood using band theory of solids.

As shown in Fig. 1.2 there are three stages responsible for the luminescence process. These are;

- a). Ionization,
- b). Trapping and
- c). Recombination.

Initially (at time t = 0) the system (crystal) is in equilibrium state, under such condition all electrons are in valance band whereas the conduction band remains empty.

Irradiation from any ionization radiation ionizes the atoms (crystal) and produces free charges, viz. electrons and holes. Most of these charges recombine instantaneously. However, a small fraction gets trapped in localized defect states (e.g. lattice defects, voids, impurities, etc.). The residence time of trapped charges depends on the binding energy (charge environment) and can range from few seconds to >Ma.

However, if the external stimulation energy exceeds the trap depth, detrapping of the charges occurs and some of these can radiatively recombine at recombination centers to produce luminescence. The escape probability (per second) of a charge from the trap is,

$$p = s . \exp(-E/kT) \tag{1.6}$$

Where, s is the frequency factor (local lattice vibrational frequency), E is the trap depth (activation energy), k is the Boltzman constant and T is the temperature.

1.4.2 Luminescence dating

Luminescence dating is the dosimetry of natural radiation environment, using natural minerals. The technique relies on the measurement of natural radiation induced trapped charges in the naturally occurring minerals. Most commonly used minerals that occur in all geological environments are quartz and feldspar, and these have appropriate dosimetric properties, that enable their application for dating. On account of mean lives of natural radionuclides being $\geq 10^9$ years, the radiation flux arising from the decay can be taken constant over million year time scales.



Figure 1.2 Schematic representations of TL and OSL phenomena, (a) ionization and trapping, (b) storage (where E_1 and E_2 represents the trap depths and τ_1 , τ_2 represents the mean life time) and (c) recombination and luminescence production (where λ_1 and λ_2 are the stimulation wavelengths (after Aitken 1985).

This implies that as a first approximation the rate of ionization remains constant and hence the total numbers of trapped charges are proportional to the elapsed time since the time irradiation began (Huntley et al., 1985; Aitken, 1998).

Luminescence measurements enable quantification of trapped charges in terms of equivalent radiation dose. Estimation of elemental abundance of natural radioactivity, enables computation of annual radiation dose and ratio of the two provide the age. Three type of geological events can be dated using the luminescence technique (Singhvi and Wagner, 1986) these are, i) the most recent daylight exposure of the minerals in the sediment, ii) heating event and iii) authegenic precipitation event (mineral formation). All these events refer to the "zeroing" of preexisting geological luminescence to zero or near zero (residual value).

In the first case, when minerals are exposed to day light during their weathering and transport, which results in to photo-bleaching of the trapped charges to a zero or near zero residual level. On burial, further day light exposure ceases and reacquisition of the trapped charges is initiated by irradiation from ambient radioactivity. Acquisition of trapped charges continues till the mineral is exposed to daylight or is stimulated in the laboratory. The event dated is the time of burial (last deposition of the sediment e.g. loess deposits, dune sand and glaciers). In sediment dating the most important criteria is geological luminescence should be zero or residual level before burial. This is largely achieved for sediment deposited by wind. However, for sediment transported by water (aqueous sediments) there are chance of inadequate photobleaching or it could be heterogeneous. The reason being water column and sediment load can attenuate the day light flux. In the second case the luminescence clock is reset to zero by heating, such as pottery fired by ancient men, burnt bricks, sediment contact backed by lava flows or forest fires when temperature goes to 500°C or so. The third case is authegenic precipitate, where the accumulation of luminescence signal initiated at time of crystal nucleation, and the event dated is the formation time of minerals (gypsum, halite, carbonates, etc.).

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1.4.3 The age equation

The luminescence age equation can be written as,

 $Age(T) = \frac{Lum. acquired (L)}{Lum./year} = \frac{Lum. acquired (L)}{(Lum./radiation dose) x (radiation dose/year)} (1.7)$

$$T = \frac{L}{\sum_{i} \chi_{i} \frac{D}{D_{i}}}$$
(1.8)

Where, $i = \alpha$, β , γ and cosmic rays

 χ = Luminescence sensitivity (luminescence/radiation dose) and

D = dose rate (radiation dose/year)

The linear energy transfer (LET) of alpha is higher than that of beta and gamma on account of higher charge and mass. This leads to a higher ionization density along the α -tracks and leads to charge saturation effects such that charge produced exceeds the trap available. Thus a major fraction of charge produced is wasted. Consequently the efficiency of luminescence production per Gy of dose is reduced. Beta, gamma and cosmic rays have low LET and hence the luminescence production is higher.

Thus,

$$\chi_{\alpha} \neq \chi_{\beta} = \chi_{\gamma} = \chi_{c} \tag{1.9}$$

This enables defining an alpha efficiency parameter $a = \chi_{\alpha} / \chi_{\beta}$, which permits to write an age equation as,

$$T = \frac{P}{a_{D_a} + D_{\beta} + D_{\gamma} + D_{c}}$$
(1.10)

Where, P $(L/\chi\beta)$ is the laboratory dose (from a calibrated source) that produces the luminescence equal to the natural luminescence and known as paleodose (P) or equivalent dose (D_e); 'a' is the alpha efficiency factor.

1.4.4 Evaluation of D_e

Several methods have been proposed for D_e determination. The basic principle of all the methods is same, i.e. to compare natural luminescence with the luminescence induced by artificial (laboratory) irradiation using a dose response curve. Two analytical methods, multiple aliquot additive dose method (MAAD) and single aliquot regeneration (SAR) method have been used widely. These methods are discussed in chapter 2.

1.4.5 Dose rate

The amount of nuclear (ionizing) radiation delivered per unit time to a material is called dose rate and for dating application is usually expressed as Gy/ka. The dose rate is estimated by measuring concentration of natural radioactive elements (U, Th, and K). U and Th concentration can be measured using thick source ZnS(Ag) alpha counting whereas ⁴⁰K is estimated by gamma spectrometry. Cosmic rays contribution is computed using the latitude, longitude, altitude and the average burial depth and equations provided by Prescott and Hutton (1994). The dose rate computation assumed an infinite matrix. This implies that within a volume having dimensions greater than the ranges of the ionizing radiations (α , β , γ and cosmic rays), rate of energy absorbed per unit mass is equals the rate of energy emitted per unit mass (conservation of energy) (Aitken, 1985). Another assumption is that the dose rate is constant since the luminescence clock reset to zero. This would mean that radioactive elements uranium (²³⁸U) and thorium (²³²Th) and their daughter nuclides were in equilibrium and there was no change in the potassium (⁴⁰K) concentration through time. Any deviation from this would imply that dose rate is time dependent and need additional computation.

1.4.6 TL/OSL of Quartz and Feldspar

Quartz: Quartz and feldspar have been the most common minerals used for luminescence dating. TL glow peaks and emission spectrum of quartz mineral have been summarized by a number of authors e.g. McKeever, 1985; Franklin et al., 1995; Prescott et al., 1995; Krbetschek et al.; 1997 and Bøtter-Jensen et al., 2003. Quartz has TL peaks at 95–110°C, 150–180°C, 200–220°C, 325°C and 375°C. Quartz has three main TL

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emission bands at 360–440 nm (UV-blue), at 460–500 nm (blue-green) and at 600–650 nm (orange-red) and all of these have been used for dating applications.

There are only few studies concerned with emission spectra from quartz OSL. The only information available is that quartz has an emission band centered at 365 nm (Huntley et al., 1996). The similarity between the emissions wavelengths suggest that quartz OSL originates from the same recombination centers as those from TL arises.

Feldspar: Most feldspar classified in three groups, (i) sodium feldspars, (ii) potassium feldspars and (iii) calcium feldspars. Feldspar has TL peaks at 120°C, 250°C and 330°C when measured using a blue filter (Strickertsson, 1985; Mejdahl, 1989; Balescu and Lamothe, 1992). Huntley et al., (1985) suggested that the optical stimulation of feldspar is possible, and Hutt et al., (1988) published the first stimulation spectra for feldspar. Huntley et al., (1991) suggested that TL and Infrared stimulated luminescence (IRSL) emission spectrum were similar, implying that the same recombination centers are being used by the two processes.

1.5 ESR dating

Electron Spin Resonance (also called as Electron Paramagnetic Resonance (EPR)) involves the measurements of paramagnetic ions in a sample. ESR is a non-destructive method of measuring the concentration of paramagnetic species and free-radicals in liquid and solids. ESR dating relies on measurement of radiation induced paramagnetic ions. The concentration of these centers in a given sample is measure of the total radiation dose to which the sample was exposed. Thus, the paledose (or D_e) of the natural radiation can be estimated in a similar fashion as that used in luminescence dating. The age can be calculated from geological dose by estimating the annual dose of the natural radiation from the content of natural radioactive elements (²³⁸U, ²³²Th, ⁴⁰K, and cosmic rays).

1.5.1 ESR

EPR or ESR detects species that have unpaired electron; generally it must be free radical or transition metals. Irradiation from natural radiation causes ionization and the

migration/trapping of free charges (Figs.1.3a and 1.3b). These ionized electrons are trapped in lattice defects which are termed as the electron trapping center and hole trapping center. Some of these trapped charges lead to paramagnetic center. Presence of a net unpaired electron spin implies a net magnetic moment (μ).



Figure 1.3 (a) Radiation and non-magnetic paired electron, (b) Ionization and (c) unpaired electron (after Ikeya, 1993)

Observation of ESR is based on the fact that a charged particle spins around its axis and acts like a tiny bar magnet as shown in Fig. 1.3c. In a magnetic field, the degeneracy of a particular energy state that depends on the value of m_l (magnetic quantum number) as well as of total quantum number (n), is breaks and leading to the Zeeman splitting.

In a magnetic field **H**, spin states of a paramagnetic system are quantized in directions parallel and antiparallel to the field resulting in a splitting of the energy levels, so that the interaction of magnetic moment with magnetic field gives rise to an additional energy contribution E,

$$\Delta \mathbf{E} = -\mathbf{\mu} \cdot \mathbf{H}$$
or

$$\Delta E = -\mu_{s} H = -g\beta m_{s} H$$

The value of E corresponding to the two possible states as shown in Fig. 1.4

$$\mathbf{E} = \pm (1/2)\mathbf{\mu} \cdot \mathbf{H} = \pm (1/2)g\beta H$$
$$\Delta \mathbf{E} = \mathbf{g} \beta \mathbf{H} (1/2 - (-1/2)) = \mathbf{g} \beta \mathbf{H}$$

To move between the two energy levels, the electron needs energy, ΔE such that,

$$\Delta \mathbf{E} = \mathbf{h}\,\mathbf{v} = \mathbf{g}\,\boldsymbol{\beta}\,\mathbf{H} \tag{1.11}$$

This is the fundamental equation of ESR spectroscopy and represents the resonance condition. Here v is the frequency of electromagnetic radiation (microwave).

Under a magnetic field Zeeman splitting occurs. The electrons can move from the lower energy states to higher energy state by absorbing the incoming radiation hv. The incoming radiation is, however, also absorbed by the electrons in the higher energy level causing them to move down to the lower level (stimulated emission).

Since the coefficients of absorption and stimulated emission are equal, no net value would be observed if the spin population was equally distributed between these two levels. Einstein probablity suggets that the population in the lower energy state is higher, because of that there is a net absorption of microwave radiation. If this population of center is in thermodynamic equilibrium, its statistical distribution is described by the Boltzmann distribution.

$$N_{j+1} / N_j = \exp(-(E_j - E_{j+1}) / kT)$$

= exp(-\Delta E/kT) (1.12)

Where, k is the Boltzmann's constant (= $1.38 \times 10^{-23} \text{ J K}^{-1}$) and T is temperature in Kelvin.

In principle resonance absorption can be obtained by sweeping the magnetic field H, and maintaining the frequency v constant (Fig. 1.5). Conversely, ESR signals can be generated by resonant energy absorption measurements made at different electromagnetic radiation frequencies v in a constant external magnetic field.



Figure 1.4 Splitting of the energy levels in a magnetic field (Zeeman splitting).



Figure 1.5 Electron spin resonance, microwave frequency bands.

1.5.2 ESR dating

The principles of ESR Dating are similar to luminescence dating. The events which can be dated by ESR techniques are i) mineralization, ii) biomineralization, iii) thermal annealing, iv) geological fault and v) optical bleaching (Grun and Invernati, 1985; Ikeya, 1993 and Grun, 2006). This technique is mostly used to date minerals and been used to date fossilized teeth, burnt flints, calcium carbonate, coral and egg shells. A basic advantage of Electron Spin Resonance dating is that it is a non destructive technique and can be repeated a number of times. This is because an ESR measurement does not involve movement of charge.

Other comparative advantages are;

- 1. ESR is less sensitive to surface effect than TL/OSL, which means grain size of the sample does not make any difference in ESR results.
- Sample preparation and ESR measurements are quite simple at room temperature. ESR measurements can be made on small quantity of samples.
- 3. ESR can probe different phases of a mineral.
- 4. ESR is a center dependent method and hence the age assigned is center specific.
- 5. Dating range is >100Ma (Odom and Rink, 1989).

1.5.2.1 The age equation

ESR is a dosimetric dating technique similar to luminescence dating technique and the age is determined by the following equation;

$$Age(T) = \frac{D_e}{\dot{D}}$$
(1.13)

1.5.2.2 Basic assumptions

ESR dating assumes,

At time T = 0, the ESR signal was zero at the time of formation of mineral (in case of tooth enamel, speloethems, travertine, calcrete, mollusk shell, coral, bones and gypsum) or was reduced to zero by thermal zeroing (e.g. volcanics, fault gauge, burnet flint)
- 2. It is essential that the trapped electron and holes should remain stable over a geological time scale, implying that the mean life of the ESR signal must be longer than the age of the sample being dated.
- 3. The accumulated dose is smaller than the saturation dose of the sample.

1.5.2.3 Paleodose (De) measurements

To obtain a realistic growth curve the additive dose method (Aitken, 1985) is commonly used. In this method sample is exposed to different known artificial doses (using a strong calibrated radiation source) and the ESR response is measured. To obtain growth curve, ESR intensity is plotted against the applied dose.

Paleodose or equivalent dose (D_e) is calculated after extrapolating the growth curve to zero dose or known initial dose.

1.6 Objectives and scope of the Thesis

The present thesis explored the luminescence and ESR dating potential for providing the chronology for gypsum occurrences in two different contexts. As an additional input the paleoclimate and paleohydrological implications of gypsum in Thar Desert, India and White Sands, New-Mexico, USA were also examined. The scope of the present thesis is,

- Characterization of the sample using techniques such as X-ray diffraction, Fourier Transform Infrared (FT-IR) Spectroscopy, Thermogravimetry (TG) and Differential Thermal Analysis (DTA),
- 2. Luminescence characterization of signals including study of their kinetics,
- 3. Methodological aspects of dating of the quartz associated with gypsum,
- 4. Methodological aspects of ESR dating and characterization of ESR centers,
- 5. Inferences on the formation episodes of gypsum in the Thar Desert, Rajasthan, India and depositional events of gypsum in White Sands, New Mexico, USA.
- 6. Inferences on the formation path ways and formation environment of the gypsum

1. Characterization of the sample

In low temperature aqueous environment (T < $\sim 100^{\circ}$ C), along with the gypsum (CaSO₄.2H₂O) some other evaporatic minerals e.g. anhydrite (CaSO₄), magnesite (MgCO₃), halite (NaCl), and sylvite (KCl) are also formed. Gypsum is one of the most common minerals in sedimentary environments. It is a principle evaporatic mineral that produces massive beds, by evaporation of highly saline waters. Since it forms easily from saline water, gypsum can have many inclusions of other minerals and even trapped fluids. The purity of samples was ascertained using DTA, TG, XRD and FT-IR spectroscopy.

2. Luminescence Characterization related to dating and dosimetry

In view of the ease of dehydration of gypsum, it was necessary to understand the effect of heating on luminescence properties of gypsum and for identifying the signal that could be used for dating. Extensive studies for radiation sensitivity (OSL and TL) for effect of heating, and the kinetic parameters (E, s and τ) were carried out. Optically Stimulated Luminescence (OSL) and Thermally Stimulated Luminescence (TL) behavior of gypsum were explored for dating and dosimetry.

3. Dating of gypsum: indirect via luminescence

Indirect age estimate for gypsum formation by dating the associated sediments (quartz) using the luminescence dating technique were obtained. The associated sediments (indirect dating) were dated using the traces of quartz extract from gypsum (concentration 0.1%) and the underlying and overlying quartz sand in playa.

4. Dating of the gypsum: direct via ESR

In the direct dating of gypsum, ESR behavior of gypsum was explored. This includes identification of the ESR centers and their use to geochronology. Direct dating of gypsum using the Electron Spin Resonance dating technique was employed on the gypsum crystals.

5. Formation episodes of gypsum: Thar and White Sands

Gypsum occurrences of Thar Desert and White Sands were dated using Luminescence and ESR techniques. The ages of the quartz extracted from the sand horizons and the ages from the gypsum itself provided the information of formation episodes of gypsum in Thar Desert and White Sands.

6. Formation path ways of gypsum

In nature, gypsum can form through two pathways. The first one is through direct precipitation of gypsum with out any changes. In the second case, gypsum precipitation occurs through sulfur produced by microbial activity in the form of dimethyl sulphonio propionate. Using the ESR analysis and FT-IR investigation possible pathways of gypsum are discussed from two different localities viz. White Sands, New Mexico, and Thar Desert, India.

1.7 Chapter wise details

<u>Chapter-1</u>: Introduction

This chapter describes the evaporite deposits and the importance of dating these deposits. Various methods to date evaporites are discussed in brief. Basic principles and methodology of luminescence and ESR dating is discussed in some detail. Measurement protocols, such as the single aliquot method and multiple aliquot methods, are examined.

<u>Chapter-2:</u> Experimental procedures and protocols

This chapter describes the experimental methods and protocols that are used in the measurement of OSL and ESR. These include sample preparation, measurement protocol, analysis and the description of instruments used.

<u>Chapter-3:</u> Material characterization

This chapter describes techniques and results of sample characterization. Experimental methods such as Fourier Transform Infra-red (FT-IR) spectroscopy, Differential Thermal Analysis (DTA), Thermogravimetry (TG), and X-ray diffraction (XRD) analysis are discussed along with the results and their implications are presented,

<u>Chapter-4</u>: Dating of gypsum: Results-I (Thar Desert, India)

This chapter provides detailed description of the sample location and the sampling regions. These include account of 12 locations in the Thar desert. The results of dating are presented and their implications are discussed. As an aside, the implication and comparison with the present understanding of the region is presented. A comparison of the direct and indirect dating is also presented.

<u>Chapter-5</u>: Dating of gypsum: Results-II (White Sands, New Mexico)

This chapter provides the first dating results using possibility of both the direct and indirect dating of gypsum by ESR technique (on gypsum itself) and Luminescence techniques (quartz) from the White Sands Dune Field which is the largest,(\sim 700 km²) known field of gypsum dunes in world.

<u>Chapter-6</u>: Conclusions and Future Perspectives

This chapter gives the conclusions and summary of the results obtained from the present study and also gives the future prospect of the work described in the thesis.

EXPERIMENTAL PROCEDURES AND PROTOCOLS

2.1 Dating techniques and sample preparation

This section describes the techniques employed in luminescence dating. Samples in the field were collected after freshly exposing sections. Specially designed cylindrical metal tubes (~20 cm long and 5 cm diameter) made of aluminum or galvanized iron were used for sample collection (Chandel et al., 2006). A black cloth was used to create the dark room like conditions during the sampling process. These tubes were opened in laboratory under subdued red light conditions and the outer ~ 5 cm from both sides of the tube were used for the radiometric purpose. Central 10 cm portion was processed for luminescence analysis. For luminescence dating either of fine and coarse grain fractions were used, the choice of analysis was dictated by the mean grain size.

2.1.1 Fine grain technique

In fine grain technique, proposed by Zimmerman (1971), fine silt fraction $(4-11 \ \mu m)$ is used for dating. The fine grain extracted after a sequential pretreatment of the sample with 1N HCl (to remove carbonates) and 30% H₂O₂ (to remove organic matter) followed by de-flocculation in 0.01N sodium oxalate solution (to remove the clay fraction). In general, multiple cycles of the above treatments were given and at each stage samples were kept in ultrasonic bath for desegregation. This was followed by suspension of the samples in 6 cm column of acetone or alcohol and 4-11 µm grain size fraction was separated using Stoke's settling times of 1.5 and 15 minutes respectively. The 4-11 µm size fraction was re-suspended in acetone or alcohol and equal volumes (~1 ml) were pipetted onto 9.65 mm diameter aluminum discs kept in a glass vial with ~ 1 cm acetone/alcohol, which were then oven dried at $< 50^{\circ}$ C temperature for ~ 16 hours. Considering the difficulty in mineral separation at this grain size level, the luminescence is taken to be from entire polymineralic assemblages, where K-feldspar signal generally dominates. Consequently at time undesirable property of any of the mineral phases can render the sample unsuitable for dating. On the other hand, the presence of alpha dose dilutes the uncertainties due to environmental dose particularly in complex environments.

2.1.2 Coarse grain technique

Coarse grain technique was originally proposed by Ichikawa (1965) and later developed by Fleming (1970 and 1979). In this technique both quartz and potassium feldspar minerals are used for dating. Chemical pretreatment is similar to the fine grain technique except that, after removal of carbonates and organic matter sediments are dried and sieved in order to obtain the desired grain size. Given that the dose absorbed from the beta source is grain size dependent, a narrow size distribution (90–150 µm) is generally used. Following this, quartz is separated using sodium polytungstate ($\rho \ge 2.58$ gm/cm³) solution where quartz ($\rho = 2.65$ gm/cm³) sink and feldspar ($\rho = 2.56$ gm/cm³) float. The quartz fraction thus separated was etched with 40% HF for 80 min to remove the outer, alpha dosed 10–15 µm skin followed by 12N HCl treatment for 30 minutes to convert insoluble fluorides to soluble chlorides. Mejdahl (1979) suggested that due to etching a

small attenuation in external beta also occurs and proposed appropriate correction factors for various grain sizes. Typical attenuation of beta dose is ~ 5%, for a 100 μ m grain size (Aitken, 1985). Etched and cleaned quartz grains were deposited using silicon oil (silkosprayTM) onto stainless steel disc (~9.65 mm diameter). Stainless steel disc was chosen over aluminum disc because it is reported that silicon oil on aluminum discs can give spurious signal especially after irradiation. The basic advantage of using quartz over feldspar is it lack internal radioactivity and that it does not show anomalous fading. On the other hand feldspar provides a possibility of higher dating range due to its significantly higher saturation dose.

2.2 Normalization procedures

Variation in luminescence sensitivity (counts/mg/Gy) of individual grains, imply that the luminescence output of the different sub-samples of the same sample is not same and significant intra sample differences in luminescence yield are observed. In multigrain aliquots this scatter arises either due to the variation in the number of luminescence emitting grains and due to the variability in the luminescence properties of these grains. In order to circumvent this problem, several normalization methods have been proposed (Aitken, 1985; 1998; Jain et al., 2003). The most common and routinely used methods are;

- 1. Weight normalization
- 2. Zero glow normalization (ZGN) and
- 3. Short shine normalization

2.2.1 Weight normalization

In this method aliquots are normalized by the weight of the sample and assume that all grains have identical luminescence output. Given that individual grains have variable luminescence sensitivity and that in general less then few percent of the grains provide a major fraction of luminescence of an aliquot, weight normalization often results in a scatter of ~10% or more (Aitken, 1985 and Jain et al., 2003).

2.2.2 Zero glow normalization (ZGN)

ZGN method was suggested by Aitken and Bussell (1979), and was meant for TL applications. In this method a small test dose on natural sample is given and luminescence output corresponding to 110°C TL peak is used for normalizing the higher temperature peak. This method works as in natural samples there is no TL signal up to 200°C, however, variations in the supralinearty correction of individual grain implies variation in the TL yield of these grain for a test doses. This can cause scatter up to 10–15%. It has been demonstrated that a close correspondence exists between the OSL and 110°C TL peak (Stoneham and stokes, 1991; Stokes, 1994) and hence occasionally 110°C peak is also used to normalize OSL signal.

2.2.3 Short shine normalization

Also known as natural normalization, in this method a 0.1sec OSL signal is recorded before the measurement (long-shine). The stimulation flux is adjusted such that there is only a marginal (<1%) depletion of the natural luminescence signal from the sample. This method assumes that the luminescence sensitivity of the first 0.1 sec and the rest of the shine down curve are correlated, such an assumption however does not hold over large dose ranges (Jain et al., 2003).

2.3 Luminescence: experimental

This section deals with the instrumentation used in luminescence measurement. Commercial systems are now available that enable both the optical or thermal stimulation, irradiation and luminescence detection. A typical TL/OSL-reader comprises,

- 1. A detector (Photomultiplier tube)
- 2. A filter combination
- 3. Stimulation source(s)
- 4. Irradiation system
- 5. Heater control
- 6. A system controller / interface / readout system

2.3.1 Photomultiplier Tube

The luminescence signal is detected by EMI 9235 QA (bi-alkali type) photomultiplier tube (PMT). Figure 2.1a shows the Quantum efficiency of EMI 9235 QA PMT as a function of wave length. The maximum detection efficiency (~380 nm) makes it possible to detect the entire luminescence signal from quartz and feldspar grains in the UV–near red orange signal. The maximum photon counts rate was kept below $5x10^5$ counts/second in order to avoid pulse pileup effects. For bright signals, either the stimulation power was reduced or quartz neutral density filter were employed.

2.3.2 Filters

Luminescence signal used for dating is usually very low and spans several emissions from UV to blue. In view of this use of optical filters becomes necessary to; i) isolate the desired emission band, ii) discriminate against the stimulation light and iii) reduce black body radiations. Quartz has a strong emission centered around 365 nm (Huntley et al., 1996) whereas feldspar emission centered around 410 nm (Krbetschek et al., 1997). The luminescence signal was detected by an EMI 9235 QA PMT attached to a filter pack consisting of the following filter assemblies;

- 1. Schott BG-39 + Hoya U-340, in case of UV emission for Quartz (blue light stimulated luminescence; BLSL).
- Schott BG-39 + Cs 7-59 (or 5-58), in case of blue (or violet) emission for feldspar (infra red stimulated luminescence; IRSL).
- 3. For very bright samples, fused silica neutral density (ND) filters were used.

The transmission curves for the filters, BG-39, U-340, and 7-59 are shown in Fig. 2.1b.

2.3.3 Stimulation source

Systems used in the present study are; i) Risoe TL/OSL-reader (12 and 15), and ii) Daybreak TL/OSL-reader (1150 and 2200). A block diagram of Risoe-12 system is shown in Fig. 2.2.



Figure 2.1 (a) Response of the EMI 9235 QA PMT and (b) transmission curve for the Filters, BG-39, U-340 and CS 7-59.



Figure 2.2 (a) Block diagram of Risoe TL/OSL-reader and (b) block diagram of beta irradiator (after Botter-Jensen et al., 2003).

Sample stimulation is done by an array of Light Emitting Diodes (LED'S). For quartz, blue LED's are used whereas feldspar grains are stimulated by the Infrared LED.

Risoe-TL-OSL reader: In this system 28 Blue LEDs are arranged in 4 clusters each containing 7 LED and emitting at $\lambda = 470 \pm 30$ nm. The total power delivered at the sample is > 40 mW/cm². Stimulation intensity can be changed by varying the power to LED's (Botter-Jensen et al., 2003). The IR LEDs ($\lambda = 880 \pm 80$ nm) are arranged in 3 clusters of 7 LEDs each and the total power delivered at the sample position is 135 mW/cm² (Botter-Jensen et al., 2003).

Daybreak TL-OSL-reader: The maximum power delivered by 20 Blue-Green LED's (arranged in two parallel rows each containing 10 LEDs), with the peak wavelength at \sim 515 nm is 60mW/cm² to the sample at 45° from vertical. For IR excitation, 10 LED's (arranged in two rows each containing 5 LEDs) were used with the peak wavelength at 880 nm, and the maximum power can be delivered is 50 mW/cm² (Bortlot, 2000).

2.3.4 Irradiation

Risoe reader: Majority of the experiments were carried out on a Risoe TL/OSL TL/DA-15 which has a mounted beta irradiator (90 Sr/ 90 Y beta source) on the top of the system. The block diagram of the beta irradiator is shown in Fig. 2.2b. The distance between the radiation source and the sample is 5 mm. The calibration of the source on the system using calibration quartz supplied by Riso yielded the beta source strength to be 0.109 Gy/sec.

Daybreak system: Daybreak-2200 TL-OSL reader has the beta irradiator with source strength of 0.016 Gy/sec as on October 2005. The distance between the irradiation source and sample is 15 mm. For the samples analyzed in Daybreak-1150 system, beta irradiations were performed using a 20 slots beta irradiator manufactured by Daybreak-Nuclear and medical systems. The source was calibrated for fine grain $(4-11\mu m)$ and coarse grain $(90-150 \mu m)$ samples using MBLE super CaF₂: nat from Oxford and Quartz supplied by Risoe National Laboratory, Denmark. The calibration of Daybreak beta irradiator gave a dose rate of 0.061 Gy/sec and 0.041 Gy/sec for Quartz $(90-150 \mu m)$ and fine grains $(4-11 \mu m)$, respectively.

2.4 D_e measurement

In the present study two methods viz. multiple aliquot additive dose (MAAD) and single aliquot regeneration (SAR) were used to evaluate D_e as discussed below.

2.4.1 Multiple aliquot additive dose method (MAAD)

This method was first developed for the Thermoluminescence dating of archeological pottery (Aitken, 1985). This method uses several identical aliquots of same sample. In order to obtain appropriate paleodose, these aliquots divided into several groups, the very first group is used for the measurement of natural luminescence (i.e. sample as received) and other groups are given increasing laboratory dose (e.g. $\beta_1, \beta_2, \beta_3,...$) over and above the natural signal. The luminescence signal thus obtained is plotted against the applied dose and a growth curve is reconstructed. The Paleodose is obtained by extrapolation of the growth-curve to zero luminescence intensity (Fig. 2.3) and the distance of this intersection point to the origin gives the paleodose. This method assumes that all aliquots have identical radiation history and that the radiation response of the sample. This method while ensures against sensitivity changes, requires a priori assessment of the nature of the growth curve. Further in MAAD, growth curve is extrapolated on to the x-axis; hence the result depends quite significantly on the choice of the mathematical function used (linear, exponential or polynomial). In addition to this, problem arises when the extrapolation is to be made over a large dose-span, where the growth is nonlinear and/or there is a large scatter between the data points. As the construction of growth curves involves a large number of aliquots, appropriate normalization (discussed in section 2.2) is needed. Monte-Carlo simulations by Felix and Singhvi (1997) provide practical guidelines for construction of growth curves and extrapolations.

2.4.2 Single aliquot regeneration method (SAR)

Single aliquot regeneration (SAR) of Murray and Roberts (1998) enables D_e estimation on single aliquots. This method provides for improved precision by combining measurements of several discs.



Figure 2.3 Multiple aliquot additive dose growth curve. Luminescence intensity as photon counts per second is plotted against the applied laboratory doses. Paleodose is evaluated by extrapolating the curve on to the dose axes. Multiple aliquots for each dose points are measured.

In SAR method, D_e is estimated on a single aliquot by recording its natural luminescence and then a regeneration growth curve is made through a cycle of measurements that involve, increasing irradiation, preheat and measurement. At each stage a sensitivity measurement is included to ensure that any lab induced sensitivity is corrected for. The intensity of the natural sample is then read on the regenerated growth curve to obtain a D_e . Recording D_e on many such aliquots and appropriately treating the data provide statistical firmness and also helps to identifying poor/heterogeneous bleaching.

The change in sensitivity caused due to OSL readout, preheat and irradiation of the samples is monitored via the response of 110°C peak to a fixed test dose (Murray and Roberts, 1998). The natural and regenerative OSL measurements are carried out at 125°C in order to keep the 110°C trap empty during the OSL stimulation (Murray and Wintle, 2000). Table 2.1 gives the details of SAR protocol, which was used.

A SAR protocol starts with preheat followed by the measurement of the natural OSL (L_N) signal. Any changes in luminescence sensitivity during preheat and OSL measurement is corrected by measuring the OSL output (T_N) from a small test dose (10-20% of natural D_e). Afterward, the aliquot is given incremental regenerative doses which are recorded after preheating the sample. In the procedure test dose is kept constant so that any change in sensitivity can be corrected provided 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 the present work, five regeneration dose (R₁, R₂,...., R₅) responses were recorded. The first three doses constrained the natural signal and were such that, $R_1 < N$, $R_2 \sim N$ and $R_3 > N$. The fourth regeneration dose (R₄) was a zero dose point and was used to monitor the recuperation due to thermal transfer from optically insensitive traps which are partly drained by the 240°C preheat. The fifth regeneration dose (R_5) is kept equal to R_1 and the ratio R_5/R_1 enabling in examining the reproducibility of the signal hence provide a mean to further check any change in the sample sensitivity during the cycles of measurements (Murray and Wintle, 2000). A growth curve between the test dose corrected luminescence (L_x/T_x) and laboratory regeneration doses $(R_1, R_2 \text{ and } R_3)$ is then constructed (Fig. 2.4).

Step	Treatment	Observation
1	Preheat (160–300° C) / 10 (s)	
2	OSL (Natural)	L_N
3	Test dose	
4	Cut heat (160° C) / 10 (s)	
5	Test dose OSL	T_N
6	Illumination (240–280° C) / 100 (s)	
7	Regeneration dose (R ₁)	
8	Preheat (160–300° C) / 10 (s)	
9	$OSL(R_1)$	L_1
10	Test dose	
11	Cut heat (160° C) / 10 (s)	
12	Test dose OSL	T_1
13	Illumination (240–280° C) / 100 (s)	
14	Go to position, 7 and repeat it for R_2, R_3	

 Table 2.1 Single aliquot regenerative protocol (Murray and Wintle, 2000)



Figure 2.4 Single aliquot regeneration method, sensitivity corrected luminescence is plotted against the incremental doses (R_1 , R_2 , R_3 ...). Paleodose is measured by interpolating the (L_N/T_N) on to the dose axis (Murray and Wintle, 2000).

The natural signal (L_N/T_N) is read onto that growth curve to get the laboratory equivalent paleodose (D_e) as shown in Fig. 2.4.

2.4.3 Experimental details

Indirect dating of gypsum using the OSL technique was employed on the quartz extracted, from the sediments underlying and overlying gypsum beds and from the gypsum sand. Single aliquot regeneration (SAR) method Murray and Wintle (2000) was employed. The resulting shine down curve was collected over 40 or 100 seconds, the first 0.8 seconds were used for signal integration and the final 4 seconds were used for background subtraction. The growth curves were appropriately fitted with a linear or saturating exponential equation.

For samples with dominance of fine silt fraction, fine grain technique using 4–11 μ m grain size were used by their infrared stimulated luminescence (IRSL). Samples were analyzed using multiple aliquot additive (MAAD) dating method in Daybreak 1150 automated TL/OSL system. Short shine normalization and preheat of 200°C, for 1min was used. For each sample 4–6 discs per dose point were taken and additive dose points were extended up to six times the anticipated paleodose for optimum precision (Felix and Singhvi, 1997). The alpha efficiency was estimated by giving additive alpha and beta doses to daylight bleached aliquots, then reconstructing beta dose growth curves and reading alpha induced intensities on the beta dose growth curves. The prescription of Aitken (1985) was used to get alpha efficiencies.

2.4.4 Selection of paleodose for age estimation

The event dated by OSL technique is the most recent exposure to sunlight which reset the geological luminescence signal to zero or near zero values. If the sediment grains were completely bleached (to a zero or a near zero level) then every grain or set of grains should yield the same paleodoses. However, this does not happen in some of depositional environments and in general, at individual grain level all samples are heterogeneously bleached. In case of the fluvial transport, the bleaching of the sediment grain is likely to be partial and heterogeneous due to attenuation of sun light due to depth of water column, turbidity, and transport duration. Further, sediment coagulation by clay and retarded bleaching efficiency with stimulating wavelength makes the entire bleaching process complex. This would imply that at the time of deposition different grain had varying amount of doses in them.

Compare to the water lain sediment, in principle the wind transported (aeolian sand) are adequately bleached because the sediments are transported either in suspension or saltation. However, it may not be true as observed in the present study that aeolian samples showed wide D_e spread. In such situations selection of actual D_e needs care. Towards this, several proposals have been suggested and these are summarized below.

In case of well bleached aeolian sediments dose distribution approximate Gaussian distribution and in such cases mean value of the D_e is used. In samples where the dose distribution is positively skewed minimum dose values are preferred which are likely to represents the most bleached grains. Olley et al., (1998) suggested that use of lowest 5–12 % of the D_e obtained from small aliquot (<50 grains) can provide accurate D_e . Further it was shown that if the D_e distribution is asymmetric there is a greater probability that aliquots with the lowest D_e closely represent the true burial dose. This was successfully demonstrated in a known 6 years old flood sample (Olley et al., 1999).

Fuchs and Lang (2001) suggested that only those aliquots should be considered for D_e estimation whose relative standard deviation (RSD) is ~ 4%. For a distribution of paleodose the RSD defined as percentage ratio of standard deviation of the dose distribution to the mean value of the paleodoses. They applied this method on fluvially transported quartz on a small number of aliquots (N = 10) and 4% was selected taking into consideration the error associated with the dose recovery test (discussed in section 2.4.7).

Lepper et al., (2001) developed the leading edge method in which the experimental error is first deconvoluted from the measured D_e distribution that arises from geological processes (weathering, transportation and sediment flux). According to him, deconvolution of experimental error that arises due to geological processes helps in obtaining a correct D_e value.

Galbrith (1988; 1990 and 1994), and Galbrith et al., (1999) suggested the use of radial plot to select the appropriate D_e value. In this approach the D_e values are plotted against their related precision. The value can be traced by a radial line on to D_e scale and the method works well with well bleached samples.

Based on the foregoing it can be suggested that for a narrow Gaussian distribution the mean value can be taken whereas for the positively skewed distribution the lowest D_e value can be considered.

In the present study, the minimum 10% of the D_e distribution, and the weighted mean of all discs in the range defined by minimum dose and the minimum paleodose + 2σ , (where σ is the experimental error) were used.

2.4.5 Dose visualization methods

Dose visualization is the pictorial representation of D_e distribution. Several methods have been proposed in order to visualize results from a set of D_e 's. In this study, i) plotting histograms and ii) radial plot have been used.

2.4.5.1 Histogram

Histogram is a graphical display of D_e values. A histogram is simply a mapping that counts the number of observations which fall into various disjoint categories, known as bins. A histogram can be constructed by segmenting the range of the data into equal sized bins. The bin width (Δ) or the number of bins of a histogram can be selected by using the formula ($2k - \xi$) / Δ^2 , where k and ξ are the mean and variance of the number of data points in the bins, the optimal bin width is the one that minimizes this formula.

The y-axis of the histogram is represents frequency (the number of counts for each bin), and the x-axis of the histogram is labeled with the range of D_e values (Fig. 2.5a).

Histograms have been used successfully in luminescence dating for visualization the width and the skewness of dose distributions and to detect poorly/heterogeneously bleached samples (Murray et al., 1995; Olley et al., 1998).

2.4.5.2 Radial plot

Radial plot is a graphical representation of D_e values, especially for comparing several estimates which have different precisions. The circles represent the individual data point in the plot (Fig. 2.5b).



Figure 2.5 (a) Histogram constructed for the sample MOH-2 (Thar), number of aliquot used is also shown and (b) Radial plot of the sample BHB-3 (Thar Desert). Data is from dose recovery test, after bleaching the signal to residual level followed by the known dose (20 Gy). Shaded region is the band of 2σ on the y-axis

The value of an equivalent dose measured for an aliquot can be read by drawing a line from the origin of the y-axis through the intersection point of the right hand circular scale (Fig. 2.5b).

The x-axis represents the precision, expressed as relative standard error (%). The precision, by which an individual D_e is obtained, can therefore be read from the intersection with the x-axis by a vertical line drawn through the data-point. The y-axis is the standardized estimates of equivalent dose, which is,

$$\frac{\log\left(D_e - w'\right)}{E'} \tag{2.1}$$

Where, w' is the weighted average of all the aliquots, and E' is the standard error of $logD_e$. Equivalent doses that are statistically consistent at the 2σ (95% of the data points) level are easily recognized, as these will fall within a band of ± 2 units around a radial line.

2.4.6 Preheat plateau

A heat treatment to remove unstable OSL components is an integral part of any luminescence dating protocol. It is now well known that the luminescence sensitivity is affected by heat treatments. In view of this it is important to assure that the luminescence sensitivity should not change for the natural sample (as received) and the artificially irradiation (laboratory). This is done by measuring D_e at different preheat and seeking a constancy (the preheat plateau). Thus, if the D_e value does not change with preheat, then it can be assumed that sample is not affected by preheat treatment and vice-versa. In the present study a preheat plateau test was carried out by taking about 30 aliquots these are divided into 7 subgroups (each subgroup contain 3–5 aliquots). For every subgroup SAR D_e was determined by using different preheat temperature ranging from 160°C to 280°C at 20°C intervals.

2.4.7 Dose recovery test

In SAR protocol, the first regenerative dose (R₁) was repeated (R₅) and the OSL signal and the associated OSL test dose response were measured. Ideally R₁ and R₅ should be identical, and the ratio (R = (L₁/T₁) / (L₅/T₅)) of these two, corrected

regenerated OSL signals, is called the recycling ratio and should close to unity. The deviation of the recycling ratio from unity can be used as a criterion for acceptance or rejection of aliquots. In the present case only those values were considered where the recycling ratio ranged from 0.95 to 1.05.

In the present study the dose recovery test was carried out by recovering a known dose by using the SAR protocol. In the dose recovery test about 10 aliquots are bleached using blue LED's for 100s at room temperature. This is followed by a laboratory dose which is equivalent to the D_e value of the sample. Other condition such as preheat, cut heat and test dose are kept same as done for the D_e estimation for the respective sample. In the present study all samples which were dated by OSL were analyzed for dose recover test (chapter 4 and 5).

2.5 Dose rate estimation

Dose rate (annual dose) is the rate at which the sediment has adsorbed the energy from the naturally occurring radionuclide i.e. 238 U, 235 U, 232 Th, 40 K, and 87 Rb. These radionuclide have long life (half life ~10⁹years) and decay by emitting alphas, betas and gamma rays (Figs. 2.6 and 2.7). The ionization power and the range of ionizing radiation play an important role in luminescence/ ESR dating technique as discussed below.

When radiation interacts with matter its intensity decreases as a function of distance travelled. The attenuation of radiation along its track in a solid implies that the dose delivered is spatially heterogeneous. The heterogeneity arises due to higher charge and mass. Thus α , β , γ produced from the same radionuclide deposit energy over different scale lengths and thus needs to be accounted for.

Additional complication arises from the fact that the radioactivity is also heterogeneously distributed in the sediment. For example quartz has no internal radioactivity, whereas feldspar has up to 14% potassium. This implies that, the distribution of dose in sediments and its partitioning at a grain level is crucial for radiation dosimetry and hence dating. The range of the alpha particles is $\sim 10-20 \ \mu m$, β particles is 3 mm and for gamma rays it is 30 cm.

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Figure 2.6 Decay schemes of the Uranium series, (a) Uranium-235 and (b) Uranium-238.





Figure 2.7 Decay schemes of the radioactive series, (a) Thorium-232, and (b) Potassium-40 and Rubidium-87.



Figure 2.8 Scheme of the interaction of radiation with sample, and its environment (after Grun, 1991).

This is shown schematically in Fig.2.8. The annual dose can be calculated by two methods; i) computation the dose rate using infinite matrix assumption, by determining the concentration of U, Th, and ⁴⁰K and ii) field γ -ray dosimetry.

The age equation assumes that the annual dose remains constant over time span that is being dated. This assumption holds in cases where the decay chain in secular equilibrium. However, this may not always be true particularly for the fluvial sediments. Several workers (Ikeya, 1993; Krbetschek et al., 1994; Prescott and Hutton, 1995 and Olley et al., 1996) have found that fluvial samples suffer from radioactive disequilibrium which can affect the dose rate significantly. The most common disequilibrium is in the ²³⁸U series, with the escape of ²²²Rn (half life 3.82days), and the disequilibrium of ²²⁶Ra, ²³⁴U, ²¹⁰Pb.

In addition to this, dose rate can be affected by the presence of water, which though devoid of radioactivity has a property to attenuate the radiation flux. The absorption coefficient of water is 50% higher for alpha particles, 25% higher for beta particles and 14% for gamma radiation (Zimmerman, 1971 and Aitken, 1998). The correction factor is determined by measuring the water content of the sample as received (or as perceived to be in the nature) and the saturation water content measured in laboratory.

$$D_{\alpha} = \frac{D_{\alpha, dry}}{1 + 1.50 \times W \times F} \tag{2.2}$$

$$D_{\beta} = \frac{D_{\alpha, dry}}{1 + 1.25 \times W \times F}$$
(2.3)

$$D_{\gamma} = \frac{D_{\beta, dry}}{1 + 1.14 \times W' \times F} \tag{2.4}$$

Where, W refers for sample, W' for the environment and F is the fraction of saturation.

Thick source alpha counting (Aitken, 1985) was done for measuring the uranium and thorium concentrations using Daybreak 582 alpha counters. Samples were gently crushed to thickness less than 10 μ m, and spread onto a ZnS(Ag) scintillation screen. The counting system was calibrated using NBL Uranium standard BL-3 (1 ppm Uranium) and sand NBL105A (10.2 ppm Uranium). The counting threshold was set at 83.5 % efficiency to allow the efficiency of counting for the two decay chains to be nearly equal (Aitken, 1985). Typical background count rate is ~0.2 counts/kilo second for a counting area of 13.85 cm². Typical s alpha count rates are ~8–10 counts/ kilo second for the

samples. Usually samples are counted for a period so that a total count of greater than1000 is achieved.

For potassium estimation the gamma spectrometry NaI(Tl), and liquid nitrogen cooled hyper pure Germanium detector was used. The K concentration was estimated by measuring the ⁴⁰K gamma lines (1.4675MeV). In case of NaI(Tl), "3x3" well type geometry was used. The count rate of 10 gram of standard (AR grade KCl) was ~ 58 counts/min. For comparison, only the photo peak counts (up to the full width at half maximum) were used. Typically sample weights of ~10 gm gives a count rate of 4–7 counts/minute for sample compared to a background of 1–2 counts/minute. The hyper pure Germanium planar detector (Relative efficiency 25.6%) housed within a 10 cm thick lead shield has typical background of 0.025 cpm for ⁴⁰K. The measurements were carried out using a laboratory standard (STD. 107-Basalt as well as KCl standard) in which the K concentration is 2.63%.

The cosmic ray dose rate was computed using latitude, longitude, altitude, burial depth of the sample and equation proposed by Prescott and Stephan (1982) and Prescott and Hutton (1994). The total dose rate was finally calculated using the correction factors suggested by Ademic and Aitken (1998).

2.6 a-value

The luminescence efficiency of alpha particles is less as compared to beta and gamma. The alpha efficiency factor 'a' can be determined by the formula suggested by Aitken and Bowman (1975),

$$a = \frac{\beta}{13 \, s. \, y} \tag{2.5}$$

Where, s (μ m⁻²min⁻¹), is the strength of alpha source and β , is the beta dose (Gy) which induces the same amount of luminescence as y minutes of alpha dose.

2.7 ESR: experimental and methods

2.7.1 ESR Spectrometer

The block diagram of an ESR spectrometer is shown in Fig. 2.9. A typical ESR spectrometer consists of, i) an electromagnet, ii) an electromagnetic wave generator (Microwave Bridge) and iii) a detector assembly to measure the power absorption from this wave. A microwave bridge consists of a Klystron or a Gun-diode that generates the microwave and an attenuator, which controls the power level. Microwaves entering from the Klystron or Gun-diode are directed by a wave-guide towards the resonant cavity (where the sample is mounted) in a static magnetic field. Microwaves reflected back from the cavity are measured using a diode-detector.

Resonance absorption can be obtained by sweeping the magnetic field, and maintaining the frequency v constant. Conversely, ESR absorption can also be generated by varying the microwave frequencies in a constant external magnetic field. Since it is easy to change the magnetic field, normally the magnetic field is varied.

Most spectrometers work with frequency v in the microwave region. The detector (diode) is mounted in such a way that a current proportional to the microwave power reflected from the cavity is produced in it. So the microwave absorption can be detected by noting the change in current.

In general, a constant magnetic field is modulated by an 100 kHz sinusoidal magnetic field of smaller amplitude. Therefore, the microwave absorption is modulated by a high frequency of 100 kHz and synchronously amplified electronically (using a lock-in-amplifier system). The modulation amplitude is normally less than the line width hence the detected signal is proportional to the change in sample absorption. The recorder showed the rectified output, which is a mathematical differentiated line of microwave absorption (dP/dH), as shown in Fig. 2.10. To read out the first derivative spectra is bit different (concentration of the unpaired spins can be taken by reading the minimum and maximum magnitude). Nonetheless there is a various advantage, that, a first derivative spectrum has much better resolution than absorption spectra. Sample is mounted in the microwave cavity, which is a rectangular or cylindrical metal box. Cavities are characterized by the Q (quality factor).



Figure 2.9 Block diagram of the ESR spectrometer (after Jonas, 1997).



Figure 2.10 ESR absorption signal microwave power is recorded as a function of magnetic field, (b) first derivative of (a).

In the present study, Bruker Emx-6/1 X-band (a; frequency 9-10GHz, b; magnetic field, for g = 2, 3400G) spectrometer was used for ESR measurements at room temperature.

Typically, 30–40 mg samples loaded in Wilmad quartz tubes with 3.5 mm OD (outer diameter) were used for ESR measurements.

This spectrometer has a fully computer controlled, high sensitivity X-Band Gunn-Oscillator Bridge with automatic tuning capability, Q-factor (quality factor) and power measurements are standard. This spectrometer is equipped with water cooled magnets with pole diameters from 6" to 18", air gaps from 62 mm to 160 mm and power supplies from 1 kW to 40 kW. The standard cavity on this spectrometer is the ER 4119HS highsensitivity cavity. This X-Band resonator has an unloaded Q of more than 12000. It features high modulation amplitudes of up to 50 G. The spectrometer can be operated at any modulation frequency between 6 kHz and 100 kHz. The data collection and analysis were done using a computer controlled data acquisition system. The spectra were analyzed using the WIN-EPR/SIMFONIA software.

2.7.1.1 WINEPR/SIMFONIA

WIN EPR is a window based software package. All types of ESR/EPR spectra, obtained by Bruker EMX spectrometer can be handled by this software package. SIMFONIA is a spectral simulation program. Some of the important feature of WINEPR/SIMFONIA, which have been used in this study, are listed below,

- 1. Integration and differentiation
- 2. Deconvolution of overlapping lines
- 3. Lorentzian and Gaussian line shape fitting
- 4. Exponential fitting
- 5. Peak picking
- 6. Baseline correction
- 7. Double integral
- 8. Easy transfer of simulated spectra

2.7.2 ESR spectrum and parameters

The ESR spectrum can be described by the following parameters (Maurfunin, 1979):

- 1. g-factor (spectroscopic splitting factor)
- 2. Fine structure parameters and
- 3. Hyperfine structure parameters

1. g-factor

The g-factor (spectroscopic splitting factor) provides the information about the electronic structure of the paramagnetic centers. In the fundamental equation of ESR spectroscopy (the resonance condition) $\Delta E = hv = g \beta H$, the g factor determines the line position in ESR spectrum. In a ESR experiment the field H and the frequency v at which resonance occurs leads to estimate g.

The g-factor of a free paramagnetic ion can be calculated by The Lande formula;

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$
(2.6)

Where, L is orbital angular momentum quantum number, S is spin angular momentum quantum number and J is total angular momentum quantum number $(J = L \pm S)$.

For most of the organic radicals and radical ions, unpaired electrons have L close to zero and the total electron angular momentum quantum number J is spin quantum number, S. The g-value of a free electron, when L = 0 (no orbital moment), is 2 but the actual "free spin" value is 2.0023. The variation in g-value is because of the relativistic corrections. Free radicals and radical ions ordinarily have g-factors close to the free electron value of g_e = 2.0023, e.g. the most common standard in ESR, diphenyl-picryl-hydrazyl (DPPH) which is ((C₆H₅)₂N-NC₆H₂ (NO₂)₃) has the g-value 2.0036. The other standards used in ESR spectroscopy are peroxyamine disulfonate (g = 2.00537), tetracyanoxy methane (g = 2.0026) and tanol (g = 2.0055) (Ikeya, 1993). If a radical shows the g factor slightly lower or slightly higher than the g_e, it means that the radical have excess of electron or deficient of electron respectively (electron-hole centers). The accuracy in g-value measurements is normally ± 0.001 and ± 0.0005 (Maurfunin, 1979).

2. Fine structure parameters

In ESR, the absorption occurs when the resonance condition $hv = g\beta H$ is satisfied and the spectra is obtained in the form of an absorption line. For an ion in the simple cubic symmetry, the g-value is the only parameter which is determined by substituting the appropriate values in resonance equation.

The value of g is different for electron or hole with lowering the crystal field symmetry, in result there are several absorption lines instead of one (Fig. 2.11). This is because of the initial splitting (in absence of magnetic field) by crystal field, so when the direction of magnetic field is changed there are three principle values of g_{xx} , g_{yy} . and g_{zz} (anisotropy of g) instead of one. The splitting of the levels in ESR generally occurs by two type of fields, 1) internal crystalline field and 2) applied magnetic field (Marfunin, 1979). The symmetry (cubic or noncubic) of the crystalline field plays a vital role in ESR, because the understanding of number of lines and the splitting by the crystalline field depends upon it.

3. Hyperfine structure parameters

Hyperfine interaction is the interaction between the magnetic moment of an electron with the magnetic moment of the nucleus. The hyperfine interactions are basically two types, isotropic or contact interaction and anisotropic or dipole interaction. Nuclei independently linked with the electron spin system often have a magnetic moment I which also has different permissible orientations (2I + 1) in H.

Because of this interaction there is a week splitting of the electron's spin level, so the original electron resonance line is split into (2I + 1) components. For example, when the electronic spin of a paramagnetic ion interacts with its own nuclear spin the hyperfine interaction is described as,

$$H_{hfs} = ASI$$

Where, *A* is the coupling constant.

Hyperfine structure parameter plays an important role to characterize the electronhole centers and for identifying the paramagnetic ions.



Figure 2.11 splitting of spin levels in crystalline and magnetic field.

2.7.3 Methodology

This section comprises the procedures for ESR dating viz. paleodeose measurement, annual dose rate estimation based on the radionuclide (U, Th and K), measurement techniques, spectrum readout and sample preparation.

2.7.3.1 Paleodose measurement: Single sample additive dose method

For paleodose or equivalent dose (D_e) measurement, the additive dose method (Zeller et al., 1967; Aitken, 1985) is usually used. In this method, the ESR response is measured after exposing the sample for different artificial doses (from calibrated source). Paleodose is measured by extrapolating the growth curve (dose response curve) to zero or near zero value on the dose axis.

2.7.3.2 Dose rate estimation

As discussed earlier, the ESR dating falls in the radiometric dating category such as luminescence (TL/OSL) dating technique.

Extensive studies have been made for the dose rate measurements for ESR dating materials, when the system is in equilibrium (Bell 1979; Fleming 1979; Aitken, 1985; Nambi and Aitken, 1986; Adamiec and Aitken, 1998), and the corrections have been applied (when system is in disequilibrium) for closed system (Wintle 1978; Ikeya 1982; Gosler and Hercman 1988).

2.7.3.3 Measurement techniques

Several techniques have been developed for measuring the ESR spectra. The most popular methods to measure the ESR are;

- 1. Continuous Wave spectrum (CW-ESR)
- 2. Pulsed ESR and electron nuclear double resonance (ENDOR)

1. Continuous Wave spectra (CW-ESR)

The application of the ESR is based on the measurement of its spectra; this involves the collection of conventional field sweep or continuous wave (CW) spectra. ESR spectra is obtained by measuring the absorption of microwave power while, the magnitude of the external magnetic field was continuously increased. An ESR spectrum is the curve of
microwave absorption P versus the magnetic field strength (H). Actually, the output of the ESR is the first derivative of the ESR intensity (dP/dH) against the magnetic field strength (H). In continuous wave ESR, sample is exposed continuously to microwaves.

Most of the spectra are recorded in this study using CW–ESR by keeping the sample into a MW field of constant frequency v and sweeping the external magnetic field H until the resonance condition is fulfilled. The measurement parameters used in this study are shown in Table 2.2.

2. Pulsed ESR and Electron Nuclear Double Resonance (ENDOR)

In pulsed ESR, microwave is applied in very short and high-power pulses. ENDOR (Electron-Nuclear Double Resonance) is a spectroscopy tool, often called as EPR detected NMR (combined ESR with nuclear magnetic resonance). ENDOR is very practical tool for understanding the structure of paramagnetic molecules. It is very useful for learning about the structure of paramagnetic molecules, as well as information about the distances and orientations of atoms surrounding paramagnetic centers (e.g. defects in solids). Electron-nuclear hyperfine couplings between the unpaired electrons and neighboring nuclei can be measure with high precision with the use of ENDOR. In this technique, the sample experience a constant magnetic field and a constant microwave frequency, and the spectra are obtained by sweeping the sample with another wave in the radiofrequency range (energy is in the range of nuclear spin transition). The technique uses two frequencies; a fixed microwave frequency to partially saturate electronic Zeeman transitions and monitor the intensity of the EPR signal, and a strong radiofrequency which is varied in order to excite nuclear (NMR) Zeeman transitions. The double resonance technique can highly simplify a spectrum since every additional nucleus with spin I multiply the number of lines in the ESR spectrum by (2I+1) but only add two lines to the ENDOR spectrum. ENDOR can enhance the spectra to a large extent from the fact that two resonance conditions have to be fulfilled simultaneously (one for the electron spin transition (ESR), and one for the nuclear spin transition (NMR). ENDOR lines are sharper than ESR lines, therefore, hyperfine coupling constants, untraceable by ordinary ESR spectroscopy, can often be determined.

	Sample	
Parameters	Thar	White Sands
Field		
Central field Sweep width Resolution <u>Microwave</u>	3470.000 24.000 1024	3465.000 50.000 1024
Frequency Power	9.717 GHz 0.799 mw	9.717GHz 5.029 mw
Receiver gain Phase Harmonic Mod. Freq. Mod. Amplitude Signal channel	54dB 0.00 deg. 1 100.00kHz 1.00 G	54dB 0.00 deg. 1 100.00 kHz 1.00 G
Conversion Time constant Sweep time	40.960 ms 163.840 ms 41.643 s	40.960 ms 327.680 ms 41.943 s

Table 2.2 Measurement parameters used in ESR study of Thar as well as WhiteSands.

2.7.3.4 Spectrum Readout

Towards ESR dating and dosimetric application, several methods have been suggested for spectrum processing. The basic principle of all the methods is same, as to read out the concentration of the unpaired spins and plot against the applied doses to construct an ESR growth curve. The methods generally used for spectrum readout are listed below;

- 1. Peak-to-peak method
- 2. Peak-to-baseline method
- 3. Double integral method
- 4. Spectrum deconvolution

1. Peak-to-peak method: This is the most commonly used method to determine the ESR intensity from the first derivative spectrum of the absorption curve. The ESR intensity is determined by reading the amplitude difference between maximum and minimum value (peak-to-peak) of the absorption curve (differential form) as shown in Fig. 2.12.

2. Peak to baseline method: The ESR intensity is determined in this method by reading the amplitude between a maximum and a baseline as shown in Fig.2.12.

3. Double integral method: In this method the ESR intensity is determined by double integrating the original ESR spectrum. This gives the total spin concentration.

4. Spectrum deconvolution: Spectrum deconvolution is the process by which the signal can be separated in several components, where each component has its physical significance (trap species). Several methods have been proposed for spectrum deconovolution over time, viz. i) non-linear least square fitting (Press et al., 1992; Jonas, 1995; Lidja et al., 1996; Lund, 2004 and Lund et al., 2006), ii) Fourier self deconvolution (Kouppinen et al., 1981) and c) Maximum likelihood common factor analysis.



Figure 2.12 ESR absorption spectrum, (a) double integral and (b) peak – to- peak and peak to baseline amplitudes

2.7.4 Experimental details

In case of Thar, gypsum crystals collected from the sites (discussed in chapter 4) were initially cleaned for detrital contamination with hand brush and then gently grounded to $10-20 \ \mu m$ size. In case of White Sands, samples were initially treated with 1N HCl and $30\% H_2O_2$ for removal of carbonates and organic matter, respectively.

ESR measurements were done at room temperature using, Bruker Emx-6/1 X-band (a; frequency 9-10GHz, b; magnetic field, for g = 2, 3400G) spectrometer. Typically, 30-40 mg samples loaded in Wilmad quartz tubes (3.5 mm outer diameter) were used for ESR measurements.

The spectra were analyzed using the WIN-EPR software. D_e 's were determined for each sample using, the additive dose method (Zeller et al., 1967; Aitken, 1985). In this method, the ESR response is measured after exposing the sample for different artificial doses (from calibrated gamma source-⁶⁰Co). Equivalent dose is measured by extrapolating the Growth curve to zero or near zero value on the dose axis. ESR spectra were measured in continuous wave ESR mode, and the spectrum readout was performed by using the peak-to-peak or double integral method. The parameters used are shown in (Table 2.2).

2.8 Estimation of Errors

Error estimation is equally important for accurate age estimation. Luminescence and ESR dating involves several measurements, and each measurement has their associated errors which can be categorized broadly into random errors and systematic errors. The error estimation in the present case was based on the calculation proposed by Aitken (1985) and Murray and Olley (2002). The total error in luminescence/ESR techniques can be divided into two parts

- 1. Random errors: that comprises error in estimation of D_e, error in a-value, error in annual dose
- 2. Systematic errors: that comprises error in the calibration of the alpha and beta source, error in calibration of alpha and gamma counters, parameters used in converting the U and Th concentration to dose rate, error in water content.

Material Characterization

3.1 Introduction

Gypsum is one of the most common mineral in sedimentary environments. It is a major rock forming mineral that produces massive beds, usually by evaporation of highly saline waters. Since it forms easily from saline water, gypsum can have many inclusions of other minerals. In nature gypsum occurs as;

- 1. Selenite: a well-crystallized, colorless and transparent variety of gypsum. In desert environment selenite formations can have the shape of desert rose, or as bladed crystals.
- 2. Satin spar: a compact fibrous aggregate
- 3. Alabaster: fine grained gypsum that occurs as massive body in a sedimentary environment.

In general, these varieties are colorless and transparent, but occasionally they can be white, gray, red, brown and yellow, due to the presence of iron-oxide or clay impurities. Gypsum have the monoclinic structure and have the crystal habits; massive, flat, elongated and generally prismatic crystals. The gypsum structure consists of layers parallel to 010 planes. Each layer comprises SO_4^- tetrahedral linked by Ca^{2+} ions and faces a layer of H₂O groups on each surface (Fig. 4.1). The specific gravity of gypsum is 2–2.31. Gypsum is sparingly soluble in water. In geological context, several calcium sulfate minerals are found, but gypsum is the principle form.

3.2 Studies on the loss of water

On heating gypsum loses its water in two stages. Gypsum (CaSO₄.2H₂O) converts to the hemi hydrate (CaSO₄.½H₂O) at about 90–150°C, and at 190–200°C it converts to anhydrite (CaSO₄). At 290°C a phase change in gypsum occurs due to structural inversion to β -CaSO₄. The behavior of bound water was characterized by the thermal methods such as Thermogravimetry (TG) and Differential Thermal Analysis (DTA).

- 1. Thermogravimetry (TG) is a technique in which the mass of substance is measured as a function of increasing temperature whilst the substance is subjected to a controlled temperature program. In this technique the mass changes of a sample is continously recorded, as a function of a combination of temperature with time. A TG thermogram is a plot of the weight loss vs. the temperature. Thermogravimetry is useful in investigating of the processes like; dehydration, oxidation, thermal stability decomposition and high-temperature gas corrosion.
- 2. Differential thermal analysis (DTA) measures the temperature difference between a sample and an inert reference material under identical heat treatments. This differential temperature is then plotted against temperature. Changes in the sample which lead to the absorption or evolution of heat can be detected relative to the inert reference. DTA can therefore be used to study thermal properties and phase changes. A DTA curve consists of peaks corresponds to the evolution (exothermic) or absorption (endothermic) of heat.



Figure 3.1(a) Crystal structure of gypsum (CaSO₄.2H₂O) and (b) structures projected to the planes perpendicular to c-axis (i) and to a-axis (ii) of the unit cell (after Ikeya, 1993).

The purity of samples for the present study was ascertained using Differential Thermal Analysis and Thermogravimetry using the facilities of the Analytical Chemistry Division, at Bhabha Atomic Research Center (BARC), Mumbai. Figure 3.2 show the TG/DTA spectrum of Samples from White Sands, New Mexico, USA (2b, 4b, and 6b), and Thar Desert, India (BJ-11, BJ-12, MILA-8). The TG/DTA thermograms for all the samples, indicated loss of water in two stages between 150°C and 220°C. Gypsum (CaSO₄.2H₂O) converts to the hemihydrate (CaSO₄.½H₂O) at about 150°C, and at 220°C it becomes anhydrite (CaSO₄). This suggested that the Thar and White Sands samples were gypsum with their waters of hydration intact. The percentage loss of weight in TG and the amplitude changes in DTA were \leq 30% which is consistent with the stocheometry.

3.3 X-ray diffraction (XRD)

In a crystal lattice the distribution of atoms is a regular spaced three-dimensional. These are arranged so that they form a series of parallel planes separated from one another by interplaner distance (d). The interplaner distance (d) varies according to the nature of the material and the planes exist in a number of different orientations (each with its own specific *d*-spacing). When a monochromatic X-ray beam is incident onto a crystalline material with an angle θ , diffraction occurs only when the atomic planes of a crystal cause an incident beam to interfere with one another as they reflected back (if the wavelength is of order of the interatomic distance).

If the path difference between the two waves is $2d\sin\theta$, then for constructive interference between these waves, the path difference must be an integral number of wavelengths. This relation is termed as the Bragg's equation,

$n\lambda=2dsin\theta$

Diffraction occurs whenever this equation is satisfied. XRD is widely used for characterization of crystalline materials and to determine their structure. When the incident beam strikes a powder sample, diffraction occurs in every possible orientation of 20.



Figure 3.2 Thermograms with simultaneous measurements of thermogravimetry (TG) and differential thermal analysis (DTA) of Gypsum samples: (a–c) White Sands and (d–f) Thar Desert samples.

The diffracted beam is detected by using a movable detector such as Geiger counter, which is connected to a chart recorder. In normal use, the counter is set to scan over a range of 2θ values at a constant angular velocity.

For XRD measurement, samples were ground with mortar and pestle down to ≤ 100 µm. All the XRD analysis was conducted with a powder X-ray diffractometer using copper target. The data were collected from 5 to 80° (20), using the scanning speed of the counter 2° per min.

Figure 3.3 show the typical XRD spectrum of White Sands samples. This suggested that gypsum (CaSO₄.2H₂O) is the major phase with traces of quartz (SiO₂). There are 5 well defined peaks at 11°, 23°, 48°, 31° and 44° in spectra. In case of Thar Desert samples, additional features of calcite (CaCO₃) at 20 value and hannebachite (CaSO₃.¹/₂H₂O) were observed (Fig. 3.4). The signal due to calcite is shown at 24° and 29° and the signal due to hannebachite (at 27° and 33°) is less intense as compare to gypsum and calcite, and agreed with those in the literature (Laperche and Bigham, 2002).

3.4 Fourier Transform Infrared (FT-IR) Spectroscopy

At times the XRD techniques do not provide quantitative information of the materials. Fourier transform infrared (FT-IR) spectroscopy is a powerful tool for characterizing and identifying materials. FT-IR has been used for quantitative measurements of components of an unknown mixture, and is applicable to solids, liquids, and gasses. FT-IR method works on the principle of infrared spectroscopy.

Infrared spectroscopy is the study of the interaction of infrared radiation with matter. When a matter is exposed to infrared radiation, some of the infrared radiation is absorbed by the matter depending on the molecular structure.

The instruments used for infrared spectroscopy were originally of the dispersive type. These instruments separate the individual frequencies of energy emitted from the infrared source. This was accomplished by the use of a prism or grating.



Figure 3.3 XRD spectrum of White Sands sample; (a) sample 2b and (b) sample 4b. In both of the figures, G represents for gypsum



Figure 3.4 XRD spectrums of Thar sample; (a) sample, BJ-11 and (b) sample, BK-1.G represents for gypsum, C is for calcite and H is for hannebachite.

FT-IR techniques have several advantages over the dispersive type infrared spectral analysis such as:

- 1. Sensitivity of the measurements can be improved with FT-IR for many reasons e.g. the detectors employed are much more sensitive, the optical throughput is much higher which results in much lower noise levels, and the speed of the scanning process enable the co-addition of several scans in order to reduce the random measurement noise to desired level.
- 2. It provides a precise measurement method which requires no external calibration.
- 3. FT-IR is a non destructive technique.

The FT-IR spectrum is plotted as transmittance/absorbance on the ordinate and wave number (cm⁻¹) on the abscissa. The instrument used to obtain the infrared spectrum is named as infrared spectrometer. Most infrared spectrometer works on the principle of Michelson interferometer. Infrared energy is emitted from a glowing black-body source. This beam passes through an aperture which controls the amount of energy presented to the sample (and, ultimately, to the detector). Interferometer normally take a beam of light, split it into two beams with the help of beam splitter, and make one of the light beams travel a different distance by moving the mirror to a very short distance (typically a few millimeter). This difference is known as the optical path difference (δ). The resultant signal, from the spectrometer is the signal of two beams interfering with each other, known as interferogram. An interferogram consist of large number of sinusoidal signals added together. When interferogram signal is transmitted through or reflected from the sample surface, the specific frequencies of energy are adsorbed by sample due to excited vibration of function groups in molecules. The infrared signal after interaction with the sample is uniquely characteristic of the sample. The beam finally arrives at the detector and is measured by the detector. This interferogram can not be interpreted directly, because for analysis an individual frequency spectrum is required. There is a need of decoding the individual frequency, and this can be done by a mathematical technique termed, Fourier transformation. Fourier theorem tells that, any mathematical function can be expressed as a sum of sinusoidal waves. An interferogram is a sum of sinusoidal waves, each of which contains information about the frequency of a given

infrared peak and amplitude information about the peak intensity at that frequency. The Fourier transform simply calculates the infrared spectrum from the summed sinusoidal waves in the interferogram. Because of this mathematical theorem the absorption spectroscopy is named as Fourier transform infrared spectroscopy.

In the present study, the Fourier Transform Infrared Spectral data were obtained in the range 700-4500 cm⁻¹ using a BOMEM DA8 FT-IR spectrometer in an evacuated mode. The spectrometer was equipped with a globar source, a KBr beam-splitter and liquid nitrogen cooled (77°K) HgCdTe (MCT) detector. The KBr pellet method was used and the samples were mixed in concentrations of 1% and 0.5% by weight in 200 mg of anhydrous KBr and ground thoroughly using a pestle and mortar. KBr pellets were prepared using a hydraulic pressure. A pellet of pure KBr served as the background reference for calculating the absorbance. Spectra were obtained in transmission mode and converted to an absorbance versus wave number plot using standard software supplied with the system. Typical spectral resolution was 2 cm⁻¹.

Figures 3.5 and 3.6 show the FT-IR spectra in 700-2400 cm⁻¹ region for White Sands and Thar samples. The FT-IR spectra for the White Sands were nearly identical with bands at 1115, 1140, 1630, 21-2200 and 3550 cm⁻¹ and these agreed well with the values in literature (Hentschel et al., 1985; Alpers et al., 2000; Laperche and Bigham, 2002; Prasad et al., 2005).

The FT-IR spectra from Thar samples (viz. BJ-11, BJ-12 and MILA-8) had additional peaks. Sample MILA-8 had an absorption peak at 870 cm⁻¹ and an absorption band in 1410-1460 cm⁻¹ range suggesting the presence of calcite.

For sample BJ-11 and BJ-12, peaks due to hydrated lime and a prominent absorbance around 1060 cm⁻¹ due to CaSO₃.¹/₂H₂O (Hentschel et al., 1985) were observed. Signals due to CaSO₃.¹/₂H₂O and calcite were more intense than those from gypsum. Their relative concentration varied with the depth of location of these samples. These observations suggest that BJ-11, BJ-12 and MILA-8 (Thar) gypsum formed via a reaction intermediate calcium sulphite CaSO₃.¹/₂H₂O (hannebachite).



Figure 3.5 Fourier Transform Infra-red (FT-IR) spectra of White Sands samples in absorption mode (a) 2b, (b) 4b and (c) 6b.



Figure 3.6 Fourier Transform Infra-red (FT-IR) spectra of Thar samples in absorption mode (a) BJ 11; (b) BJ-12 and (c) MILA-8.

3.5 Luminescence Characterization

Calcium sulfate doped with the dysprosium (CaSO₄:Dy) has been widely used for personal dosimetry. Considerable attention has been focused on the luminescence properties and parameters of CaSO₄: Dy (Pradhan and Ayenger, 1976; Juan and Alicia, 1986; Botter-Jensen et al., 2003 and the references there in). Nambi (1982) characterized the Thermoluminescence (TL) properties of natural marine gypsum for dating. He observed a main TL peak at about 350°C in natural sample and peaks around 120°C, 180°C and 260°C on irradiated sample. Based on a study of kinetics of TL peak at 345–350°C, he estimated that the life time of this peak is 10^{12} – 10^{14} years at 25°C.

3.5.1 Luminescence studies

Gypsum samples for the present thesis were from lacustrine environments. In view of the dehydration of gypsum, it was necessary to understand its effect on luminescence properties of gypsum, and on the dating. This involved ascertaining the radiation sensitivity in terms of OSL and TL, effect on heating, and the kinetic parameters (E, s and τ).

A White Sands sample WS–03–01 (~99% gypsum) and a Thar Desert sample BK-1 (crystalline gypsum) were analyzed. UV and blue emission windows were examined for OSL and TL measurements. It was found that BLSL signal in UV window was measurable but in blue window (with IRSL) the luminescence yield was below the detection limit. In TL, a 380°C TL peak in blue window (Fig. 3.7 a) and 220°C TL peak in UV window (Figs. 3.7b and 3.8a) were observed.

We could not observe 345-350°C TL peak as reported by Nambi, (1982) in marine gypsum (Fig. 3.7a). Further, the OSL signal in UV window was radiation sensitive (Fig. 3.9a). Since the study was primarily focused on the dating of gypsum, hence it was important to check the thermal stability of the OSL signal. The temperature dependence of OSL was investigated to check, if there were any change in the OSL decay curve due to water loss (dehydration).



Figure 3.7 Typical glow-curve of White Sands sample (WS-03-01), (a) natural glow curve in blue window and (b) natural glow curve in ultra-violet window



Figure 3.8 Typical glow-curve of Thar Desert smple (BK-1), (a) natural glow curve in ultraviolet window and (b) activation energy calculated by initial rise method.

A series of measurement were made in which samples were irradiated and preheated at different temperatures <190°C for 10 sec followed by blue light stimulation. Measurements were made up to 190°C as going above this temperature would have caused significant thermal loss of the 220°C peak. There was no change observed in the OSL counts from 100–190°C (Fig 3.10). The trap depth of 220°C TL peak was measured by initial rise method. The trap depth of 220°C TL peak (0.85–1.1eV) would translate into a lifetime of <10 years (Fig. 3.8b). This would imply that such a short lifetime in naturally occurring gypsum (CaSO₄.2H₂O) could not be used for dating by luminescence technique.

3.5.2 Dose response

The dose response of gypsum was investigated in a sample which is dated by OSL technique in the present study. In order to asses the dose response curve Single aliquot regeneration (SAR, discussed in chapter 2) method was used. In the measurement cycle 190°C preheat for 10 second was used followed by a 40s OSL measurement conducted at 125°C. A typical dose response is shown in Fig. 3.11, which shows that signal grows linearly with dose.



Figure 3.9 Typical BLSL shine down curve of, (a) White Sands gypsum after exposing to 5, 10 and 15 Gy of beta dose and (b) Thar Desert gypsum. In both of the cases the filter combination of U–340 and BG-39 was used.



Figure 3.10 BLSL measured at different temperatures.



Figure 3.11 Typical growth curve of White Sands gypsum (6b).

3.6 Conclusions

Following inferences are drawn from the above studies,

- DTA/TG analysis of both the White Sands and Thar Desert samples indicated water loss in two stages. Gypsum (CaSO₄.2H₂O) converts to the hemihydrate (CaSO₄.¹/₂H₂O) in air at about 150°C, and at 220°C it becomes anhydrite (CaSO₄). Further, at 290°C a phase change to β-CaSO₄ (Monoclinic to Trigonal system) takes place.
- 2. XRD analysis of the bulk White Sands samples indicate that these samples comprise gypsum (CaSO₄.2H₂O) with traces of quartz (SiO₂). The Thar Desert samples comprise gypsum along with calcite (CaCO₃) and hannebachite (CaSO₃.¹/₂H₂O). The signal due to hannebachite is weak as compared to gypsum and Calcite.
- 3. The FT-IR spectra for the White Sands comprise absorption bands at 1115, 1140, 1630, 21–2200 and 3550 cm⁻¹. These conform to the published values (Alpers et al., 2000) and suggest the samples are nearly gypsum. The FT-IR spectra of the Thar Desert has bands at 870, 1060, 1140, 1115, 1410-1460, 1630, 21-2200, and 3550 cm⁻¹. Additional absorption bands at 870 cm⁻¹, 1060 cm⁻¹ and 1410-1460 cm⁻¹ indicate presence of calcite, CaSO₃.¹/₂H₂O, and hydrated lime (Hentschel et al., 1985).
- 4. The OSL and TL behavior shows that the natural gypsum is sensitive to radiation.
- 5. Dose response behavior indicates the stability of OSL signal.
- 6. These studies suggest that gypsum can be used as an environmental dosimeter, but the study based on the kinetic parameters (activation energy and tarp life time) led to the inference that, the naturally occurring gypsum (CaSO₄.2H₂O) can not be used for geochronology by Luminescence technique using TL peak of 220°C.

Dating of Gypsum: Results I (Thar Desert, India)

4.1 Introduction

The Thar Desert, Rajasthan in north-west India, is the easternmost extension of midlatitude desert belts comprising the Sahara and the Arabia. It lies mostly in the Indian state of Rajasthan, and extends up to the southern part of Haryana, Punjab and northern Gujarat. Geomorphologically it is bounded by the Sutlej River in northwest, Aravalli range in the east, the salt marsh known as the Rann of Kutchchh in south and Indus River in the west. The regional geology of Rajasthan is shown in Fig. 4.1. The spatial distribution of the present-day annual rainfall in the Thar Desert ranges from 500 mm in the east to 100 mm in the west (Fig. 4.2). Numerous playas across this rainfall gradient exist. The region has a negative water balance with potential evapo-transpiration in the range 1500–2000 mm/year. The playas (dried lake beds) are hydrologically closed, saline and are fed only during the monsoon months through centripetal drainage.



Figure 4.1 Regional geology of Rajasthan (after Choudhary et al., 1984).

It has been suggested that majority of the playas were once part of relict fluvial regimes and were formed either due to, (i) the development of basin troughs by reactivation of lineaments (Sinha-Roy, 1986; Roy, 1999) or (ii) siltation of paleo drainage by aeolian activity (aeolian segmentation) (Agarwal, 1957; Ghosh et al., 1977; Kar, 1990; Singhvi and Kar, 1992). The Regional geology, climate, soil type, and geomormological process of Thar Desert has been summarized by various authors (Singhvi and Kar, 1992, Sinha-Roy et al., 1998). Geomorphologically Thar Desert can be divided into five geomorphic zones viz. i) Western plain, ii) Eastern plain, iii) ridge and valley province iv) Aravalli hill range, and v) Vindhyan upland. Similarly based on the soil texture, soils of the Thar Desert are classified in to five groups viz. i) sandy, ii) sandy loam, iii) loam, iv) clay loam, and v) skeletal soil (Sinha-Roy et al., 1998). In the present study samples from 12 playa sequences distributed in between 500 mm to <150 mm annual rainfall contours were investigated for chronometric studies (Fig. 4.2).

4.1.1 Gypsum in Thar

Gypsum deposits are invariably associated with dry land environment; hence their occurrence in geological record can be used to interpret past episodes of extended dry periods. In the Indian context, extensive gypsum deposits occur in the playas formed in shallow interdunal depression or around the deranged paleo-drainage courses in Thar Desert. In the field gypsum is invariably associated with sand, silt or clay which differentiates the gypsum rich layer with that of the gypsum deficit layer. Spatially pervasive sand and silty clay horizons alternating with gypsum occurrences thus imply fluctuating hydrological condition with high seasonality. The southwest monsoon is the principal source for moisture and hence fluctuation in gypsum in a stratigraphic column can serves as surrogate for monsoon performance through time. The major gypsum deposits occur in Jaisalmer, Barmer, Bikaner, Nagaur, Ganganagar, and Churu districts of Rajasthan (Fig. 4.2). In the present study, gypsum and adjoining sediments from the following sites were analyzed for chronology; i) interdunal depressions at Jamsar, Khichiyan, and Nursar-Bharu (Bikaner), Chittarpar (Barmer), Nachna, Phalsund, Mohangarh (Jaisalmer) and ii) rocky catchments region at Phulera, Bhalisar, Pokaran, and, Pachbhandra.



Figure 4.2 Major gypsum deposits in Thar Desert and site investigated along with annual rainfall contour (Isohyets). The dotted line provides the gross extant of the region examined.

4.2 Direct dating of gypsum: ESR

Electron Spin Resonance (ESR) of radiation induced paramagnetic defects is used in geochronology for samples like inorganic sulphates, carbonates, silicates, phosphates etc. (Marfunin, 1979; Ikeya, 1993). In case of gypsum, radical ions like SO_4^- , SO_3^- and CO_2^- are the major constituents and were used in the present study. Further, the studies also suggested that ESR could provide additional information in determining formation pathways of gypsum.

ESR dating of authegenic precipitate is based on the assumption that the radiation induced paramagnetic centers are abinitio zero at the time of precipitation of the mineral. ESR analysis enables a quantitative measurement of the concentration of radiation induced paramagnetic centers. In nature, natural radiation environment due to decay of U, Th and K provides the radiation field which induces paramagnetic centers in the sample in a cumulative manner. Using appropriate laboratory calibration experiments, the ESR intensity of the sample as received is converted into radiation dose units and is termed as the equivalent dose (D_e).

As a first order approximation, the natural radiation field is assumed to be constant through time. The annual rate of ESR production called the dose rate per annum. The age is calculated by dividing the D_e by annual dose.

4.2.1 ESR dating of gypsum: Present status

ESR-dating of gypsum was made for the first time by Ikeya (1978). Kasuya et al., (1991) systematically investigated the radiation induced paramagnetic centers in a single crystal of gypsum and identified four signals (G₁ to G₄). Using the hyperfine structure of ³³S, they observed that SO₃⁻ radical had a nearly isotropic spectrum with g = 2.003. The SO₃⁻ center is a trapped electron center at an oxygen vacancy and was designated as G₁ center. The second center G₂ had $g_{xx} = 2.0084$, $g_{yy} = 2.0088$ and $g_{zz} = 2.0192$. The z-axis of g-tensor was perpendicular to c-axis and is 10° away from b-axis in (a, b) plane. However, their study did not identify the species responsible for this center except for suggesting that it could be an electron deficient center. The G₃ center had g-values: $g_{xx} = 2.0029$ (parallel to c-axis), $g_{yy} = 2.0027$ (parallel to b-axis) and $g_{zz} = 1.9973$ (parallel to a-

axis). In case of G_4 center, a doublet hyperfine structure was identified which was attributed to the presence of O_2H .

Nambi (1982) used the center G_1 (g = 2.004) for ESR dating of gypsum from Marine origin (India) and provided the age estimates of 63 ka and 71 ka for the two gypsum samples. Ikeda and Ikeya (1992), investigated the ESR signal in natural and synthetic gypsum samples and found that the intensity of G₂ center ($g_{\parallel} = 2.0196$, $g_{\perp} = 2.008$) increased with carbonate doping and attributed the G₂ center to CO₃⁻ radical. Using this center, an ESR age of 260-300 year was estimated for a tectonic event at San Andreas Fault. More recently, G₂ center was also used by Mathew et al., (2004) for dating the gypsum in Indian context, and obtained the ages of marine gypsum ranging from 70–200 ka. Kasuya et. al., (1991) found that the sample integrity was lost when heated beyond 90°C, and the ESR signal of all the centers disappeared around 160°C. This was due to loss of water of hydration and implied that the intrinsic thermal stability of these centers in gypsum can not be assessed at temperature above 90–100°C. Kasuva et. al., (1991) also reported that the intensity of SO₃⁻ increased with temperature, as observed in anhydrous alkaline earth sulphates (Dalvi et al., 1984 and Seshagiri et al., 1988). The mechanism for the anomalous increase of SO3⁻ radical with temperature is yet not understood.

In the present work, the nomenclature of Kasuya et al., (1991) and Ikeya (1993) is used to maintain conformity with the designations used in literature. A summary of the species responsible for the corresponding centers is given in Table 4.1.

4.2.2 Present work: Results

Sample details, location and stratigrphy are given in the appendix of this chapter (Appendix A). ESR spectrums for crystalline and powdery gypsum both sample as received (natural) and after irradiation were examined. Two samples viz. BJ-11, powdery gypsum collected from Jamsar and crystalline gypsum BK-1 from Khichiyan were analyzed in detail. Figures 4.3a and 4.3b show the typical ESR spectrum of natural and after 50 Gy gamma dosed for sample BJ-11 and, Figs 4.4a and 4.4b is the ESR spectrum obtained for sample BK-1.

Center	Identification of the center	
	Previous work	Present Work
G1	SO ₃ ⁻	SO ₃ ⁻
G_2	CO ₃ ⁻ /O ₃ ⁻	SO_4^-
G ₃	CO ₂ -	CO_2^-
G_4	O ₂ H	-
С	SO ₂ ⁻	SO_2^-

Table: 4.1 Radiation induced ESR centers in gypsum and their identificationvis a vis prervious assignments (Kasuya et al., 1991 and Ikeya 1993).



Figure 4.3 ESR spectrums of Gypsum samples (BJ-11) from Thar Desert: (a) sample as received and (b) sample exposed to 50Gy of additional external gamma dose.



Figure 4.4 ESR spectrums of gypsum samples (BK-1) from Thar Desert recorded at room temperature: (a) sample as received and (b) sample exposed to 50 Gy of external gamma dose.

Signal reproducibility in ESR depends on the location of sample in the sample cavity particularly for crystalline gypsum; minor changes in the orientation of the crystal during the measurements can affect the reproducibility of the ESR spectrum. However in case of powdered sample (filled in quartz sample vial) the orientation problem is circumvented because the ESR signal comes from multiple grains. The later method was used in the present study. Reproducibility of the ESR spectrum was obtained after tuning the sample to 180° in the sample cavity. Reproducibility measurements on gypsum show that the intensity of the main signal (SO₃⁻) can be measured with precision of ~ 5%. After heating the sample at 120°C for 60 min, no changes were observed in the SO₃⁻ signal. This suggests that SO₃⁻ signal should be stable and usable for dating. The growth curve for this centre was linear up to 100 Gy, the maximum applied dose in this study. Typical growth curves for gypsum samples are shown in Fig. 4.5. The growth curves in ESR were constructed using either peak-to-peak or double integral method. Based on the precision and the reproducibility measurements, obtained D_e had an error of \pm 5–10%.

ESR spectrum of Thar samples comprised, an intense Mn^{2+} spectrum including the $\Delta m_I = \pm 1$ forbidden transitions. All the radiation induced free radical signals of gypsum however appear between the central hyperfine lines of Mn^{2+} . An obvious problem, is the overlap of tail of $(SO_4^-)_{\perp}$ line with the low field line of Mn^{2+} ($\Delta m_I = \pm 1$) doublet around 3455G. In one sample, BK-1, an intense line due to $(CO_3^-)_{\perp}$ at g = 2.016 with characteristic features of a perpendicular line was also observed (Fig. 4.4). The g value and the line shape illustrate that line G₂ is not due to CO_3^- but due to SO_4^- . The ESR of White Sands samples (Chapter 5) had the absence of Mn^{2+} signal, and relative predominance of SO_3^- signal compared to SO_4^- . However, during irradiation, SO_3^- signal did not show any increase in the White sand whereas a significant increase was observed in the samples from Thar Desert.

In anhydrous alkaline earth sulphates, it has been reported that radiation induced defects show a striking and yet unexplained buildup of SO_3^- signal on heating at the expanse of SO_4^- signal (Dalvi et al., 1984; Seshagiri et al., 1988 and Kasuya et. al., 1991).



Figure 4.5 Dose response curves of SO₃⁻ centers, for sample BJ–11 (powdery gypsum) and NACH–1 (crystalline gypsum). The peak-to-peak intensity is plotted as a function of dose.

In view of this Ikeda and Ikeya (1992) did not consider SO_3^- as being suitable for dating as its intensity depended on factor other than radiation dose such as temperature. This was the reason for not using SO_3^- signal for dating gypsum so far. However in case of the Thar Desert samples which contained significant sulphite it can therefore reasonably assumed that sulphite is responsible for the ESR signal in Thar Desert gypsum. Further, if this was not the case, then SO_3^- signal would have increased with temperature as observed by (Dalvi et al., 1984; Seshagiri et al., 1988 and Kasuya et. al., 1991).

Summarizing this, it can be suggested that that a temperature dependent increase in SO_3^- occurs when SO_3 is in a sulphate matrix. This signal is not suitable for dating. However, when SO_3^- is in a sulphite matrix, the signal is temperature independent as well as stable and suitable for dating.

We envisaged that the SO₃ center is present as a point defect in sulphate matrix it would act as an efficient electron trap (electrons trapped at oxygen vacancy). That is because the electron trapping ability of SO₃, leads to the formation of diamagnetic SO₃²⁻ with paramagnetic SO₃⁻ as an intermediate (Marfunin, 1979). The radical SO₃²⁻ has the electronic configuration $6a^{*2}$ resulting in diamagnetic ¹A, state. The anti-bonding nature of electrons would add to the repulsive force between S⁴⁺ and O⁻ (in SO₃²⁻), increasing S–O bond distance considerably. Therefore SO₃²⁻ would produce significant local strain in alkaline earth sulphate lattice. This strain could be released only by the loss of electrons and hence it becomes a shallow electron trap, which could probably be thermally ionized around 100–150°C, generating SO₃⁻ radicals (Marfunin, 1979 and Kasuya et. al., 1991). Such a case would not be applicable for SO₃²⁻ in a sulphite matrix, where it would be a hole trap incapable of producing any strain in a lattice. In sulphite matrix, it will be a case more analogous to SO₄⁻ in sulphate and can possibly be used for dating samples containing hannebachite (CaSO₃.¹/₂H₂O) where the ESR out put will depend only on radiation dose.

Considering above it is inferred that SO_3^- signal in Thar Desert gypsum can be used for ESR dating for those samples which have the sulphite in significant proportion.
Based on this, ages thus obtained by ESR are shown in Table 4.2 along with the sample details and radioactivity data.

Out of twelve locations investigated in the present study, ESR dating was employed in the following five localities which are discussed below.

1. Jamsar

At Jamsar three samples (two powdery; BJ-11 and BJ-12 and one granular gypsum BJ-4) were dated and the ages obtained for the sample BJ-4 was 11.0 ± 2.1 (depth 2.0), BJ-11 was 8.7 ± 1.5 ka (depth 0.7 m) and for sample BJ-12 was 12.2 ± 1.4 (depth 0.5 m).

2. Khichiyan

At Khichiyan four samples were tried out of these only one sample BK-1 (crystalline gypsum) at depth 7.2 m, responded to radiation dose and yielded an age of 15.5 ± 2.2 ka.

3. Chittarpar

At Chittarpar out of four samples analysed only two (crystalline gypsum) gave the ages viz. CBR-3 dated to 18.3 ± 2.4 ka (depth 2.8 m) and CBR-5 was dated to 11.1 ± 1.6 ka (depth 2 m).

4. Mohangarh

At Mohangarh only one sample, MOH-3 at depth 1.2 m (crystalline gypsum) was dated to 6.1 ± 0.8 ka.

5. Nachna

At Nachna three samples which were analysed, NACH-1 and NACH-4 was crystalline gypsum whereas NACH-3 was granular gypsum. The ages obtained were 7.7 \pm 1.0 ka for NACH-1 (depth 1.8 m), 12.7 \pm 1.8 ka for NACH-3 (depth 1.3 m) and 5.8 \pm 0.9 ka for NACH-4 (0.5m)

Sample	Sample type	U (ppm)	Th (ppm)	K (%)	Cosmic ray (µGy/a)	De [*] (Gy)	Dose rate (Gy/ka)	Age (ka)
NACH-1	Crystalline (Selenite)	2.3 ± 0.3	5.3 ± 1.0	0.3	150 ± 30	29	3.9 ± 0.3	$\textbf{7.7} \pm \textbf{1.0}$
NACH-3	Granular	1.8 ± 0.3	2.3 ± 0.3	0.2	150 ± 30	33	$\textbf{2.6} \pm \textbf{0.2}$	12.7 ± 1.8
NACH-4	Crystalline (Selenite)	$\textbf{2.1} \pm \textbf{0.4}$	3.7 ± 0.4	0.4	150 ± 30	20	3.5 ± 0.3	$\textbf{5.8} \pm \textbf{0.9}$
CBR-3	Granular to powdery	1.7 ± 0.3	5.2 ± 0.4	0.6	150 ± 30	67	3.7 ± 0.3	18.3 ± 2.4
CBR-5	Granular to powdery	1.8 ± 0.3	$\textbf{3.8} \pm \textbf{0.9}$	0.6	150 ± 30	38	3.4 ± 0.3	11.1 ± 1.6
BJ-4	Granular	2.3±0.6	2.1 ± 0.3	0.6	150±30	37	3.4 ± 0.5	11.0 ± 2.1
BJ-11	Gypseous Earth	2.3 ± 0.6	1.9 ± 0.3	0.6	150 ± 30	30	3.4 ± 0.5	8.7 ± 1.5
BJ-12	Gypseous Earth	2.0 ± 0.3	1.1 ± 0.6	0.6	150 ± 30	35	2.9 ± 0.3	12.2 ± 1.4
MOH-3	Crystalline (Selenite)	1.2 ± 0.2	$\boldsymbol{0.9\pm0.7}$	0.6	150 ± 30	13	2.1 ± 0.2	6.1 ± 0.8
BK-1	Crystalline (Selinite)	1.3 ± 0.2	1.1±0.8	0.6	150 ± 30	35	2.3 ± 0.3	15.5 ± 2.2

Table: 4.2 Details of samples, ESR D_e, radioactivity data and computed ages

* ±10 % error was considered in De (which is solely based on the reproducibility measurements). Alpha efficiency factor (a value) 0.25 was used.

4.3 Indirect dating: Luminescence

In the present work quartz extracted from 32 samples collected from sand horizon above and below the gypsum were dated using Blue Light Stimulated Luminescence (BLSL). In order to check the suitability of the samples for luminescence dating, conventional checks like dose recovery, preheat were performed. Dose recovery was carried out for 13 samples. Bleaching and preheat plateau tests were performed on two representative samples each from the 12 sequences investigated in the present study.

Figure 4.6 show the dose response of quartz extract during dose recovery and Table 4.3 shows the result of dose recovery test. Except the samples BJ-5 and MILA-2, for all samples the given doses could be recovered within <15%. Further only those aliquots were considered for D_e for which the recycling ratios were within the range 0.95–1.05. It was also observed that the recuperation was less than 3% corresponding L_N/T_N signal induced by the lowest given dose as well for higher given doses.

The preheat temperature was chosen from the preheat plateau, which was constructed using D_e vs. preheat temperature in the range of 160–280°C. Dependence of D_e on the preheat temperature was investigated. Figure 4.7 summarizes the preheat plateau for samples BHB-3 and MOH-2.

Typical growth curves of quartz extract obtained for the samples NB-5, BK-1, MILA-1, MOH-1, BHB-3 and BJ-5 are shown in Figs. 4.8 (a–f). In SAR protocol, nature of D_e distribution indicates the extent of predepositional bleaching experienced by the sediments during their transport. All samples were examined for D_e distributions and results are shown in the form of histograms and radial plots. In order to reconstruct histogram, a minimum 26 and maximum 77 aliquots were used (Figs. 4.9–4.11).

The extent of bleaching heterogeneity can be appreciated by looking at the data obtained on fluvially reworked aeolian sand deposited in Jamsar playa. For example, samples BJ-1 at depth 2.6 m had a relative standard deviation > 26% in the D_e (Table 4.5). Similarly in radial plot 44% aliquot were outside the 2σ value for the same sample (Fig. 4.9a). The average D_e (mean of all aliquot) was 27.8 ± 7.3 Gy whereas the least 10% D_e was 17.2 ± 2.0 Gy.



Figure 4.6 The figures (a, c) on the left shows the dose recovered (10 aliquots) for sample BHB-3 and MOH-2. The figures on the right shows corresponding shine down curve dose response curve.

Sample	No. of aliquots	Dose Given (Gy.)	% of dose recovered within 2σ of dose given		
BJ-1	10	25	90		
BJ-3	10	25	91		
BJ-5	10	25	65		
MOH-1	10	37	92		
MOH-2	10	37	95		
MOH-5	10	37	85		
MILA-1	10	37	92		
MILA-2	10	18	75		
BHB-2	10	26	91		
BHB-3	10	26	98		
PHA-1	10	10	98		
PHA-2	10	20	85		
PHA-4	10	10	90		

Table: 4.3 Dose recovery results



Figure 4.7 The figures show the dependence of $D_{e,}$ on preheat. The average D_{e} is across the preheat plateau is also shown.



Figure 4.8 Growth curves constructed using the SAR protocol as discussed in chapter 2. The circles represents the sensitivity corrected regenerated OSL signal. Y-axis represents the test dose corrected luminescence (L_x/T_x) , while x-axis represents the applied dose.



Figure 4.9(a, c and e) shows the radial plots of the D_e's obtained for samples, BJ-1, BJ-2 and PHL-1 and (b, d, and f) shows dose distribution obtained for these sample. Total number of aliquots (n) is shown on the upper right corner of the figure.



Figure 4.10(a, c and e) shows the radial plots of the D_e's obtained for samples, CBR-1, MOH-2 and BK-4and (b, d, and f) shows dose distribution obtained for these sample. Total number of aliquots (n) is shown on the upper right corner of the figure.



Figure 4.11(a, c and e) shows the radial plots of the D_e's obtained for samples, MOH–1, NB–3 and MILA–2 and (b, d, and f) shows dose distribution obtained for these sample. Total number of aliquots (n) is shown on the upper right corner of the figure.

Similar observation was made for all the samples analyzed in the present study. The variation of least 10% D_e from the mean D_e is ranged from 22–68% (Table 4.4). Keeping the bleaching heterogeneity in mind, ages were computed by using the, least 10% of the D_e values.

Table 4.5 and Table 4.6 provide the radioactivity data, water content and the SAR ages obtained using the least 10% of the D_e , values. Two playas sequence viz. Pokaran and Phulera were dated using the feldspar extract from the sediments. Table 4.7 provides the details of radioactivity, dose rate, D_e , values and IRSL (MAAD) ages.

Luminescence ages that were obtained on the intervening sand horizons from different sections investigated in the present study are given below.

1. Jamsar

At Jamsar four sand horizons (Fig. 4.12) were dated. The lowermost sand horizon at depth 2.7 m (BJ-1) gave an age of 7.7 ± 2.6 ka. Second sample from the same horizon collected at depth 2.2 m (BJ-2) was dated to 4.0 ± 0.8 ka. Third sample collected immediately below the first gypsum layer at depth 2.0 m (BJ-3) was dated to 3.8 ± 0.5 ka and the forth sample immediately above the gypsum layer (BJ-5) at depth 1.8 m gave an age of 3.5 ± 0.5 ka.

2. Khichiyan

The uppermost aeolian sand at depth 2.0 m that overlies silty-clay horizon (Fig. 4.12) provides an age of 1.6 ± 0.2 ka (BK-4).

3. Nursar

At Nursar, four samples were analyzed (Fig. 4.13). The lowermost sample collected from sand horizon (NB-1) at 4.5 m depth was dated to 13.0 ± 2.6 ka. Second sample above the powdery gypsum horizon from sand layer (NB-2) at depth 2.8 m dated to 6.0 ± 0.8 ka. Upper part of this horizon at depth 2.0 m gave an age of 3.2 ± 0.9 ka (NB-3). The upper most sample collected from the sand horizon underlying the gypsum crust at depth 1.0 m gave an age of 2.8 ± 0.9 ka (NB-5).

Sample	Mean D _e (Gy)	Least 10% D _e (Gy)	% variation of D _e 's	RSD (%)
BJ-1	27.8 ± 7.3	17.2 ± 2.0	38	26
BJ-2	18.9 ± 6.3	10.0 ± 0.5	47	33
BJ-5	22.2 ± 5.9	8.2 ± 1.0	63	27
NB-1	56.2 ± 18.6	31.6 ± 1.8	44	33
NB-2	22.3 ± 5.9	13.9 ± 2.2	38	27
NB-3	19.1 ± 6.2	8.3±1.6	55	32
CBR-2	17.7 ± 6.4	10.2 ± 2.0	42	36
PHL-1	18.9 ± 3.4	13.7 ± 1.0	28	18
MOH-1	32.6 ± 7.1	20.4 ± 2.0	37	22
MOH-2	24.1 ± 3.2	18.9 ± 1.3	22	13
MOH-5	17.3 ± 0.6	5.6 ± 0.5	68	26
MILA-2	20.9 ± 1.0	12.1 ± 1.4	42	21
BHB-1	12.8 ± 3.6	8.6 ± 0.5	33	28
BHB-2	19.4 ± 3.8	13.5 ± 0.7	30	20
BHB-3	29.0 ± 7.7	16.7 ± 1.3	42	27
PHA-2	19.0 ± 5.8	12.0 ± 0.9	37	30
PHA-4	18.4 ± 7.0	8.4 ± 1.4	54	38

Table: 4.4 Computed De, average as well as least 10 % and the relative standard
deviation (RSD)

S. No.	Sample	Depth (m)	U (ppm)	Th (ppm)	K (%)	CR (Gy/ka)	Water (%)	De [*] (Gy)	Dose rate (Gy/ka)	Age (ka)
1	BJ-1	2.7	3.9 ± 0.6	10.5 ± 2.0	1.1 ± 0.9	150 ± 30	20 ± 5	17.2 ± 2.0	2.2 ± 0.7	7.7 ± 2.6
2	BJ-2	2.2	$\textbf{3.2} \pm \textbf{0.6}$	12.3 ± 2.0	1.5 ± 0.1	150 ± 30	20 ± 5	10.0 ± 0.5	2.5 ± 0.3	4.0 ± 0.4
3	BJ-3	2.0	$\textbf{3.6} \pm \textbf{0.1}$	10.4 ± 0.4	1.5 ± 0.2	150 ± 30	20 ± 5	9.5 ±0.9	2.5 ± 0.2	3.8 ± 0.5
4	BJ-5	1.8	$\textbf{3.8} \pm \textbf{0.4}$	8.1 ± 1.1	1.4 ± 0.1	150 ± 30	20 ± 5	8.2 ± 1.0	2.3 ± 0.2	3.5 ± 0.5
5	BK-4 [#]	2.0	14.9 ± 1.3	8.9 ± 5.5	1.4 ± 0.1	150 ± 30	20 ± 5	7.1 ± 0.2	4.4 ± 0.5	1.6 ± 0.2
6	NB-1	4.5	2.5 ± 0.4	7.4 ± 1.3	2.0 ± 0.1	150 ± 30	20 ± 5	31.6 ± 1.8	2.4 ± 0.5	13.0 ± 2.6
7	NB-2	2.8	2.2 ± 0.2	8.1 ± 0.8	1.9 ± 0.1	150 ± 30	20 ± 5	13.9 ± 2.2	2.1 ± 0.2	6.0 ± 0.8
8	NB-3	2.0	$\textbf{2.8} \pm \textbf{0.45}$	8.92 ± 1.62	1.8 ± 0.1	150 ± 30	20 ± 5	8.3±1.6	2.5 ± 0.2	3.2 ± 0.9
9	NB-5	1.0	1.8 ± 0.3	$\textbf{7.08} \pm \textbf{1.00}$	2.0 ± 0.1	150 ± 30	20 ± 5	6.5 ± 1.0	2.3 ± 0.2	2.8 ± 0.9
10	CBR-1	3.6	2.9 ± 0.5	10.87 ± 1.64	1.8 ± 0.1	150 ± 30	20 ± 5	17.7 ± 1.3	2.7 ± 0.2	6.6 ± 0.8

Table: 4.5 Details of samples, D_e, radioactivity data, water content (assumed) and BLSL ages

*Ages were calculated by taking the least 10% from the equivalent dose (D_e) distribution [#] For this sample age was calculated by taking the mean value of D_e . This is because the RSD of D_e was 5% and 84% values falls in 2σ band of radial plots.

11	CBR-2	3.1	1.8 ± 0.3	7.9 ± 1.1	1.4 ± 0.1	150 ± 30	20 ± 5	10.2 ± 2.0	2.0 ± 0.2	5.4 ± 1.1
12	CBR-4	2.4	2.2 ± 0.3	3.8 ± 0.8	1.4 ± 0.1	150 ± 30	20 ± 5	14.6 ±2.0	2.9 ± 0.1	5.1 ± 0.9
13	CBR-8	1.1	2.6 ± 0.3	6.4 ± 0.9	1.3 ± 0.1	150 ± 30	20 ± 5	7.0 ± 1.5	2.0 ± 0.2	3.6 ± 0.8
14	PHL-1	2.0	1.8 ± 0.3	10.6 ± 1.1	1.1 ± 0.1	150 ± 30	20 ± 5	13.7 ± 1.0	1.9 ± 0.2	7.2 ± 0.8
15	MAILA-1	5.4	2.9 ± 0.4	10.5 ± 1.3	1.1 ± 0.1	150 ± 30	20 ± 5	26.0 ± 2.0	2.1 ± 0.2	12.4 ± 1.5
16	MAILA-2	5.0	2.9 ± 0.3	10.5 ± 1.3	1.1 ± 0.1	150 ± 30	20 ± 5	12.1 ± 1.4	2.1 ± 0.2	6.0 ± 0.9
17	MOH-1	3.2	1.2 ± 0.5	6.4 ± 1.6	1.1 ± 0.1	150 ± 30	20 ± 5	20.4 ± 2.0	1.6 ± 0.2	13.1 ± 2.0
18	MOH-2	2.5	3.1 ± 0.4	4.7 ± 1.5	1.0 ± 0.1	150 ± 30	20 ± 5	18.9 ± 1.3	1.7 ± 0.2	10.1 ± 1.4
19	MOH-4	1.0	0.6 ± 0.1	0.5 ± 0.3	0.9 ± 0.1	150 ± 30	20 ± 5	6.0 ± 0.5	1.1 ±0.1	5.8 ± 0.7
20	MOH-5	0.6	0.6 ± 0.1	1.1 ± 0.4	0.9 ± 0.1	150 ± 30	20 ± 5	5.6 ± 0.5	1.0 ± 0.1	4.8 ± 0.6

Table: 4.5 Continued

S. No.	Sample	Depth (m)	U (ppm)	Th (ppm)	K (%)	CR (Gy/ka)	Water (%)	D _e * (Gy)	Dose rate (Gy/ka)	Age (ka)
1	BHB-1	0.6	3.6 ± 0.8	6.6 ± 2.9	1.2 ± 0.1	150±30	20±5	8.6 ± 0.5	2.1 ± 0.3	4.1 ± 0.6
2	BHB-2	1.2	12.1 ± 1.0	4.1 ± 3.8	$\textbf{0.40} \pm \textbf{0.04}$	150±30	20±5	13.5 ± 0.7	2.8 ± 0.3	$\textbf{4.7} \pm \textbf{0.6}$
3	BHB-3	1.7	22.6 ± 1.0	2.9 ± 1.6	$\textbf{0.40} \pm \textbf{0.04}$	150±30	20±5	16.7 ± 1.3	4.5 ± 0.3	$\textbf{3.5} \pm \textbf{0.4}$
4	PHA-1	1.6	1.7 ± 0.7	8.2 ± 2.3	1.7 ± 0.2	150±30	20±5	30.2 ± 1.0	$\textbf{4.7} \pm \textbf{0.4}$	13.7 ± 1.8
5	PHA-2	1.0	1.2 ± 1.3	21.5 ± 5.4	1.5 ± 0.2	150±30	20±5	12.0 ± 0.9	2.7 ±0.4	$\textbf{4.4} \pm \textbf{0.7}$
6	PHA-4	0.7	2.2 ± 0.5	9.4 ± 1.6	1.6 ± 0.2	150±30	20±5	$\textbf{8.4} \pm \textbf{1.4}$	$\textbf{2.3} \pm \textbf{0.3}$	$\textbf{3.7} \pm \textbf{0.7}$

Table: 4.6 Details of samples, measured D_e, radioactivity data, assumed water content and BLSL ages

*Ages were calculated by taking the least 10% from the equivalent dose (D_e) distribution.

S. No.	Sample	Depth (m)	U (ppm)	Th (ppm)	K (%)	CR (Gy/ka)	Water (%)	'a' value	D _e (Gy)	Dose rate Gy/ka)	Age (ka)
1	POK-2	0.9	3.8 ± 1.3	11.0 ± 5.0	$\textbf{2.4} \pm \textbf{0.1}$	150 ± 30	40 ± 20	0.06	21.6 ± 2.0	5.0 ± 0.7	4.3 ± 0.7
2	POK-3	0.5	$\textbf{2.6} \pm \textbf{0.9}$	10.0 ± 3.0	$\textbf{3.2}\pm\textbf{0.2}$	150 ± 30	50 ± 20	0.06	14.0 ± 1.5	5.0 ± 0.6	$\textbf{2.8} \pm \textbf{0.4}$
3	POK-4	0.4	1.5 ± 0.5	60 ± 2.0	$\textbf{3.0} \pm \textbf{0.2}$	150 ± 30	40 ± 30	0.06	12.1 ± 1.4	$\textbf{4.2} \pm \textbf{0.4}$	$\textbf{2.9} \pm \textbf{0.4}$
4	POK-5	0.3	$\textbf{2.8} \pm \textbf{0.7}$	7.1 ± 2.3	$\textbf{3.1} \pm \textbf{0.3}$	150 ±3 0	40 ± 20	0.06	6.8 ± 2.5	$\textbf{4.9} \pm \textbf{0.5}$	1.4 ± 0.5
5	PHUL-3	0.9	$\textbf{2.8} \pm \textbf{0.7}$	6.0 ± 2.0	1.3 ± 0.1	150 ± 30	20 ± 5	0.06	6.4 ± 3.6	$\textbf{3.3} \pm \textbf{0.3}$	$\textbf{2.8} \pm \textbf{0.8}$
6	PHUL4	0.6	$\textbf{2.6} \pm \textbf{0.6}$	$\textbf{7.0} \pm \textbf{2.0}$	$\textbf{2.5} \pm \textbf{0.2}$	150 ± 30	20 ± 5	0.06	9.2 ± 2.4	$\textbf{4.5} \pm \textbf{0.3}$	1.4 ± 0.8

Table: 4.7 Details of samples, D_e, radioactivity data, water content and IRSL ages

4. Chittarpar

From this section four samples were collected from sand and silty-clay horizons (Fig. 4.13). The lowermost horizon dominated by sand at depth 3.6 m gave an age of 6.6 ± 0.8 ka (CBR-1). Second sample collected immediately below the first powdery gypsum horizon at depth 3.1 m from sandy-silt rich layer was dated to 5.4 ± 1.1 ka (CBR-2). Third sample collected from silty-clay layer which overlies crystalline gypsum was dated to 5.1 ± 0.9 ka (CBR-4, depth 2.4 m). Due to the lack of coarse grains, fine grain IRSL technique was employed. The forth sample was collected from sand lens embedded in powdery gypsum at depth 1.1 m gave an age of 3.6 ± 0.8 ka (CBR-8).

5. Phalsund

At Phalsund an extensive gypsum crust sandwiched between well sorted fluvailly reworked sand at the bottom and aeolian sand on the top (Fig. 4.14). In this section one sample at depth 2.0 m (PHL-1) below the gypsum crust was dated to 7.2 ± 0.8 ka.

6. Mila

At Mila the exposed succession show cyclic occurrence of gypsum, sandy- silt and clay (Fig. 4.15). The lowermost horizon contain well sorted fluvially reworked aeolian sand at depth 5.4 m (MILA-1) was dated to 12.4 ± 1.5 ka. The second sample collected above the crystalline gypsum at depth 5.0 m (MILA-2) was dated to, 6.0 ± 0.9 ka.

7. Mohangarh

Similar to Mila the sequence at Mohangarh show frequent alterations of sandy, siltyclay interspersed with crystalline gypsum of various shape and size. A total of four samples collected from sandy layers were dated (Fig. 4.15). The lowermost sample (MOH-1) was fluvailly reworked aeolian sand at depth 3.2 m gave an age of 13.1 ± 2.0 ka. Second sample collected at depth 2.5 m (MOH-2) was dated to 10.1 ± 1.4 ka. Third sample was from a depth of 1.0 m (MOH-4) gave an age of 5.8 ± 0.7 ka and the last sample at depth 0.6 m was dated to 4.8 ± 0.6 ka (MOH-5).

8. Bhalisar

At Bhalisar sediments were dominantly sand and silty-clay with a lone gypsum horizon at depth 1.4 m (Fig. 4.16). Three samples collected from the sand dominated horizons. The first sample collected below the gypsum crust at depth 1.8 m (BHB-3) gave an age of 3.5 ± 0.4 ka, second sample (BHB-2) collected above the gypsum crust at depth 1.4 m was dated to 4.7 ± 0.6 ka (BHB-2). The topmost sample was dated to 4.1 ± 0.6 ka (BHB-1) collected from depth 0.6m.

9. Pachbhandra

At Pachpadra also three samples were dated from depths 1.6m, 1.0 m and 0.7 m which were dated to 13.7 ± 1.8 ka (PHA-1), 4.4 ± 0.7 ka (PHA-2) and 3.7 ± 0.7 ka (PHA-4) respectively (Fig. 4.16). Interestingly no gypsum horizons were encountered in this section.

10. Phulera

Sequence at Phulera was dominantly silty-clay with absence of well defined gypsum horizons. In view of the presence of silty-clay, fine grain IRSL technique was employed. The ages obtained on two samples at depth 0.95 m (PHUL-3) and 0.60 m (PHUL-4) was 2.8 ± 0.8 ka and 1.4 ± 0.8 ka respectively (Fig. 4.17).

11. Pokaran

Similar to Phulera, at Pokaran also the sequence was dominated by silty-clay hence IRSL on fine grain extract was employed (Fig. 4.17). However, unlike Phulera, at Pokharan towards the top at around 0.3 m from surface crystalline gypsum was found. A total of four samples were dated from Pokhara. The first sample was collected from silty-clay at depth 0.9 m (POK-2) was dated to 4.3 ± 0.7 ka, second sample (POK-3) collected at depth 0.5 m was dated to 2.8 ± 0.4 ka and the third sample collected immediately below the crystalline gypsum at depth 0.4 m (POK-4) gave an age of 2.9 ± 0.4 ka. The last sample taken immediately above the crystalline gypsum yielded an age of 1.4 ± 0.5 ka (POK-5).

4.4 Discussion

ESR studies indicated that the Thar gypsum is dominated by Sulphite. During the heating to 120°C, no significant increase in ESR intensity of SO_3^- suggesting it be suitable for dating. The ESR ages thus obtained in the present study are based on the signal obtained from SO_3^- radical ESR results suggest that formation were the result of gypsum formation in anoxic water beds in playas.

In succession where crystalline and powdery gypsum occurred at different depths, the ESR ages on powdery gypsum were higher and stratigraphically inconsistent e.g. sample NACH-3 (Nachana) and BJ-12 (Jamsar). Field observation suggest that powdery gypsum contains silty-sand and was weakly laminated implying deposition as detrital (transported) gypsum from pre-existing gypsum deposits. Hence in a succession, they gave higher ages compared to the crystalline gypsum (Figs. 4.12 - 4.15). The ages obtained on crystalline gypsum suggest three major phases of gypsum formation 15 ka, 8–6 ka and <6 ka respectively. Luminescence dating of quartz and feldspar extracted from the intervening sand horizons support the ESR based ages.

Geological implications

Broadly the luminescence ages obtained from the sequences investigated were stratigraphically consistent (Appendix A). Ages obtained on sand horizons indicate that majority of the playas in Thar Desert experienced fresh water condition between 14 ka to 12 ka. During this period no major gypsum formation occurred. A phase of fresh water condition with fluctuation during 8 ka and 6 ka (at Jamsar and Chittarpar) was inferred by the presence of well sorted sand with occasional gypsum. In the region with annual rainfall is <300 mm, phase of gypsum formation indicating persistent aridity appeared in the Thar desert after 6 ka and continued till < 2 ka. Similarly, at Mohangarh, (located west of 200 mm isohyets), prevalence of fresh water condition around 13 ka accords well with the other sites investigated. However, after 13 ka, the presence of gypsum around 10 ka and its persistence with minor fluctuations till <5 ka, suggests drying up of the region.

This when compared with Phulera playa (situated in 500 mm mean annual rainfall region) where no evidence of gypsum formation was observed between, 3 ka and 1 ka.

Instead the prevalence of aridity was manifested by the changes in sediment texture (dominantly silt and clay).

The spatial and temporal changes in the events of gypsum formation should reflect the rainfall gradient which in turn controls the ratio of potential evaporation and mean annual precipitation (E/P ratio). Thus, for Phulera where no gypsum was observed the E/P ratio is 3 whereas at Mohangarh where gypsum precipitation occurred early the E/P is 10.

A broad concordance can be seen when the limited ESR ages are compared with the luminescence ages. The former provides direct age on the gypsum formation, whereas the later limit the periods of gypsum formation. The ESR age of 15 ka could not be validated due to the lack of sand horizons. There is a reasonable concordance with the ESR age estimate (8–6 ka) with that of the luminescence age showing development of dispersed gypsum crystals. However, ESR age of 6 ka accords well with the luminescence age (6– <2 ka) which has been identified as a regionally extensive gypsum formation event in the Thar Desert.

In view of the limited ESR ages, climatic of the gypsum in Thar Desert is based on the luminescence chronology as discussed here. Paleoclimatic and paleohyrological changes during the Late Quaternary, playas sediments in Thar Desert were investigated by various workers in the recent years (e.g. Swain et al., 1984; Singh et al., 1990; Enzel et al., 1999; Thomas et al., 1999; Deotare et al., 2004). Swain et al. (1984) based on pollen study suggested high lake level in the Thar desert between 10 ka and 5 ka. According to Singh et al., (1990), lacustrine record in Thar Desert indicate a phase of desiccation and hyper saline conditions from last glacial maxima (LGM) to until around 13 ka followed by fluctuating hydrological condition between 13 ka to 7 ka. Enzel et al., (1999) based on sedimentology, mineralogy, stable isotope and radiocarbon dating suggested that that during 10 ka to 4.8 ka, though the lake level fluctuated but never dried. It was only after 4.8 ka dry playa conditions with episodic lake existed. Thomas et al., (1999) observed a regionally extensive aeolian phase between 6 to 3 ka in the Thar Desert implying prevalence of Mid-Holocene aridity. Recently, Deotare et al., (2004), carried out detailed geochemical and palynological studies at Bap-Malar and Kanod

playa located in the western Thar Desert. According to them, playa condition was initiated around 15 ka BP and based on the appearance of gypsum around 11 ka suggested initiation of aridity in the region. However, they inferred full of water condition during 8.0 ka BP to 5.5 ka BP and suggested earlier desiccation (~1 ka) of the western margin playa compared to the eastern margin.

The above observations accord well with the present study which has a larger spatial coverage and secured chronology which allowed constraining the periods of major gypsum forming events.

Mechanism of gypsum formation

The sulphur chemistry in lakes including, i) gypsum formation, ii) the different pathways gypsum takes to exist both in higher oxidation state and as sulphate and, iii) its transformation to lower oxidation state in the form of mineral such as pyrite, FeS₂, or native sulphur, have been extensively investigated (Deprez et al., 1986, Vairavamurthy et al., 1985, Gibson et al., 1991, seal et al., 2000). The role of sulphate reducing bacteria (such as Desulfo-x) under anaerobic conditions plays a vital role in bacterial sulphate reduction (BSR) process, and it can be operative at temperatures less than 80-110°C. A typical reaction may be shown as:

 $Ca^{2+}+2SO_4^{2-}+2CH_4+2H^+ \rightarrow 2H_2S+CaCO_3+3H_2O+CO_2$

In this reaction CH_4 is representative of the host of possible hydrocarbons and SO_4^{2-} represents dissolved sulphate. The sulphate reducing bacteria flourish in anoxic water bodies immediately beneath hyper saline environments and, contribute to the formation of early pyrite framboids. When H₂S accumulates at near surface redox interface, where oxygen is present and metallic-ferrous brines are absent, it can form accumulations of native sulphur rather than metal sulphides. Bio-geochemical considerations suggest that H₂S does not escape to atmosphere. Instead is subjected to microbial oxidation, i.e. aerobic condition or it may be phototropically oxidized under aerobic conditions. In well-oxygenated waters, the stable form of common transition metals Fe and Mn exist in higher oxidation states Fe (III) and Mn (III/IV), as hydrolyzed oxides in the form of colloids or particles. In the absence of oxygen, the lower redox states Fe (II) and Mn (II) are formed. In view of this, in seasonally or permanently stratified lakes where the

bottom waters are anoxic, Fe (II) and Mn (II) can accumulate to a high concentration. However, when these conditions change due to change of salinity and/or change in the amount of oxygen in water, the reverse process viz. the oxidation of sulphur and eventual precipitation of gypsum takes place.

$$CaSO_3. \frac{1}{2} H_2O + \frac{1}{2} O_2 + 1.5 H_2O \rightarrow CaSO_4.2H_2O$$

The presences of significant amount of divalent Mn impurity in all Thar samples, along with hannebachite suggest low oxidative conditions. Presence of intense ESR spectrum of Mn²⁺ in all of the Thar Desert samples suggests that the starting material for Thar gypsum may have pyrite or any other metal sulphide formed in anoxic waters concomitant with low valent transition metal ions. Metal sulphides in rock record and fossil fuels constitute largely inert sulphur reservoir. In natural geological systems, it is observed that formation of pyrite framboids is favored when dolomite (Ca Mg $(CO_3)_2$) is precipitated under higher pH condition. Samples (e.g. BK-1), from Bikaner revealed the presence of intense (CO₃)_{\perp} signal along with (SO₄)_{\perp}, and relatively weaker Mn²⁺. In addition to the presence of Mn²⁺, Thar Desert samples contained significant amounts of sulphite. Intermediate sulphoxy anions such as sulphite were also reported in the oxidation of sulphur moiety in pyrite giving rise to sulphate and thereby gypsum on reaction with calcite. Despite these suggestive factors on possible metal sulphide / pyrite weathering, this is considered less probable due to available geological evidences for absence of pyrite deposit in Thar. An alternative possibility for the occurrence of calcium sulphite, along with Gypsum could be the following reaction (Laprerche and Bigham, 2002),

$$SO_2 + CaCO_3 + H_2O \rightarrow CaSO_3 \frac{1}{2} H_2O + CO_2 + \frac{1}{2} H_2O$$

The calcium sulphite may be partially or fully oxidized to form calcium sulphats at these sites, at the time of gypsum formation.

4.5 Conclusions

Based on the present study, the following inferences are drawn;

- ESR study on Thar Desert samples indicates the presence of SO₃⁻, SO₄⁻, CO₃⁻, and SO₂⁻ centers.
- 2. SO_3^- signal is radiation sensitive and did not increase with heating.
- 3. ESR studies suggest that SO₃⁻ is in sulphite matrix and suitable for dating.
- 4. The ages obtained on the powdery gypsum were higher and straitigraphicaly inconsistent as compare to well develop crystalline gypsum. ESR studies suggested that the powdery gypsum (or gypsite) in Desertic environment is not good for chronometric studies.
- SAR ages on sand were ranged from 14 ka to <2 ka. These ages on sand were in stratigraphic sequence, and these constrain the timing of gypsum formation in the Thar.
- Ages obtained by Luminescence and ESR suggest three major events of gypsum formation 15 ka, 8–6 ka and <6 ka respectively.
- 7. Based on the Luminescence ages the following three major inferences can be drawn; i) Thar Desert experienced fresh water condition between 14 ka and 12 ka during this period no gypsum formation occurred, ii) a fresh water condition with fluctuation during 8 ka and 6ka, and iii) a regionally extensive phase of gypsum formation indicating persistent aridity after 6 ka and continued < 2 ka.</p>
- ESR studies additionally help to understand the formation pathways of gypsum in Thar Desert. Presence of Mn²⁺ signal in ESR analysis suggesting reducing conditions at the time of their formation.

<u>APPENDIX A</u>

A1. Stratigraphy

Samples were collected during two field trips conducted in the eastern and western Thar Desert. First field trip was undertaken during 10–14 March, 2004, wherever second field trip was conducted during 2–9 March, 2005.

A 1.1 Jamsar (Bikaner)

Jamsar playa is located at the northern fringe (28°14.64'N, 73.24°07'E) of the Thar Desert in Bikaner district of Rajasthan (Fig 4.12) surrounded by the linear dunes. Mean annual precipitation is ~250 mm and majority of the rainfall occurs during summer South-west monsoon. Stratigraphy of the exposed succession began with pale-yellow fine grain well shorted mottled sand at the bottom. This was capped by, 0.15 m buff color sandy silt overlain by, 0.10 m crudely laminated light to dark gray fine sand. This horizon was overlain by, 0.6 m buff color marly gypsum with occasionally mm to cm thick sand lamina, around, 5 sand lamina (2 cm thick) could be seen. This horizon was capped by 0.10 m grayish-brown friable clay-silt, and was overlain by 0.35 m granular gypsum (crystalline), containing faint lamination of dirty clay partings. Overlying this horizon was the granular gypsum with clay-silt intercalation. A total 8 intercalations were observed, which was capped by 0.40 m white powdery gypsum. The succession terminates with gypsum crust at the top.

Four samples for luminescence chronology was collected from bottom most well sorted sand and silty-sand horizons at depth 2.7 m, 2.2 m, 2.0 m and 1.8 m (Fig 4.12).

A 1.2 Khichiyan (Bikaner)

Khichiyan is located at the northern fringe (28°13'N, 73°20'E) of the Thar Desert in Bikaner district of Rajasthan (Fig. 4.12). Mean annual precipitation is ~250 mm. From the bottom upwards the sequence began with 3.3 m crystalline gypsum horizon. At places the laminae were contorted, up warped and contained infrequent silt and clay lamina. This was followed by 0.10 m greenish silty sand and was overlain by 1.0 m horizon containing impersistent Gypsum with partly developed crystallinity.



Figure 4.12 Location and Stratigraphy of the Jamsar and Khichiyan Playa with the ages obtained by OSL and ESR (shown in brackets).

Due to the inaccessibility only one sample from uppermost aeolian sand (2.0 m depth) was collected for luminescence dating (Fig. 4.12). In the exposed section small channel activity could be seen. The gypsum horizon was overlain by, 1.0 m bluish grey silty sand showing swelling and pinching character. The succession is terminated with the deposition of ~ 2.5 m aeolian sand having sharp basal contact.

A 1.3 Nursar (Bikaner)

Nursar playa located (28°13'N, 73°11'E) of the Thar Desert in Bikaner district of Rajasthan (Fig. 4.13). At Nursar the succession contain alternating layers of gypsum and clayey-silt. From bottom upwards the succession began with reddish-brown friable sand, which continues below up to 12 m. This is overlain by a 0.02 m reddish- brown to dark-gray fine sand containing discreet gypsum crystals. Overlying this horizon 1.0 m well developed gypsious earth (powdery gypsum) horizon, which is laterally massive and persisted. Gypsious earth horizon was overlain by, 1.0 m reddish-brown friable sand containing mega rhizoconcretions (2–3 cm, in diameter) and was again overlain by, 0.4 m thick and crudely laminated gypsious earth. This horizon was capped by, 1.0 m thick dark-grey to reddish-brown well sorted sand containing rihzoconcretions. The sequence terminates with the deposition of crystalline gypsum.

Four samples from sand horizons were collected for luminescence dating at depth 4.5 m, 2.8 m, 2.0 m and 1.0 m (Fig. 4.13).

A 1.4 Chittarpar (Barmer)

Chitar-Ka- par playa is an interdunal depression located at the south-west fringe (25.45°N, 71.25°E) of the Thar Desert in Barmer district of Rajasthan (Fig. 4.13). Dunes that surround the playa are parabolic in nature. In the exposed section alternating gypsum and clay intercalations could be seen. From bottom upwards this succession began with dark gray sand containing dispersed gypsum crystals. This was overlain by a 0.4 m mottled silty-sand containing impersistent granular gypsum lamina.



Figure 4.13 Location and Stratigraphy of the Nursar and Chittarpar Playas with the ages obtained by ESR (shown in bracket) and OSL.

This was overlain by 0.25 m crudely laminated crystalline gypsum in which iron staining around the gypsum crystals could be seen. The horizon was overlain by a 0.05 m impersistent clay lamina followed by, 0.05 m gypsum lamina. The gypsum-clay intercalations was caped by, 0.1 m granular to massive gypsum horizon containing, toothspar gypsum, which in turn caped by, 0.1 m motteled bluish-green clay horizon. This horizon was overlain by, 0.2 m well developed ~5cm selenite gypsum which shows up warping. This horizon was succeeded by, 0.2 m massive granular gypsum with dispersed columnar crystals and was again caped by, 0.2 m horizon of the selenite crystals with clay partings. Following this a, 0.1 m massive powdery gypsum with dispersed gypsum crystals was observed, which was overlain by, 0.7 m ash grey gypsious earth. This playa succession was covered with aeolian sand.

Three samples from sand horizons (at depth 3.6 m, 3.2 m, 1.1 m) and one sample at depth 2.0 m from silty-clay horizon was collected for luminescence dating (Fig. 4.13).

A 1.5 Phalsund (Jaisalmer)

Phalsund playa is located at the south-west fringe (26°14'N, 71°12'E) of the Thar Desert in Jaisalmer district of Rajasthan (Fig. 4.14), and is surrounded by parabolic dunes. Phalsund comes into the ~170 mm annual rain fall region The bottommost exposed sediment comprised reworked pale-yellow aeolian sand with discrete gypsum crystals towards upper part. This horizon was overlain by a 1.0 m gypsum duricrust (crystalline aggregate) with silty-clay intermixing. Duricrust is caped by, 0.3 m grayish–green sand and clay.

At Phalsund the bottom sand horizon (at depth 2.0 m) was sampled for luminescence chronology (Fig. 4.14).

A 1.6 Nachna (Jaisalmer)

Nachna (27.30°N, 71°43'E) is the place in Jaisalmer district of Rajasthan, Western India. Nachna comes into the ~170 mm annual rain fall region (Fig. 4.14). From bottom upwards sediment comprised reworked pale-yellow aeolian sand containing discrete gypsum crystals.



Figure 4.14 Location and Stratigraphy of the Phalsund and Nachna Playas with the ages obtained by and OSL ESR (shown in brackets).

This was overlain by; 0.25 m massive light grey selenite gypsum which in turns was caped by 0.25 m layer of crudely laminated cm size crystalline gypsum. This horizon was caped by a 0.1 m well developed dark grey selenite body (desert rose) followed by a massive 1.1 m thick granular gypsum. This horizon was overlain by, 0.3 m powdery gypsum covered by the aeolian sand.

A 1.7 Mila (Hanuman-garh)

Mila is a small village near to Pallu, which is located at the northern fringe (28.59°N, 74.14°E) of the Thar Desert in Hanumangarh district of Rajasthan, and is located in rain fall region of ~ 250 mm (Fig. 4.15) From bottom upwards the sequence began with well sorted sand (base unexposed) followed by a 0.35 m dark-gray granular gypsum intercalated with clay. This was overlain by a, 0.4 m thinly laminated mm to cm scale pale-yellow to dark grey silty-clay sand horizon. This horizon was overlain by 1.15 m granular gypsum and silty-clay intercalations This horizon was caped by a, 0.1 m granular to dispersed well developed selenite gypsum, which was overlain by a, 0.05 m layer of well developed selenite gypsum filled with medium to fine sand. This selenite gypsum layer was overlain by a, 0.2 m crudely laminated coarse to medium gypsious sand, followed by a 0.25 m layer of sylinite gypsum filled with silty sand. This selenite band was overlain by, 0.2 m granular selenite gypsum towards top. This horizon is overlain by 0.80 m thick selenite granular gypsum with intercalation of silty-clay could be seen. This was followed by a, 0.4 m crudely laminated medium to fine pale-yellow mottled sand containing rhizoconcretions. A 0.05 m light grey silty sand showing pinching and swelling characters overlying this. The succession terminated with the deposition of 1.2 m thick massive gypsum covered with aeolean sand.

Two samples were collected for luminescence dating one from the bottom sand (5.4 m depth) and another from silty-clay above the gypsum horizon at depth 5.0 m depth (Fig. 4.15).

A 1.8 Mohangarh (Jaisalmer)

Mohangarh playa (27.17°N 71.18°E) is located in Jaisalmer district of Rajasthan. This is considered to be the largest (about 501hectare) gypsum quarry in India.



Figure 4.15 Location and Stratigraphy of the Mohangarh and Mila (Maila) Playas with the ages obtained by OSL and ESR (shown in bracket).

The exposed playa sediment shows the rhythmic alterations of gypsum-sand-clay-silt. The bottommost horizon comprised moderately grey medium to fine sand, overlain by 0.25 m dark brown to light grey medium to fine sand with lenticular clay chips. This was followed by a, 0.03 m selenite gypsum layer, followed by a, 0.15 m planner laminated sandy gypsum. Overlying this horizon there was a 1.3 m thick sequence of selenite-sand (coarse to medium) couplets. This sequence is overlain by, 0.2 m thick laterally persistent selenite horizon. This horizon was caped by a, 0.05 m granular gypsum followed by a, 0.02 m selenite layer which in turns was caped by, 0.02 m light grey clay (swelling pinching). This horizon was overlain by 1.06 m thick gypsum layer containing alternating layers of granular gypsum and selenite gypsum.

In this section four samples were collected for luminescence chronology from the sandy horizons at depth 3.2 m, 2.5 m, 1.0 m and 0.6 m (Fig. 4.15)

A 1.9 Bhalisar

Bhalisar playa is located in Barmer district of Rajasthan and lies in ~200 mm annual rain fall region (Fig. 4.16). From bottom upwards the sequence began with, 0.3 m friable desiccated brown clay, which is caped by a, 0.5m calcareous silty-clay. This horizon is overlain by 0.2 m crudely laminated light brown gypsious silty-clay, which in turns caped by 0.2 m layer of gypsum. Overlying this there was a, 0.2 m horizon of brown clay containing dispersed gypsum. This horizon is overlain by 0.6 m friable light gypsious silty-clay in which at places faint parallel laminations of gypsious earth could be seen. The succession terminated with the 0.6 m moderately brown fractured silty-clay.

Three samples from fine sand layers at depth 1.8 m, 1.2 m and 0.6 m were collected for luminescence chronology (Fig. 4.16).

A 1.10 Pachbhandra

Pachbhandra playa (25.55°N, 62.21°E) is located in Barmer district of Rajasthan. Pachbhandra lies in 250 mm annual rain fall region (Fig. 4.16). Section below 1.8 m could not excavate due to the water table. From bottom upwards the succession began with, 0.2 m thick micaseous, crudely laminated coarse to medium sand. This was capped by 0.1 m thick layer of ash grey medium to fine sand, which in turns followed by 0.2 m thick poorly sorted crudely laminated gritty sand.



Figure 4.16 Location and Stratigraphy of the Bhalisar and Pachbandra Playa with the OSL ages.

This was followed by a 0.2 m thick light grey silt clay and was overlain by 0.1 m bantonite clay mixed with pale yellow to dark brown medium to fine sand. This was overlain by 1.2 m thick alternating pale yellow to dark brown medium to fine sand caped by cherry brown impersistent sandy clay (total four). The succession terminates with 0.3 m massive aeolian sand.

A 1.11 Pokaran

At Pokaran, NNE-SSW (26.55°N, 71.58°E) tending, playa ((~12km²) is located in a depression surrounded by Pokaran sand stone hills (Fig. 4.17). The basin received around 200 mm of mean annual precipitation. The lake is fed by the ephemeral stream having catchments in the surround flat topped hills. We have excavated the playa surface up to the basement rock. In the exposed pit, from bottom upwards 0.6 m thick gritty sand overlies the bedrock. This is succeeded by a 0.2 m angular to sub-angular gravely sand overlain by a 0.4 m thick dark grey, massive, poorly sorted gritty sand. A 0.5 m thick faint laminated sticky bentonitic clay dispersed with halite crystals succeed this horizon. Following this was a 0.1 m thick reddish brown silty-clay containing randomly oriented gypsum and prismatic selenite crystals followed by a 0.1 m thick reddish brown carbonaceous silty-clay which marks the termination of the playa.

For luminescence dating four samples were collected from silty-clay horizons at depth 0.9 m, 0.5 m, 0.4 m and 0.3 m respectively (Fig. 4.17).

A 1.12 Phulera

Phulera is an oval shaped (~6 km²), E-W trending playa, located at the eastern margin (26.52°N, 75.16°E) of Thar Desert, which received around ~500 mm annual precipitation (Fig. 4.17). Samples were collected after excavating a fresh pit up to 1.4 m depth on the dry playa bed. Excavation below this depth was prevented due to the presence of water. In the exposed section four sedimentary successions were identified in a 1.4 m thick. These were from bottom upwards a 0.3 m thick light grey, fine grained laminated calcareous mud followed by a 0.6 m thick sticky clay contained angular calcrete clasts. The horizon was overlain by a 0.35 m thick intercalation of dark brown silty clay and medium to fine pale yellow sand. The upper part contains desiccation cracks filled with

sand. This is followed by a 0.3 m thick faintly laminated blocky silty- clay containing sand lenses and marks the termination of the playa sedimentation (Fig. 1.7).

For luminescence chronology two samples from silty-clay horizons at depth 0.95 m and 0.60 m were collected (Fig. 4.17).



Figure 4.17 Location and Stratigraphy of the Phulera and Pokaran Playas with the IRSL ages.
Chapter 5

Dating of Gypsum: Results II (White Sands, New-Mexico, USA)

5.1 Introduction

The White Sands dune field in Tularosa basin of the Rio Grande Rift between the San Andres and Sacramento Mountains in southern New Mexico is the largest known gypsum dunes in the world covering an area of \sim 500 km² (Kocurek et al., 2006). Gypsum that was formed in a lake was blown away by the winds as gypsum sand following the lake desiccation. More details on geology are provided in the appendix of this chapter (Appendix B).

The choice of this region for sampling was made due to its importance on the methodological aspects of ESR dating. The reasons were,

- 1. It provided pristine natural gypsum where origin could be traced.
- It provides both gypsum and traces of quartz, s.t. the ESR ages on gypsum could be examined against the quartz BLSL ages (serving as controls)
- The comparison of the ESR ages with control BLSL ages provided prospects of ascertaining the life time of SO₄⁻ signal.
- 4. It provides a way to examine if gypsum had any light sensitive signal s.t. both, the time of formation and transportation could be examined.
- 5. A comparison with quartz ages would also pave a way to provide an estimate on the alpha efficiency factor (a-value).

5.2 Chronology

5.2.1 Direct dating: ESR dating

Electron Spin Resonance (ESR) dating technique was employed on two samples viz. 1b (depth 1 m) and 6b (depth 6 m) (Appendix B). Figs. 5.1a and 5.1b give the ESR spectra for sample 6b as received and after 100 Gy of gamma dose respectively. Figure 5.2 provides ESR spectra of sample 6b exposed to day light for 3 hours followed by 100 Gy gamma dose.

Irrespective of the kind of pretreatment (chemical) given to the samples, a total of five centers (G₁–G₃, C and LS) could be identified. The g-value of the ESR lines and associated centers are marked in Fig. 5.1b. Intense lines at $g_{\parallel} = 2.019$ and, $g_{\perp} = 2.008$ together form the center G₂.

A comparison of Figs. 5.1b and 5.2 indicates that the intensity of line marked LS (light sensitive) at g = 2.001 is reduced to ~30% on exposure to 3 hour daylight. Based on earlier work (Marfunin, 1979 and Prasad et al., 2005) this center is assigned to dynamic O_3^- .

Figures 5.3a and 5.3b show dose response curves of the sample 6b, for SO_4^- and light sensitive centers. In case of SO_4^- , the peak-to-peak intensity of perpendicular component (G₂) is plotted as a function of applied dose.



Figure 5.1 Room temperature ESR spectrum of sample, 6b (a) sample as received (b) sample exposed to 100 Gy of gamma radiation. Centers identified are shown with their corresponding species.



Figure 5.2 ESR spectrum of sample, 6b after exposed to 100 Gy of gamma radiation and then exposed to sun for 3 hrs (measurements were made on room temperature).



Figure 5.3 (a) Growth with gamma dose of SO_4^- centers, for sample 6b.The peak-to-peak intensity of perpendicular component (G₂) is plotted as a function of dose and (b) Growth with gamma dose of light sensitive Center (O₃⁻ at g=2.001) in the sample 6b. The double integral in a width of 0.8G around g=2.00 is plotted as a function of dose. This yields the total number of spin contributing to the absorption.

Due to low intensity (compared to SO_4^- center) of the light sensitive center, double integral of the derivative spectra in a width of 0.8G around g = 2.001 is plotted as a function of dose. The dose response was linear up to 100 Gy for both SO_4^- and the light sensitive centers.

Irrespective of its chemical identity, the suitability of a signal for dating primarily depends on its lifetime and radiation sensitivity. If such a center is an integral part of the major matrix being dated, it can be expected that it would be stable. Ikeda and Ikeya (1992) and Mathew et al., (2004) considered that centre G_2 corresponds to CO_3^- center and used for dating gypsum. We have suggested that G_2 center corresponds to SO_4^- and this was the centre used for dating the White Sands.

Since gypsum looses its trapped water at 90 –150°C, thermal stability of radiation induced centers or their isothermal decay characteristics can not be probed. The thermal activation energy for SO_4^- in anhydrous alkaline earth sulphates is around 1eV, with frequency factors varying between10¹¹–10¹³ (Dalvi et al., 1984 and Seshagiri et al., 1988). These values suggest a short lifetime for this center. However, consistency of ages based on this center in White Sands samples with Blue light Stimulated luminescence ages on syn-sedimentary quartz (Table 5.1), suggests that life time should be ~100 ka. This implies that either the frequency factors based on Thermoluminescence measurements are significantly lower than those reported (Dalvi et al., 1984) or the activation energy of SO_4^- in gypsum is significantly higher compared to that in anhydrite. It is not uncommon that the frequency factors obtained by Thermoluminescence show orders of magnitude variation for the same trap depth (Ulusoy, 2004).

This implies that, unlike in anhydrite, the water molecules in gypsum contribute to higher stability of the SO₄⁻ center through hydrogen bonding between sulphate oxygen and the water proton (Marfunin, 1979). The intensity of SO₄⁻ signal increased with applied dose in both of the White Sands samples. The O₃⁻ center was reported to be thermally stable, well beyond that of SO₄⁻ in CaSO₄ matrix (Dalvi et al., 1984 and Seshagiri et al., 1988). The radiation response of the light sensitive center was monitored by taking the double integral of the signal of width \pm 0.85G at g = 2.001. Hence it is expected to be suitable for ESR dating.

The White Sands gypsum samples were well sorted fine sands. Since U and Th are dispersed in the volume of gypsum grains, fine grain dose rate was used with an alpha efficiency factor, a-value, of 0.25, Singhvi and Aitken (1978). The ages so obtained are shown in Table 5.1 which is tabulated along with the BLSL ages for comparison. The dates obtained, using these centers matches well with the ages obtained by BLSL technique for the same sample.

Table 5.1 provides the signal used, radioactivity data, water content, and computed ages. The presence of light sensitive center at g = 2.001 suggests that ESR ages obtained using SO₄⁻ and light sensitive centers in principle provide the potential of formation event of gypsum and its subsequent transportation.

5.2.1.1 Discussion and conclusion

Compared to the gypsum of Thar Desert, the ESR signal of the White Sands (which did not have Mn^{2+} signal), the ESR signals are due to the presence of SO_4^- and SO_2^- centers (Table 5.2). Summarizes the results obtained on the samples for Thar Desert gypsum contain hannebachite (chapter 3) which was absent in the White Sands. The White Sands samples gave clear FT-IR spectra (chapter 3) of pure gypsum (Table 5.1). It would therefore be reasonable to suggest that the gypsum formation in White Sands gypsum belongs to a typical case of evaporites where the pristine gypsum formed through a simple precipitation of calcium sulphate. Based on the above evidences it can be suggested that gypsum precipitation in White Sands area occurred from brine under redox free environment.

Using the SO₄⁻ center samples 1b (depth 1 m) was dated to 2.1±0.2 ka while using the light sensitive center the age obtained was 1.8 ± 0.3 ka. Similarly for sample 6b (at depth 6 m) the SO₄⁻ center gave an age of 5.5 ± 0.6 ka whereas light sensitive yielded an age of 4.5 ± 0.5 ka. It can be seen that two different enters gave straitigraphically consistent age (Table 5.1). SO₄⁻ center is insensitive to light hence the dose accumulated after its formation (gypsum precipitation) does not bleach during the aeolian transport.

On the other hand, light sensitive center though formed simultaneously with the SO_4^- center, but due to its sensitivity towards light, it is likely to bleach during the transport.

Sample	Depth	U	Th	K (%)	CR	Water	ESR age	Luminescence age	
Sambre	(m)	(ppm)	(ppm)	(/0)	(Gy/ka)	(%)	(ka)	(ka)	
1b (SO ₄ ⁻)							2.1 ± 0.2		
	1	$0.05{\pm}0.004$	0.21 ± 0.15	$0.21{\pm}0.02$	0.197± 0.019	5±1		2.1 ± 0.2	
1b (LS)							1.8 ± 0.3		
6b (SO ₄ ⁻)	6	1 49+ 0 10	0 20+ 0 38	0 10+ 0 003	0 097+ 0 009	13+3	5.5 ± 0.6		
6b (LS)	U	1.7/1 0.10	0.201 0.30	0.101 0.005	0.097± 0.009	1010	4.5 ± 0.5	5.2 ± 0.4	

Table 5.1 Details of radioactivity*, water content, computed ESR ages and the corresponding luminescence ages

*Alpha efficiency factor (a-value) = 0.25 was used.

S. No.	Sample	Constituents of the sample (from FT-IR)	ESR centers		
			SO ₃		
			SO ₄		
			SO ₂		
1	White Sands	Gypsum	O_3		
			С		
			SO ₃		
•	Thar	Gypsum +	SO_4		
2		CaSO ₃ . ¹ / ₂ H ₂ O	SO ₂		

Table 5.2 A summary of the FT-IR and ESR results obtained in gypsum samples(White Sands and Thar).

In view of this, it is expected that the ages obtained using SO_4^- center should be higher (accumulated dose in playa plus dose acquired after burial as gypsum sand). On the contrary, identical ages obtained using both the centers implied that there was the time lag between gypsum precipitation and its subsequent deflation by the winds as sands was <1 ka.

5.2.2 Indirect dating: Luminescence dating

In order to ascertain the mineral assemblages, XRD analysis was carried out in all samples. Besides the presence of gypsum the sediment show traces of detrital quartz. This prompted us to employ the OSL dating technique on the quartz extract from the gypsum dominated dune sand. The extraction of the quartz from gypsum sand was non-trivial and towards this, three methods were employed which involved (i) a treatment with Ethylenediamine Tetraacitic Acid (EDTA), (ii) floatation and (iii) dissolution of gypsum in hot concentrated 12N HCl. Out of these three methods extraction of quartz by HCl dissolution was most successful since it was rapid and provided clean quartz grains. This method is discussed below.

5.2.2.1 Extraction of Quartz by Hydrochloric Acid and Results

In this method, quartz is extracted by dissolving gypsum in hydrochloric acid. Nearly 250 gm of gypsum sand was taken in a 500 ml beaker, and decarbonated by treating with 1N HCl followed by 30% H_2O_2 treatment to remove organic matter if any. This is followed by washing using distilled water and dried at 50 degree centigrade. The dried sample was homogenized and ~ 20 gm sample was dissolved in 500 ml of 12N HCl for 1 hour at 70°C with continuous stirring. This was repeated till the gypsum dissolved completely. Supernatant solution was decanted and the insoluble fraction was treated with 200 ml of 1N NaOH solution for 20 minutes (to remove precipitated sulphate). This was followed by a wash with double distilled water. Figure 5.4 gives the flow chart of the extraction protocol.

The insoluble residue was sieved and 90–125 μ m fraction was etched with 40% HF for 40 minute (removal of alpha affected skin) and 12N HCl for 40 minutes to convert insoluble fluorides to soluble chlorides. The samples were washed, dried and mounted on 9.65 mm diameter stainless steel discs.



Figure 5.4 Protocol for extracting the quartz from gypsum sand.

Before subjecting the sample for dating, presence of quartz in the insoluble residue was checked using the routine TL glow curve characteristics as discussed below. A routine TL glow curve indicated that sample comprised only quartz (Fig. 5.5). This is because gypsum provides a TL peak at 220°C with low sensitivity (TL/mg/Gy). On the other hand the extracted samples yielded the typical, quartz glow peak at 110°C.

Figures 5.6a and 5.6b show the typical shine down curves for sample 6b and basal clay respectively. Figures 5.7a and 5.7b show the growth curves for the sample basal clay and 6b and Fig. 5.8 show the dose recovery test. For samples which showed wide D_e distribution, minimum 10% D_e value, whereas, for tightly clustered D_e distribution, mean value was taken. A total of eight samples analyzed responded linearly to radiation dose hence a linear function was fitted to estimate the D_e values and the maximum dose applied was 12 Gy. D_e distribution of the samples is shown in Figs. 5.9–5.11. The RSD in the D_e obtained for the basal clay was 40%. When D_e data was analyzed in radial plot, 40% aliquots were outside the 2σ value. Similarly for sample 4b the RSD 64% and 36% of D_e values were outside the 2σ .

In the dose rate computation radioactive equilibrium in the decay series was assumed. Appropriate correction was made for cosmic ray dose using the equation proposed by Prescott and Hutton (1994).

An interesting observation was that the quartz extract from gypsum sand was highly sensitive as a result it was possible to obtain a minimum D_e of 0.1 Gy for the topmost sample at depth 0.25 m from the surface. Table 5.3 provides the details of the sample, radioactivity, D_e , dose rate and ages obtained on White Sands. The BLSL ages on quartz ranged from 7.3±0.5 ka (for basal clay) at depth 9 m and 0.3±0.04 ka (for upper most aeolian sand) at depth 0.25 m from the surface. The first aeolian sand lying immediately above the basal clay at depth 6 m was dated to 5.2±0.4 ka. This was followed by two consistent ages of 4.3±0.3 and 4.3±0.4 ka at depth 5 m and 4 m respectively. Following this 3.6±0.3 ka at depth 3 m, 3.2±0.2 ka at depth 2 m, 2.1±0.2 ka at depth 1 m and 0.30±0.04 ka at 0.25 m were obtained (Table 5.3). Two identical ages of ~4 ka between 5 and 4 m depths could either be due to the mixing of sediment due to liquefaction and flowage within the drill hole or phase of rapid accumulation (Kocurek et al., 2006).



Figure 5.5 (a) TL glow curve for the gypsum sand (6b) as received and (b) TL glow curve of the same sample after dissolution of gypsum in HCl.



Figure 5.6 BGSL shine down curve for the quartz extracts from (a) basal clay and (b) 6b



Figure 5.7 Growth curves constructed by using the SAR protocol as discussed in chapter 2. The cubes represent the sensitivity corrected regenerated OSL signal. Y-axis represents the test dose corrected luminescence (L_x/T_x) , while x-axis represents the applied dose.



Figure 5.8 Growth curves constructed by using the SAR protocol as during dose recovery test.



Figure 5.9 (a) Dose distribution obtained for sample 2b, total number of aliquots (n) are shown on the upper left corner of the figure, and (b) radial plots of the D_e 's obtained for n=16.



Figure 5.10(a) Dose distribution obtained for sample 4b, total number of aliquots (n) are shown on the upper left corner of the figure, and (b) radial plots of the D_e's obtained for n=18.



Figure 5.11 (a) Dose distribution obtained for sample basal clay, total number of aliquots (n) are shown on the upper left corner of the figure, and (b) radial plots of the D_e 's obtained for n=20.

sample	Depth (m)	U (ppm)	Th (ppm)	K (%)	CR (Gy/ka)	Water (%)	D _e (Gy)	Dose rate (Gy/ka)	Age (ka)
Surface	0.25	0.42±0.03	0.11±0.13	0.020±0.001	0.232±0.023	18±4	0.10±0.01	0.30±0.01	0.3±0.04
1b	1.00	0.05±0.04	0.21±0.15	0.021±0.002	0.197±0.019	5±1	0.50±0.03	0.24±0.02	2.1±0.2
2b	2.00	0.13±0.00	0.00±0.00	0.020±0.002	0.168±0.016	14±3	0.70±0.06	0.22±0.02	3.2±0.2
3b	3.00	0.20±0.01	0.07±0.07	0.042±0.011	0.145±0.014	13±3	0.80±0.06	0.22±0.02	3.6±0.3
4b	4.00	0.30±0.10	0.06±0.06	0.050±0.013	0.126±0.012	13±3	1.00±0.01	0.23±0.02	4.3±0.4
5b	5.00	0.12±0.04	0.29±0.14	0.101±0.030	0.103±0.010	9±2	1.10±0.08	0.25±0.02	4.3±0.3
6b	6.00	1.49±0.10	0.20±0.38	0.101±0.031	0.097±0.009	13±3	3.01±0.28	0.58±0.10	5.2±0.4
Basal clay	9.00	1.12±0.07	0.29±0.27	0.220±0.102	0.068±0.007	20±5	4.10±0.30	0.56±0.10	7.3±0.5

 Table 5.3 Details of the sample, radioactivity, De, dose rate and ages obtained

5.3 Discussion

Comparison of the ESR and OSL data, suggests that the stability of SO_4^- signal is of the order of 100 ka (Fig. 5.12). Straitigraphicaly consistent quartz ages obtained from the White Sands suggests that dune accumulation in Tularosa basin began around 7 ka and continued till <0.3 ka. Based on archaeological evidence and radiocarbon dating Langford (2003) reasoned that basin deflation from L1 to L2 shorelines (Appendix B) and initiation of the dune field occurred around 7 ka is reasonable. Further the ages suggest that the accumulation rate varied from 0.5 mm/yr to 2.5 mm/yr. The highest accumulation rate of 2.5 mm/yr was observed during 3.6 and 3.2 ka indicating a major deflationary event corresponding to ~4 ka as speculated by Langford (2003). The dune field formed in response to the onset of progressive arid conditions around 7 ka, a stepwise drop in the water table (i.e., lake level) can be invoked which caused an increase in sediment availability of previously stored lacustrine sediment (i.e., lagged influx).

A component of contemporaneous influx derived from gypsum precipitation from existing playas has probably occurred throughout the history of the dune field (Kocurek et al., (2006). A close correspondence between the ESR age obtained on gypsum and quartz is encouraging and opens up possibility for the direct dating of White Sands gypsum in future.



Figure 5.12 Comparisons between ESR (Gypsum) and BLSL (Quartz) ages from the same sample.

5.4 Conclusions

Following inferences are drawn from this;

- 1. Paramagnetic centers SO_4^- and SO_3^- and a photo sensitive O_3^- paramagnetic center were produced in gypsum by irradiation.
- The SO₄⁻ signal in gypsum is more stable compared to gypsum anhydrite and can be attributed to hydrogen bonding with lattice water molecules.
- 3. The ESR Signal of SO_4^- , SO_3^- and photosensitive O_3^- enable direct age determination. The ages are consistent with control ages based on BLSL of quartz.
- 4. By using the SO_4^- signal from the major matrix and the light sensitive signal, it is possible to determine both the event, formation of gypsum and its subsequent aeolian transport.
- 5. For the White Sands samples the intensity of SO₃⁻ radical, increased on heating which was not observed in Thar Desert gypsum. This further suggests that for Thar samples, SO₃⁻ was in a sulphite phase whereas for White Sands it is in sulphate matrix.
- TL/ESR correlation suggests that the stability of SO₄⁻ centre is of the order of 100 ka.
- 7. Additionally ESR results help to understand the formation path ways of gypsum in White Sands area, which appeared to be result of simple Gypsum precipitation.
- 8. This study provides the first detailed chronology of White Sands.

<u>APPENDIX B</u>

Tularosa basin is an enclosed, N-S trending extensional basin that formed as a part of the Rio Grande Rift (Langford, 2003). The basin has a restricted ground water outlet and the water table is near the surface at Lucero lake (Basabilvazo et al., 1994) forming dense brine and resulting in the deposition of evaporites during the Quaternary (Allmendinger, 1972). The gypsum dunes field comprises crescentic dunes in the north and east and the parabolic dunes in the south and terminates abruptly against the Alkali Flat (deflationary gypsum). Towards the west of the Alkali Plain are the active playas in which gypsum along with other evaporite precipitation is taking place. These playas rest upon the sediments that were deposited in pluvial Lake Otero. Lake Lucero is the largest playa which occupies the topographically lowest area of the Tularosa basin (Kocurek et al., 2006).

It has been suggested that there are two sources of gypsum sand which led to the formation of dunes viz. the Alkali Flat and Lake Lucero (Allmendinger, 1972). According to Allmendinger (1972), downwind deflation of precipitated salt produced the White Sand dunes during the Pleistocene. Several patches of parabolic dunes were found extending downwind from Lake Lucero and partially burying the paleo shoreline L1 and L2 (Fig. 5.13a). Langford (2003) have shown evidence to suggest that main source of White Sand dune was the margins of the deflation basin along the L1 shoreline. Recently, Kocurek et. al., (2006) have suggested that dune sand was derived through the deflation of evaporite beds of Lake Otero and the younger playa lakes. Considering the unique mineralogical composition (dominantly gypsum rich sand) and their association with the playa lakes, attempts were made in the past to use these sediments towards understanding the past climatic fluctuations. Numerous studies pertaining to the evolution of dune field and its regional context. Langford (2003) suggested that dune field initiate during specific events that were triggered by basinal deflation associated with the regional aridity.



Figure 5.13 (a) White Sands dune field, showing a zone of active playa, including Lake Lucero, paleo-shorelines L1, L2, and Lake Lucero shore-line. Position of the core which is studied in present thesis is marked as UT-1(after Kocurek et al., 2006), (b)Cross-section A-A' as shown in Fig.1, showing a deflationary basin progressively down cut into Lake Otero. The sampling site (UT-1) is 17 km from the lake Lucero (after Kocurek et al., 2006).

Based on archaeological evidence and radiocarbon dating Langford (2003) reasoned that basin deflation from L1 to L2 and initiation of the dune field occurred around 7 ka and deflation of L2 to the Lake Lucero surface was estimated to be around 4 ka. Preliminary Thermoluminescence dates from quartz grains determined by Stokes and reported in Fryberger (2000) for river sediment related to paleolake Otero was 14 ka, for relict dune16 ka, for relict arm of parabolic dune6.5 ka and for dune sediment underlying Alkali Flat it was 2.1 ka. Summarizing the above chronometric study, it can be inferred that the data is too meager to be used to draw any meaningful inference both towards the genesis their climatic significance. In view of this, present study is the first attempt to provide chronology to the dune sediments by using the luminescence and ESR dating of the embedded quartz in gypsum as also directly dating the gypsum crystal.

Sample Collection

Samples for luminescence dating were collected from a crescentic dune field located at 1216 m (32°48'W, 106°15' N) using a truck-mounted rotary drill with an inner 7.6 cm in diameter, pre-slit PVC coring tube in 75 cm long segments. The drilling site was located 17 km from the Lake Lucero (Fig. 5.13b) where drilling was performed at two localities which were 10 m apart. The first core collected from a depth of 3.75 m and the core recovery was 100%. Beyond this depth coring was abandoned due to the presence of water causing liquefaction. Sample 1b, 2b and 3b were obtained from depths 1 m, 2 m and 3 m respectively. Second core was drilled up to 9 m from surface and the core recovery was 50%. Samples 4b, 5b, 6b and basal clay, at depth 4 m, 5 m, 6 m and 9 m, were collected from this core. The sampling (splitting the core sediment) was carried out under subdued red light condition and during the sampling trailer was covered with black opaque plastic sheet to avoid any light leakage. The stratigraphy of the sequence is shown in Fig. 5.14.



Figure 5.14 Location Stratigraphy and the BLSL ages of the site studied.

CONCLUSIONS AND

FUTURE PERSPECTIVES

6.1 Conclusions

The objective of this thesis was to characterize natural gypsum (CaSO₄.2H₂O) in order to use it for by Luminescence and ESR techniques. Both the direct (using gypsum itself) and indirect (using the quartz from its sedimentary context) methods were examined. Methodological aspects of the application of these techniques such as radiation response, the long term stability of the Luminescence and ESR signals in gypsum were tested in this study. The protocols so developed were applied to the samples collected from Thar Desert, India and White Sands, New Mexico, USA.

The present study allows to draw the following inferences;

- Gypsum occurs in three phases, viz., gypsum anhydrite (CaSO₄), hemihydrite (CaSO₄.½H₂O) and gypsum (CaSO₄.2H₂O), and loses its water on heating. This aspect has implication in developing dating technique that involves a thermal treatment component. DTA/TG analysis of both the White Sands and Thar Desert samples indicated water loss in two stages at 150°C and 220°C. Gypsum (CaSO₄.2H₂O) converts to the hemihydrate (CaSO₄.½H₂O) in air at about 150°C and whereas at 220°C it becomes anhydrite (CaSO₄). Further, at 290°C a phase change to β-CaSO₄ takes place. The dehydration studies showed that White Sands and Thar samples were gypsum (CaSO₄.2H₂O) with their waters of hydration intact.
- 2. XRD analysis of the bulk White Sands samples indicated that these samples comprise gypsum (CaSO₄.2H₂O) with traces of quartz (SiO₂). The Thar Desert samples comprise gypsum along with calcite (CaCO₃) and hannebachite (CaSO₃.¹/₂H₂O). In Thar samples the signal due to hannebachite is weak as compared to gypsum and Calcite.
- 3. The FT-IR spectra for the White Sands samples comprised absorption bands at 1115, 1140, 1630, 21-2200 and 3550 cm⁻¹. These suggested that the samples were pure gypsum (CaSO₄.2H₂O). The FT-IR spectra of the Thar Desert has bands at 870, 1060, 1115, 1140, 1410-1460, 1630, 21-2200, and 3550 cm⁻¹. Additional absorption bands at 870 cm⁻¹, 1060 cm⁻¹ and 1410-1460 cm⁻¹ indicated presence of calcite, CaSO₃.¹/₂H₂O and hydrated lime.
- 4. The present study shows that natural gypsum is sensitive to ionizing radiation. It exhibit TL peak at 220°C and the study based on the kinetic parameters (activation energy and trap life time) of this peak suggested that the naturally occurring gypsum (CaSO₄.2H₂O) can not be used for dating using the TL peak of 220°C. Studies on OSL of gypsum, however, suggest a higher stability of the signal suitable for Luminescence dating application.
- 5. A total of five ESR centers viz. $SO_3^-(G_1)$, $SO_4^-(G_2)$, $CO_2^-(G_3)$, $SO_2^-(C)$ including a new center, termed as light sensitive center (LS), were identified.

ESR of SO_4^- and SO_3^- give the most recent precipitation event while the ESR of O_3^- gives the age of aeolian transport. Till the present study, the nature of center G_2 , was not clear. Kasuya et al., (1991) suggested that it could be an electron deficient center, and Ikeda and Ikeya (1992) attributed the G_2 center to be CO_3^- radical. Present study suggests that this centre corresponds to SO_4^- , based on the line shape and the g-value.

- 6. Blue light stimulated luminescence (BLSL) ages on syn-sedimentary quartz from gypsum in White Sands imply that the SO₄⁻centre is stable. Comparison of the ESR and OSL data suggests that the stability of SO₄⁻ signal is of the order of 100 ka. This leads us to suggest that either the frequency factors based on Thermoluminescence measurements are significantly lower than those reported or the activation energy of SO₄⁻ in gypsum is significantly higher compared to that in anhydrite. We, therefore, suggest that, unlike anhydrite, the water molecules in gypsum provide higher stability of the SO₄⁻ center through hydrogen bonding between sulfate oxygen and the water proton as suggested by (Marfunin, 1979).
- 7. Earlier studies though limited in extent have not considered SO_3^- center in gypsum suitable for dating as its ESR intensity was dependent on factors other than radiation dose like temperature. However, in Thar samples we have observed that SO_3^- depends only on radiation and we suggest that SO_3^- is in sulphite matrix. From the known relative intensities of SO_4^- and SO_3^- in anhydrite or pure gypsum it can be concluded that SO_3^- signal in Thar samples comes predominantly from sulphite rich regions and hence can be considered suitable center for dating.
- 8. In case of White Sands samples, a light sensitive ESR signal (O_3^-) was identified. These signals can be used for determination of time of Aeolian transport of gypsum sand. The age of gypsum precipitation can be estimated using SO_4^- , and therefore, in principle two events (formation and transportation) in the history of the same sample can be dated.

- 9. Field stratigraphy of the gypsum occurrences suggests multiple precipitation events that are differentiated by sand and silty clay horizons. Spatially pervasive sand and silty clay horizons alternating with gypsum occurrences imply fluctuating hydrologic regime with high seasonality.
- The SAR ages of the quartz extracted from the sand horizons ranged from 14 ka to <2 ka. These ages on sand were in stratigraphic sequence and constrain the timing of gypsum formation in the Thar.
- 11. Based on the luminescence ages the following three major inferences can be drawn; i) Thar Desert experienced fresh water condition between 14 ka and 12 ka during this period insignificant gypsum formation occurred, ii) a fresh water condition with fluctuation during 8 ka and 6ka, and iii) a regionally extensive phase of gypsum formation after 6 ka and continued < 2 ka indicating persistent aridity.</p>
- 12. In succession where crystalline and powdery gypsum occurred at different depths, the ESR ages on powdery gypsum were higher and straitigraphicaly inconsistent. The ages obtained on crystalline gypsum suggest three major events of gypsum formation 15 ka, 8–6 ka and <6 ka respectively. Luminescence dating of quartz and feldspar extracted from the intervening sand horizons support the ESR based ages.</p>
- 13. The overestimation of the ESR ages on powdery gypsum could be due to the contribution from older reworked gypsum with secondary over growth over them. Being a volume signal, ESR therefore represents the bulk age and hence is older than OSL ages.
- 14. The present thesis gives the first detailed geochronology of the White Sands, New Mexico, USA. The SAR ages obtained from the White Sands are straitigraphicaly consistent and ranged from 0.3 ka to 7 ka. These ages suggests that dune accumulation in the Tularosa basin began around 7 ka and continued till <0.3 ka. Further the ages suggests that the accumulation rate varied from 0.5 mm/yr to 2.5 mm/yr. Highest accumulation rate of 2.5 mm/yr

was observed during 3.6 and 3.2 ka suggesting a major deflationary event corresponding to ~4 ka arid event.

- 15. Since U and Th are dispersed in the volume of gypsum grains, fine grain dose rate was used with an alpha efficiency factor (a-value) of 0.25, Singhvi and Aitken (1978).
- 16. ESR and FT-IR additionally enable understanding of the formation pathways of gypsum. In the Thar Desert it is due to sulfur reduction via hannebachite whereas in White Sands it was direct precipitation of gypsum from saline playa. Presence of intense Mn²⁺ signal in the ESR spectrum of Thar samples suggest reducing conditions during their formation. This signal was absent in the White Sands samples implying oxidizing condition during their formation. This suggested that the gypsum precipitation in the two cases followed two different pathways. Intense Mn²⁺ signal in all of the Thar Desert samples suggests that the primordial material for Thar gypsum should have been pyrite or metal sulphide formed in anoxic waters associated with low valent transition metal ions due to reaction of sulfate with calcium carbonate.

6.2 Future perspectives

- 1. Dose response behavior of gypsum opens a new window for direct dating of gypsum by luminescence, this need to be checked in future by looking into the correlation between OSL and TL. Examination of the possibility of using red emission window for the possibility of dating a more stable signal can be taken up in future.
- 2. Theoretical explanation of the mechanism responsible, for the OSL signal coming from the gypsum samples needs to be taken up in future. Component study and the nature of components responsible for gypsum OSL signal has not been explained this can be taken up in future study.
- 3. In Thar Desert, luminescence method needs to be applied to the quartz/feldspar extracts from the same gypsum horizons which have been dated by ESR technique in this thesis. Concordance between the

Luminescence and ESR ages will further validate the direct dating of gypsum by ESR.

- 4. Towards the stability of the SO_4^- center in ESR spectra of White Sands samples recorded at 77°K, the parallel component of SO_4^- was found to be significantly broader than that reported in CaSO₄ at 77°K. This can be resolved using Electron Nuclear Double Resonance (ENDOR) study on gypsum samples. ENDOR can give the strength of proton-hyperfine interaction, and the strength of hydrogen bond of SO_4^- with water molecule of gypsum.
- 5. There is a need of systematic studies for light sensitive O_3^- center which is detected in gypsum and can be used to obtain transportation age as observed in the present study.
- 6. In the powdery gypsum of Thar samples at times ESR signal was not well separated. The signals were superimposed at each other. Future study would aim at deconvoluting of ESR spectrum for such samples so that better resolution of individual signal can be obtained.
- 7. This thesis gives the chronology of the distribution pattern of gypsum in Thar. However, the study has not addressed the problem of the source of sulfur in Thar Desert. In view of this there is a wide scope for ascertaining the source of sulfur which can be done using the sulfur and oxygen isotopic studies.

List of Publications:

Submitted:

- White Sands Dune Field, New Mexico: age, dune dynamics and recent accumulations. Gary Kocurek, Mary Carr, Rwyan Ewing, Karen G. Havholm, Y. C. Nagar, A. K. Singhvi. (In press, Journal of Sedimentary Research)
- Chronometry and formation pathways of gypsum using Electron Spin Resonance and Fourier Transform Infrared spectroscopy. M. D. Sastry, Y. C. Nagar, B. Bhushan, A. K. Barsaiyana, K. P. Mishra, A. Shastri, M. N. Deo, G. Kocurek, S. K. Wadhawan, N. Juyal, and A. K. Singhvi. (Under revision, Earth and planetary science Letter).
- Geochemical signatures of Late Holocene paleo-hydrological changes from Phulera and Pokharan saline playas near the eastern and western margins of the Thar Desert, India. P. D. Roy, Y. C. Nagar, N. Juyal, W. Smykatz-Kloss, A. K. Singhvi. (Under revision, Journal of Quaternery Sciences)
- 4. Unusual EPR Line at g=2.54 in Alkali feldspars and its consequences: Evidences of interaction of shallow Fe centres and conduction electrons. Medury Dattatreya Sastry, Yogesh Chand Nagar, Braj Bhushan, Kaushala Prasad Mishra, Ashok Kumar Singhvi. (Under revision, Solid State Communication)
- 5. Controls of Floodplain Evolution on Shallow Aquifer development and the Distribution of Groundwater Arsenic: Araihazar, Bangladesh. Beth Weinman, Steven L. Goodbred, Jr., Yan Zheng', Zahid Aziz, Ashok K. Singhvi, Yogesh Chand Nagar, Michael Steckler, Alexander van Geen. (Under revision in Water Resource)

In preparation:

- 1. Comparative study of BLSL (Quartz) and IRSL (Feldspar), 'Long term fading rate of feldspar'. Y. C. Nagar and A. K. Singhvi.
- Quaternary history of the evaporite deposits in western Thar Desert. Y. C. Nagar, A. K. Singhvi, and N. Juyal

- FT-IR investigation of the gypsum samples from Playa-lakes of Thar Desert. Y. C. Nagar M. D. Sastry, and A. K. Singhvi,
- 4. Luminescence characteristics of naturally occurring Gypsum (CaSO₄.2H₂O): Relating to dating and dosimetry. Y. C. Nagar and A. K. Singhvi,
- Source and the evolution of the sulfur in saline lake in Thar Desert, India Y. C. Nagar, A. K. Singhvi, and N. Juyal.
- Distribution pattern of the Gypsum in Thar desert Y. C. Nagar, A. K. Singhvi.
 N. Juyal, and S. K. Wadhavan.
- Limits of Applicability of the Standard Growth Curve in Single Aliquot Regeneration method in Luminescence dating. M. Jaiswal, V. Jain, Y.C.Nagar, P. Morthekai, and A.K. Singhvi.

Paper/abstracts in Conferences:

- Luminescence dating of gypsum dunes-the White Sands dune field, New Mexico,USA. Nagar, Y. C., Singhvi, A. K., Kocurek, G. LED-2005
- Luminescence dating of gypsum occurrences from western playas, Rajasthan: Palaeoclimatic Implications: Wadhavan, S. K., Nagar, Y. C., Juyal, N., Singhvi, A. K. LED-2005
- Direct and Indirect Dating of Gypsum occurrences in Desert using luminescence methods: Nagar Y. C, G, Kocurek, S. K. Wadhawan, N. Juyal and Singhvi A. K. NCLA-2005
- Late Pleistocene Holocene paleo-hydrological changes in the saline playas of the Thar Desert: A synthesis P. D. Roy, Y. C. Nagar, N. Juyal, W. Smykatz-Kloss and A. K. Singhvi. AOG-2005
- 5. Fluvio-Deltaic Processes and Geomorphic Development at the scale of 100 to 1000m: There importance in governing the heterogeneity of groundwater arsenic in Araihazar, Bangladesh. Beth Weinman, Steven L. Goodbred, Jr., Yan Zheng', Zahid Aziz, Ashok K. Singhvi, Yogesh Chand Nagar, Michael Steckler, Alexander van Geen. GSA, Philadelphia Annual Meeting, 2006
- Illumination and irradiation cross-talks in automated TL/OSL systems. M. K. Murai, A. K. Tyagi, Y. C. Nagar, and A. K. Singhvi. APLD-2006, Hong Kong.

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