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Optically Stimulated Luminescence and Thermoluminescence Dating Of Samples from Antique Structures in Mardin, Turkey

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Abstract
Luminescence dating is now widely used in archaeological and geological studies. In this study, soil and brick fragments from historical structures in different regions of the Nusaybin, the south-east of Turkey, were dated. The first construction dates of some of the structures were unknown. The preheating temperature and duration for each sample were determined separately for optically stimulated luminescence dating. Equivalent doses were measured by following the protocols of single aliquot regeneration (SAR) and multiple aliquots additive dose (MAAD). Annual doses were measured by means of a low level alpha counter and XRF system. The plateau test for thermoluminescence indicated that the peak area of dating was between 290 ° C and 410 ° C. The ages of historic buildings studied in the region, following the known age calculation method of Aitken were determined between 3830±300 and 1348±95 years.

Keywords: Luminescence Dating, OSL, TL, Dayruzzaferan Monastery, Mor Yakup Church, Nusaybin.

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Highlights

- The equivalent dose was determined from the intensity of luminescence counts.
- The preheat parameters of each sample were determined.
- An OSL and a TL reader were used to find equivalent dose.
- The radioactive isotopes in the sample were determined to find annual dose.
- The age of the sample was found by equivalent dose divided by the annual dose.

1. Introduction

The phenomenon of luminescence has been used in the archaeological studies also be used as well as used in environmental, personal and accident dosimetry (Eren et al., 2013, Fujita, 2014, Meriç et al.,2008, Atlıhan et al.,2012). Luminescence can be applied as an absolute dating method, giving ages that are independent of any other chronology. For dating the technique utilizes luminescence emitted from minerals of quartz and feldspar in soil, bricks and ceramics. Luminescence is achieved through stimulation in the visible light and thermal stimulation. First one is referred as optically stimulated luminescence (OSL); another is thermoluminescence (TL). The crystal defects in minerals play a role in both techniques. The main difference between optical and TL dating techniques is that for optical dating laboratory, light of a specific wavelength or wavelength range is used to excite electrons from traps instead of heat. Non-metal archaeological material's crystal structure contains feldspar and quartz minerals. Environmental ionizing radiation (alpha, beta and gamma) due to radionuclei (i.e. U,Th and K) electron and hole pairs are created in the crystal structure. The free electrons and holes are captured at pre-existing defects (traps) of the crystal lattice, increasing over time. When the crystals are subsequently exposed to heat or light, the stimulated electrons from release from the traps and recombine with the holes. The recombination energy is emitted as luminescence photons. The numbers of photons luminescence are proportional to absorbed (paleodose) dose by sample that is proportional to the burial duration of the sample. Luminescence dating is performed by measuring of absorbed dose and annual dose. The annual dose is caused by natural radio isotopes in contents of the sample, its surrounding environment and cosmic rays. These two quantities are divided by each other and the age is calculated.

In the determination of paleodose, mostly the two basic procedure is used, SAR and MAAD. In all protocols the ultimate goal is to find paleodose. This is carried out by irradiation with a specific artificial dose source. The luminescence counts obtained from both natural radiation and artificial radiation are compared in order to find the equivalent dose. As a principle, the SAR procedure for a single disk is sufficient; a large number of discs (aliquots) are prepared to perform the MAAD procedure.

All samples to be dated have been taken from historical buildings, Deyruzzaferan Monastery, “the Dungeon”, Mor (St.) Jacob Church, in the province of Mardin, Turkey’s southeastern. Deyruzzaferan monastery was accepted as the center of Assyrians until 1932 even though prelate had resided another place from time to time (Celik, 1993)**.** There was no written source about the first construction date of the Deyruzzaferan monastery, and there was a hesitation. Authorities in the monastery said they used the structure as monastery since fifth century; on the other hand the sun worshipers had been used as a temple of the sun in the past, without a written document. They said that the monastery was built on this temple. According to the need for the monastery, different buildings were added over time. This temple, the oldest part of the building, being descended by a stone staircase, is 2 meters below the entrance to the building. The temple hall, approximately area of 40 square meters, is in the basement of the monastery. There is a small window opened to eastern at eastern side of that. The ceiling of this hall was built of hewn stone in a meter thick. Since the soil has accumulated on floor over the centuries, the height of the ceiling of the hall is less than 2 meters today.

The soil sample was taken from a building in Dara, ancient city of province of Mardin. This structure is now called as popularly “the dungeon”. The officer archaeologist said that this structure was probably built in the Roman Period, however the date of construction was unknown. Today, the building has a height of less than 2 meters from ground level. However the structure has an interior height of 30 meters and a width a basketball court, made of large hewn stones. The entrance is large enough to allow only one person to pass. A long stone staircase goes down the floor of the building. Because of floods the ground was filled with soil. Many ceramic and brick materials in the accumulated soil on the floor were collected, but these were not considered due low paleodose for dating of building. The soil sample to be dated was taken from cavity in interval of hewn stones on the wall, and at that environment lighting was turn off. The cavity is about 2 meters above the ground. In this selection of location for dating, it was searched that the soil had been exposed to daylight during construction and considered where people had not frequently preferred in usage.

Another building is in Nusaybin town of Mardin province on the Syrian border, Mor (St.) Jacob church. The building with the functionality of a monastic was made of stones, above the main prayer hall was covered with semi-domes that support the main dome. The church was a monastery that once upon a time hundreds of students boarding is considered one of the oldest of that in the Upper Mesopotamian. The church was also used as a school and within education of the philosophy, logic, literature, geometry, astronomy, medicine, law has been provided in past. Many manuscripts in language of Greek have been translated into language of Assyrian in the school, the education has continued until receive the Sassanid Nusaybin. After that the school’s instruction staffs were scattered. In the later years the Byzantines besieged the Nestorians, the school in Urfa (Edessa) moved to Nusaybin. The school in Mor Jacob church restart its activities in A.D. 469, continued until 7. Century (Akyüz, 1998). The architectural stone adornment of the church is highly exceptional, particularly its doors and windows. The structure was renovated in past; however this renewal has been not encountered in historical records. These embroidered windows probably indicate that a renewal was made in the Byzantine era. In the church there is also the grave of Mor Jacob (also known as James of Nisibis), participating in the First Council Nicaea in A.D. 325 (Akyüz, 1998). There is also a seclusion chamber, enough size to accommodate a crouched man, in tomb room in basement of the church. A small mount of soil in cavity

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at top of the seclusion chamber was carved by hand. Primarily the surface soil was scrapped and then soil sample was collected. While collecting of sample, the light was switched off. In the excavations carried out in these buildings no organic residue was found, so it is necessary to use the luminescence dating methods.

2. Experimental Procedure

2.1. Apparatus

In dating of OSL an ELSEC 9010 Optical Dating System was used. IRSL dating was chosen because there is only infrared stimulant available to extract the luminescence in the laboratory. The system's stimulation module includes 24 pcs TEMT 484 IR diodes that run at 40 mA giving approximately 30 mW/cm^2 at sample. A Thorn EMI 9235 QA photomultiplier tube (PMT) was used to detect luminescence. A BG filter transmitting 340- 620 nm was used to separate the lower energy photons. The dose rate of Sr^{90}/Y^{90} beta source, can be attached on the system, on the sample on aluminum disc was 0,029 Gy/s for fine grain or on stainless steel disc was 0,039 Gy/s for course grain. In TL dating a HARSHAW 3500 TLD reader was used. An S-11 coded PMT on the reader detects luminescence in interval of 300-650 nm at 440 nm wavelength the most efficiently. A glass filter BG-39 in front of the PMT was also used to avoid from infrared radiation due to heating planchet.

An ELSEC 7286 low level alpha counter was used in the annual dose measurements. An EMI 6097B coded PMT plugged into the counter, attached ZnS layer in sample cup on it, operates as a scintillation detector. The contributions of U and Th to annual environmental dose were determined by means of the alpha counter. The amount of K-40 was determined with the XRF system. Furthermore the content control of feldspar and quartz mineral was carried out by an XRD system.

2.2. Sample Preparation

All sample preparation procedures were carried out in the laboratory under subdued red light to avoid of bleaching effects. 3 cm of the surface of the ceramic pieces was removed by scraping for following reasons:

-The beta dosage on the surface is transitional between that corresponding to pottery radioactivity and that corresponding to the soil radioactivity.

-Daylight may reduce the luminescence level of exterior surface

-Soil contamination on surface can result in the geological luminescence signal at a high level; hence it may increase the uncertainties.

Soil and ceramic samples were gently crushed with agate grinder until powdered. Afterwards they have been held in 10% HCl and 35%H_2O_2 acids until the end of the reaction removing carbonate and organic matters respectively. Subsequently, they were washed three times with distilled water and dried in an oven. Next dried samples were sieved to obtain the fine grains (≤20 μm). After that the sample was mixed in acetone, subsequently the solution was transferred to small glass tubes with the aid of an automatic pipette cap. The grains were suspended in acetone and deposited on aluminum discs of 10 mm diameter and 0.5 mm thickness. The aluminum discs were located on the bottom of the tubes; the suspension was put in this tube and a thin sample layer of average mass of 7-8 mg was produced by evaporation of acetone. These discs were placed into tray of OSL dating systems. The DZ1 sample was prepared from a brick piece used in the construction. To prepare the quartz-rich sample (DZ1) were 90-125 μm -size grains were selected. Following the above mentioned acid treatments, coarse-grained (90-125 μm) sample was etched in 10% HF for a few minutes 40% HF acid and then for 40 minutes. The 40-minute period was determined by duration of experiment. Coarse-grained samples were deposited on the aluminum discs by means of silicone spray. The discs, deposited coarse-grained quartz, were placed in drawer of Harshaw TL reader invidiously.

3. Applied Methodology in Detail

3.1. Preheating Procedure

The preheating procedures must be performed to eliminate the luminescence arising from unstable traps. Different preheat time and temperature parameters have been performed in OSL dating studies, long time at low temperature, high temperature short time. These parameters of each sample to be dated by OSL technique are determined by as follows.

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-50 aliquots were prepared and each was exposed to 5 Gy and normalized by 0.2 seconds of OSL signal.
-25 aliquots were divided into five/six groups as five/four.
-Each group was kept in the oven at the same time for different temperatures. After cooling OSL signals of aliquots were recorded. The middle of the plateau on graph of temperature versus luminescence was taken as the temperature of preheat.
-The other 25 discs were divided into 5 groups as fours.
-Each group was kept in the oven at the determined temperature for different duration. After cooling OSL signals of aliquots were recorded. The middle of the plateau on graph of duration versus luminescence was taken as the duration of preheat. The preheat parameters were determined as follows; 6 minutes at about 200 ^{0}C for DZ2, 5 minutes at about 230 ^{0}C for Z1 and 20 minutes at about 205 ^{0}C for MY (Fig. 1).

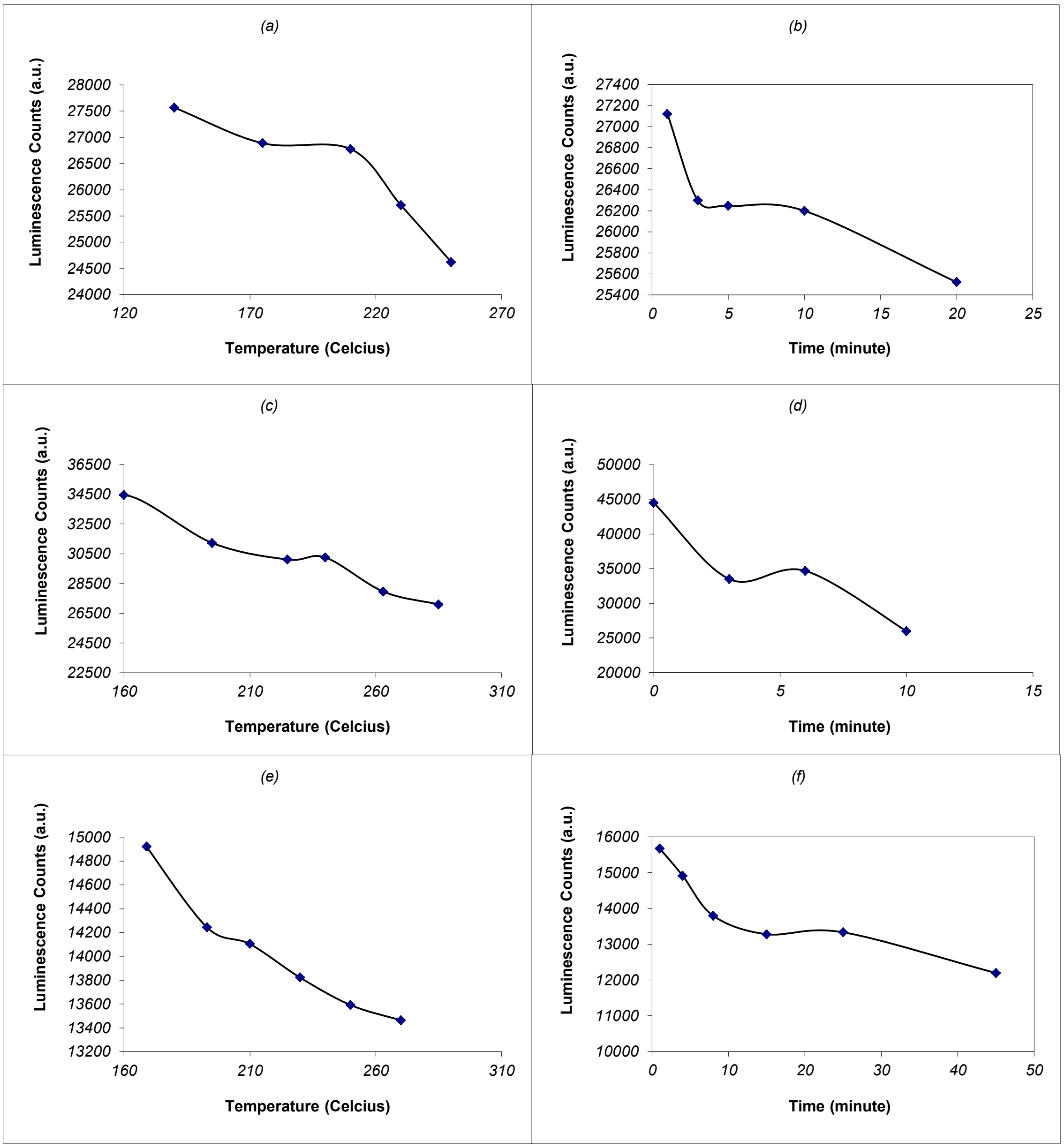

Fig.1.The graphs on finding the preheating parameters a) and b) for DZ2; c) and d) for Z1; e) and f) for MY

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3.2. Equivalent Dose (ED) Measurements in IRSL Dating

The protocols of MAAD and SAR were applied for equivalent dose measurements. MAAD was applied in samples DZ1, DZ2 and MY; also SAR was applied to samples DZ2, MY and Z1.

3.2.1. MAAD

The normalization should be carried in the protocol. The aliquots were normalized in measurements of 0.2 seconds IRSL such short shine that decrease of luminescence was very small. It could be neglected. Thirty five aliquots were prepared and equally divided into five groups.
-All aliquots were normalized with 0.2 seconds IRSL.
-The growth curves were drawn from the five points, (N), (N+3), (N+8), (N+14), (N+20) (Fig. 2).
-After the irradiation of the aliquots, they were preheated and stand for 24 hours.
-IRSL signal of each disk was measured in 250 seconds.
-Growth curves of IRSL were the plotted, the ED calculated by extrapolation to the dose axis.

3.2.2. SAR

When the amount of sample is less, it is advantageous to follow this protocol. Principally it is sufficient to prepare a single aliquot however; this number can be increased on behalf of minimizing of statistical errors. Therefore ten aliquots for DZ2, seven aliquots for MY and six aliquots for Z1 were prepared.
-IRSL of the aliquot was measured for 200 seconds to mark the original signal level. The aliquot was bleached.
-The first regeneration dose was irradiated to the aliquot, then preheat and waiting 24 hours.
- IRSL of the aliquot was measured for 200 seconds to mark the regeneration signal level. The aliquot was bleached.
These steps were repeated for 2, 4 and 8 Gy doses to the sample DZ2; 1, 3,8,13 Gy doses to the sample MY; 1,3,6,12,24 Gy doses to the sample Z1. The graph of IRSL versus the regeneration doses was drawn for each sample, the ED calculated by interpolation to the dose axis (Fig. 2).

3.3. TL Measurements

The ED was measured by integrating of the TL curves between 290 ^{0}C and 410 ^{0}C without preheat, this temperature interval was determined by means of a plateau test indicated a thermal stability between 275 ^{0}C–450 °C (Aitken, 1985).
MAAD protocol was followed to find ED by using sixteen normalized aliquots. The different additive doses were irradiated to the groups, after 24 hours the aliquots were placed on a controlled heated planchet (5 ^{0}C/s) and the TL photons were counted in interval 50-500 ^{0}C. Afterwards the growth curves were drawn and ED calculated by extrapolation to the dose axis (Fig.2.b). Therewithal the supraliniarity correction was determined with samples were annealed for two hours at 400 ^{0}C; a beta regeneration growth curve was constructed using TL signals measured after the irradiation with three different known doses (Aitken, 1985).

3.4. Annual dose rate measurements

The annual dose received by a sample is due to radiation originates from the natural radioactive isotopes within the sample and the immediate surroundings. The main sources are uranium, thorium decay series and potassium-40. Slight rubidium-87 and cosmic rays are also available. The alpha, beta, and gamma dose rates were taken into account in determining the annual dose. A calibrated low level alpha counter attached EMI 6097B as PMT, 42 mm diameter of ZnS layer placed on PMT operates as a scintillation detector was used to measure annual dose rate (Sabtu et.al. 2015). Uranium and thorium quantities were determined by the counter. The quantity of potassium 40 emitting beta was determined by XRF spectrometry (XLAB 2000 PEDXRF).

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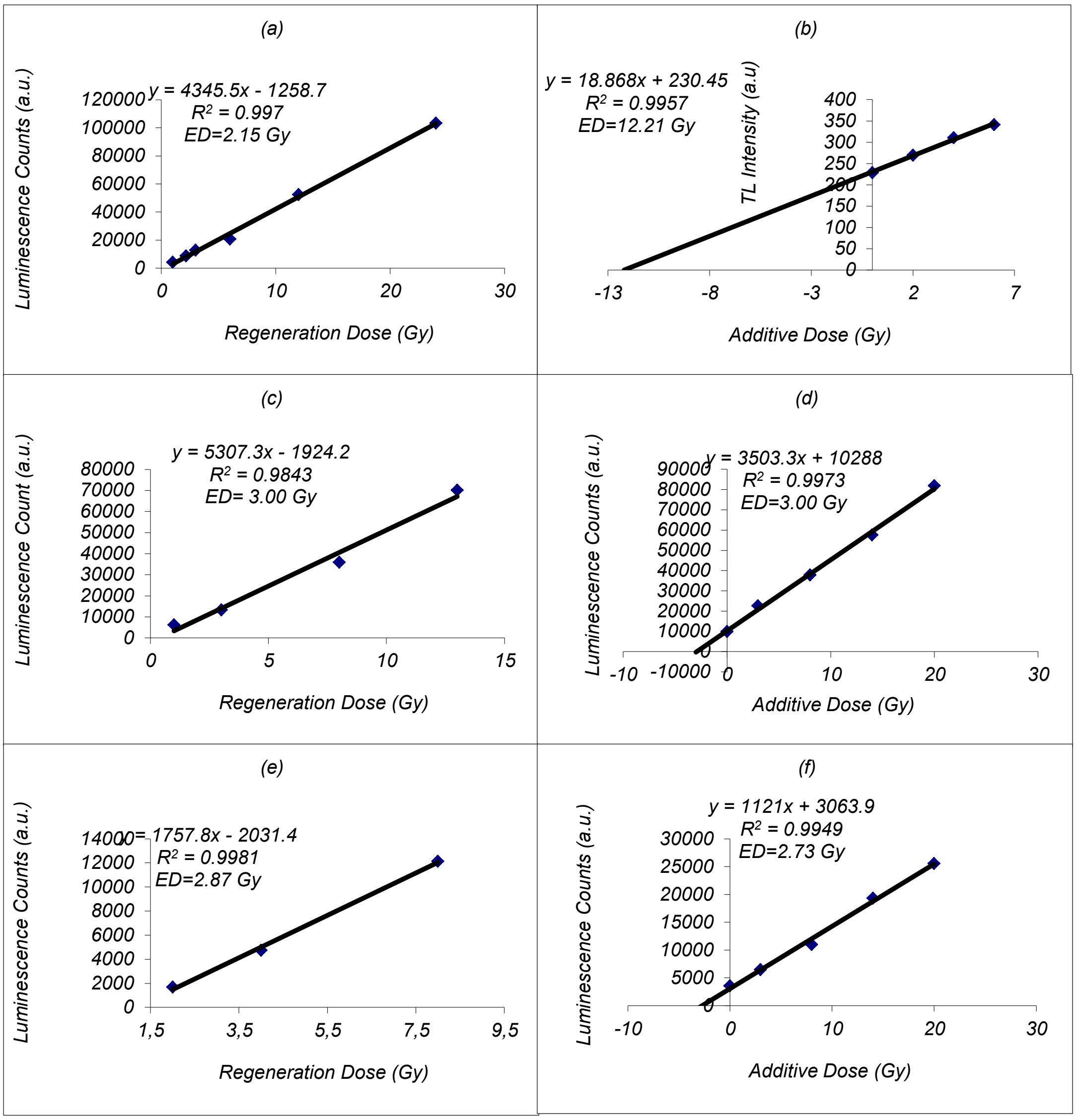

Fig.2. SAR and MAAD graphs used to find equivalent doses a) and b) for sample Z1, c) and d) for sample DZ2, e) and f) for sample MY.

The moisture content of samples, depending on the meteorological conditions of the region along burial is important to calculate annual dose. Therefore the saturation water content (W) of the samples was determined for this purpose experimentally. Water uptake during burial is taken to be (0.6 ±0.2) considering the climatic conditions of the site. The contribution of cosmic ray was taken into account 130 µGy for maximum value. In dating of all samples apart from DZ1 the alpha attenuation factor was considered as 0.15 for fine grain (Aitken, 1985). The annual dose of the brick (DZ1) was found by adding the annual dose of the surrounding soil according to the thickness of the brick. In the coarse grain dating of DZ1; the beta contribution was calculated from the sample itself and gamma dose contribution was calculated from the soil surrounding it, alpha radioactivity not taken. The beta attenuation factor was considered as 0.90 for coarse grain (Aitken, 1985). The annual dose results are given in Table 1.

Table 1: The results of annual dose for the samples

Sample	K_2O (%)	W (%)	Dose Rate (mGy/a)				Annual Dose (mGy/a)
			Alpha	Beta	Gamma	Cosmic	
DZ1	2.52±0.02	44	1.27	1.78	1.06	0.13	♣3.50 ± 0.18
DZ2	$0.25 \pm 0.05 \times 10^{-1}$	33	0.27	0.25	0.14	0.13	0.78 ± 0.04
Z1	1.47±0.03	43	0.35	0.66	0.34	0.04	1.39 ± 0.07
MY	1.54±0.03	38	0.63	0.84	0.45	0.13	2.04 ± 0.10

♣: This value includes contribution of the annual dose of the soil surrounding brick for grain dating

4. Results and Discussion

The preheat results of each sample are given in Fig.1.The midpoints of the plateau obtained in the graphs are taken as preheating parameters. These parameters for sample Z1 is 5 min at 230 ^{0}C, for sample DZ2 is 6 min at 200 ^{0}C and for sample MY is 20 min at 205 ^{0}C (Fig. 1). These values are consistent with other studies (Doğan and Meriç, 2014, Williams et al., 2006). The graphs of applied SAR and MAAD protocols to calculate ED, regeneration doses and additive doses versus luminescence counts respectively, are given in Fig. 2. As an example for sample DZ1 the fitting lines of graph were found to be equation y=18.87x+230.5. The intercept with the zero dose axis (namely x-axis) gives the equivalent dose. Hence, the equivalent doses were determined to be 12.21±Gy. In technique of SAR the graph of regeneration dose versus luminescence counts is plotted eventually interpolating of the values gives the natural luminescence counts onto a growth curve (Fig.2). For other samples these values are indicated on the graphs. Although the equivalent and annual doses of the samples taken from the monastery are very different from each other, their ages are very close. On the other hand the results of same construction are very close to each other within the limits of error.

Table 2: The results of age for the samples

Sample	Location of Sample	ED obtained by SAR (Gy)	ED obtained by MAAD (Gy)	Dose Rate (mGy/a)	Age obtained by SAR (years)	Age obtained by MAAD (years)
DZ1	Dayruzzaferan Monastery	----------------	12.21 ±0.68	3.50 ±0.18	-------------	3489±252
DZ2	Dayruzzaferan Monastery	3.00 ±0,15	3.00 ±0.15	0.78 ± 0.04	3830 ±300	3830 ±300
MY	Mor Yakup Church	2.87 ±0.14	2.73 ±0.14	2.04 ± 0.10	1407 ±100	1338 ±95
Z1	“The Dungeon” in Dara	2.15 ±0,11	--------------	1.39 ±0.07	1547 ±109	-----------

5. Conclusions

In this IRSL and TL dating study, soil and ceramic materials taken from archaeological structures in Nusaybin were discussed. For this purpose, two different protocols were followed, SAR and MAAD, to determine ED. Specimens taken from different sections of the Deyruzzaferan monastery (DZ1 and DZ2) were close to each other. Because the soil sample (DZ2) was collected from the gap between the hewn stones of the foundation wall, its annual dose is very low. At the same time, their ages from the SAR and MAAD protocols are close to one another (Table 2). Any dating technique was applied to these constructions at the first time. It is understood that the Dayruzzaferan Monastery was built on the remains of a previous possible temple.

Mor Jacob Church was constructed in A.D. 4th century; however the date we found points out 7th century. The difference indicates that the "hermitage chamber" located at corner of the tomb room was repaired at the beginning of the 7th century. On the other hand the building that the people called "dungeons" in the ruins of Dara, very close to the ancient city of Nisibis (Nusaybin) on the historic Silk Road, was dated to the middle of the 5th century. In appearance the structure was used for military purposes during the 5th century and the next centuries when the Eastern Roman Empire dominated the

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broadest boundaries in the east. On behalf of advanced archaeological studies there are many historical buildings belonging to ancient times in the region. This is the first study on the luminescence dating of ancient structures belonging to the region.

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